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SEPARATION OF TELLURIUM AND IODINE FROM OTHER FISSION PRODUCTS: APPLICATION TO LOFT SAMPLES

Myra D. Anderson and T. R. Thomas

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OTHER FISSION PRODUCTS: APPLICATION TO LOFT SAMPLES

By

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ABSTRACT

A simple and rapid procedure for the separation of tellurium and iodine from other fission products and from each other is described. Other biologically significant fission products except ruthenium may be determined in the effluent solution.

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SUMMARY

To facilitate the measurement of biologically significant fission products in LOFT containment samples, a method was developed for the separation of tellurium and iodine from other fission products and from each other. After preliminary oxidation and reduction of iodine, tellurium is reduced to the metal and separated by filtration. Iodine is then absorbed as iodide by silver chloride. The tellurium metal and the silver iodide-silver chloride are dissolved separately, and the solutions are counted in a NaI(Tl) well crystal. The procedure uses simple techniques and apparatus, and several samples can be processed concurrently. About one hour and ten minutes are required to process one sample.

The determination of chemical yield is unnecessary, because quantitative separation and recovery of both tellurium and iodine are attained. Hydrazine hydrate completely reduces and precipitates tellurium, and digestion of the precipitate makes quantitative separation by filtration possible. Complete recovery of tellurium requires only the dissolution of the tellurium metal precipitate, and this is quickly accomplished by adding an acidified solution of hypochlorite. Preliminary oxidation and reduction assure complete exchange between radioactive and carrier iodine, and the difference in the solubilities of silver iodide and silver chloride assures complete absorption of the iodide. Quantitative recovery of the separated iodine is accomplished by dissolving all the silver chloride-silver iodide in a cyanide solution.

The behavior of fission products other than tellurium and iodine was also studied. Other biologically significant fission products except ruthenium can be determined in the effluent solution from the tellurium and iodine separation, because they are not significantly retained by either the tellurium precipitate or the silver chloride. Ruthenium is significantly retained by the tellurium and variable amounts are lost, presumably by volatilization and plating out on apparatus; and therefore a separate aliquot of the initial sample will be used for the separation and determination of ruthenium. No isotopes which interfere in the determination of tellurium and iodine were observed to contaminate the tellurium and iodine fractions separated from a mixture of very young fission products.

Only one reagent, hydrofluoric acid, introduced in the tellurium and iodine separations seems likely to interfere in subsequent chemical separations of isotopes in the effluent solution. Masking the fluoride with aluminum may eliminate this interference. Conditions in the tellurium and iodine separation procedure were adjusted to avoid other interferences.

The separation procedure is very versatile and easily adaptable to most types of LOFT samples.

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CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENTS	iii
ABSTRACT	v
SUMMARY.	vii
I. INTRODUCTION	1
II. PROCEDURE FOR SEPARATING TELLURIUM AND IODINE FROM OTHER FISSION PRODUCTS	3
III. QUANTITATIVE REMOVAL AND RECOVERY OF TELLURIUM AND IODINE	4
IV. RETENTION OF OTHER FISSION PRODUCTS.	6
V. SUBSEQUENT DETERMINATION OF OTHER ISOTOPES	10
VI. ADAPTABILITY TO VARIOUS TYPES OF LOFT SAMPLES.	11
VII. REFERENCES	11
APPENDIX A. SEPARATION OF TELLURIUM AND IODINE FROM OTHER FISSION PRODUCTS.	13
APPENDIX B. SEPARATION OF IODINE FROM OTHER FISSION PRODUCTS.	19

TABLES

I. PREDICTED BIOLOGICALLY SIGNIFICANT ISOTOPES RELEASED TO THE LOFT CONTAINMENT.	2
II. PER CENT RECOVERY OF TELLURIUM AND IODINE.	5
III. PER CENT OF BIOLOGICALLY SIGNIFICANT ISOTOPES FOUND IN EFFLUENT SOLUTION	7
IV. PER CENT DISTRIBUTION OF RU-106.	9

SEPARATION OF TELLURIUM AND IODINE FROM
OTHER FISSION PRODUCTS: APPLICATION TO LOFT SAMPLES

I. INTRODUCTION

The measurement of biologically significant isotopes released to the containment in the Loss of Fluid Test (LOFT) is essential for the assessment of health hazards and for the application of these findings to other reactor systems. The measurement of iodine is particularly important because of its high volatility and its high affinity for surfaces in the containment, and several kinds of samplers are especially designed to provide information on the behavior of iodine as well as to determine its concentration. If the sampling devices perform as designed, the iodine-collecting components can be analyzed accurately by gamma-ray spectrometry; but if these components are highly contaminated with other fission products, iodine can be more accurately determined after a chemical separation.

Chemical separations are far more essential for the measurement of other biologically significant isotopes, especially in such samples as plateout coupons which will contain all the fission products, because the iodine will be contributing the bulk of the activity. This is shown in Table I, which lists the per cent of the total gamma activity in the containment contributed by the isotopes of greatest biological significance at various times after blowdown. It is apparent that many of these isotopes, especially in early samples, will be extremely difficult to measure by gamma-ray spectrometry unless iodine is chemically separated from them.

Tellurium must also be removed from the samples when it is present in large amounts because it is the precursor of iodine. If it is not removed, iodine will continue to grow in the samples from which iodine was previously separated. A second reason for the separation of tellurium is that this makes possible the accurate measurement of tellurium, information which is necessary in the determination of whether iodine found in the containment was released from the fuel as iodine or as tellurium.

If the separation procedure used to remove tellurium and iodine from the samples is to be completely satisfactory, the following criteria must be met: (1) The procedure must be simple and relatively rapid so that a large number of samples can be analyzed in a short time. Apparatus and steps in the procedure must be simple so several samples can be analyzed concurrently by one analyst. (2) The procedure must quantitatively remove tellurium and iodine and separate them from each other. This assures accurate measurement of these isotopes without the need for chemical yield determinations and prevents interference from iodine in the subsequent measurement of other fission products. (3) Other fission products ideally should not accompany the tellurium

TABLE I

PREDICTED^(a) BIOLOGICALLY SIGNIFICANT ISOTOPES
RELEASED TO THE LOFT CONTAINMENT^(b)

Isotope	Reference Gamma Energy (Mev)	Per Cent of Total Gamma Activity ^(c)		
		1.39 hr after Blowdown	27.8 hr after Blowdown	57.9 d after Blowdown
ZrNb-95	0.76	0.25	0.65	31.47
Ru-103	0.498	0.18	0.45	7.26
Ru-106	0.513	0.003	0.008	0.31
I-131	0.364	9.55	22.95	7.59
I-132	0.665	15.78	33.13	--
I-133	0.525	22.83	24.90	--
I-134	0.890	16.27	--	--
I-135	0.535, 2.42	17.85	3.03	--
Total I	--	82.28	84.01	7.59
Cs-137	0.66	< 0.002	0.004	0.19
BaLa-140	2.52, 1.60	1.40	3.56	7.53
Ce-141	0.145	0.44	1.12	14.72
Ce-144	0.134	0.06	0.17	6.24

(a) Predictions are based on the Fission Product Inventory Calculation for LOFT computed with the Radiological Safety Analysis Computer Program (to be published).

(b) Based on 25% of the iodine and 1% of the other fission products released.

(c) Not including activity from krypton and xenon.

and iodine separated fractions. This will give the most accurate determination of tellurium, iodine, and these other fission products. (4) For some isotopes, additional chemical separations will be necessary, so the procedure used to remove tellurium and iodine should introduce no reagents which cause interference in later procedures, or methods must be developed to eliminate such interference. (5) Finally, to be most useful, the procedure should be easily adaptable to the many different kinds of LOFT samples.

This report describes a tellurium and iodine separation procedure that has been developed, and discusses the procedure in terms of the above criteria.

II. PROCEDURE FOR SEPARATING TELLURIUM AND IODINE FROM OTHER FISSION PRODUCTS

Details of the following procedure are given in Appendix A.

Preliminary oxidation and reduction. Iodine, tellurium, and zirconium carriers are added to the sample. Iodine is oxidized to periodate and tellurium is partially oxidized to tellurate by hypochlorite in a caustic solution. Hydrofluoric and hydrochloric acids are added, and the sample is then heated to remove free chlorine. Iodine is reduced to iodide with bisulfite, the sample is made 3M in hydrochloric acid, and then tellurium is reduced to metallic tellurium with hydrazine hydrate.

Separation of tellurium and iodine. The tellurium precipitate is removed by filtration. The filtrate is diluted until it is 1M in hydrochloric acid, and then is passed through a column of silver chloride. Iodide replaces chloride on the column because of the lower solubility of silver iodide, and other fission products pass through the column.

Measurement of tellurium and iodine. The tellurium precipitate is dissolved with hypochlorite in acid solution, and the resulting solution is made basic and gamma counted in a NaI(Tl) well crystal. The silver chloride-silver iodide precipitate is dissolved in a basic cyanide solution, and the resulting solution is also gamma counted in a NaI(Tl) well crystal. When several isotopes of either element are present, gamma spectra analysis is required; and its use is recommended for all samples.

Time required for the procedure. Oxidation and reduction of tellurium and iodine require about 20 min, filtration of the tellurium precipitate requires about 20 min, and passage of the sample through the silver chloride column requires about 10 min. Dissolving the tellurium precipitate takes only about 5 min and can easily be done while the

sample is being passed through the silver chloride, but dissolving the silver chloride-silver iodide takes an additional 10 min. The total time required to process one sample is about 1 hr and 10 min; but if sufficient apparatus is available, a large number of samples can be run concurrently, requiring little more time than one sample.

III. QUANTITATIVE REMOVAL AND RECOVERY OF TELLURIUM AND IODINE

Table II shows the results obtained when ten samples containing I-131 and ten samples containing Te-127 were processed according to this procedure. These results indicate that removal and recovery of tellurium and iodine are essentially quantitative. Features of the procedure which make this possible are discussed below.

Quantitative removal of tellurium. In the preliminary oxidation, some of the tellurium is oxidized to tellurate by hypochlorite, causing the subsequent reduction to free tellurium to be more difficult. It is especially important to remove all the free chlorine from the sample before attempting to reduce tellurium. Heating for 30 sec is sufficient to remove chlorine when only iodine is to be reduced, but heating for 10 min is necessary before reducing tellurium. Even then, bisulfite alone will not reduce the tellurate; but addition of hydrazine hydrate to the hot solution completely reduces all the tellurium, even in the presence of nitrate. After quantitative precipitation of tellurium, the precipitate must be digested until the particle size is large enough to permit quantitative, yet rapid, filtration. Thorough washing of the filter paper is necessary to prevent the retention of other fission products, but the wash solution must contain a reducing agent to prevent losses of tellurium through oxidation.

Quantitative recovery of tellurium. The tellurium precipitate is rapidly oxidized and dissolved by hypochlorite in acid solution, and thorough washing of the filter paper is again necessary, this time to insure that all the tellurium is washed from the paper. If a dilution of the tellurium solution is necessary before counting, it may be collected in a volumetric flask; but otherwise it should be collected directly in a plastic counting tube. In either case, sodium hydroxide should be present in the container before the tellurium solution is added, in order to decrease gas formation which otherwise would cause inaccuracies in volume measurements and might even cause the counting tube to overflow and damage the well crystal. The presence of sodium hydroxide before the tellurium solution is added is particularly necessary when the tellurium solution is collected directly in a plastic counting tube, because free chlorine being generated in the acid hypochlorite solution will react with the plastic if the acid is not promptly neutralized. If this reaction occurs, tellurium will plate out on the etched plastic surface, reproducible counting geometry will not be obtained, and high tellurium answers will result.

TABLE II
PER CENT RECOVERY OF TELLURIUM AND IODINE

<u>Sample No.</u>	<u>Te-127^(a)</u>	<u>I-131^(b)</u>
1	96.7	95.4
2	99.3	98.2
3	96.5	96.5
4	96.9	102.6
5	103.1	100.9
6	99.9	99.7
7	100.5	96.4
8	99.7	98.1
9	99.3	97.2
10	99.5	97.5
Avg	99.1	98.4
Std Dev	2.1	2.3

(a) Found in the tellurium precipitate.

(b) Found in the silver chloride column.

Quantitative removal of iodine. Preliminary oxidation and reduction of iodine are necessary in any radiochemical determination of iodine, even when chemical yield is measured, to insure that all the radioactive iodine in the sample is in the same chemical state as the iodine added as carrier. Oxidation with hypochlorite and reduction with bisulfite are very commonly used,⁽¹⁾ and involve little risk of loss of iodine through volatilization. After preliminary oxidation and reduction, quantitative removal of iodine is possible because silver iodide is much less soluble than silver chloride. However, the silver chloride in the column must be packed tightly enough to prevent channeling, but not so tightly that flow rates are excessively slow. Adding a small amount of iodide to the last solution used to wash the column before passage of the sample will indicate if channeling is such a problem that the column must be re-packed before use.

Quantitative recovery of iodine. Quantitative recovery of iodine is assured by dissolving all the silver chloride-silver iodide precipitate in a cyanide solution made basic for the sake of safety. The empty column should also be rinsed with cyanide solution to dissolve small amounts of silver iodide which may have been overlooked when the precipitate was transferred from the column. The final iodine solution may be collected in a volumetric flask if dilution before counting is desired, or in a plastic counting tube if the entire solution is to be counted.

IV. RETENTION OF OTHER FISSION PRODUCTS

The procedure was modified considerably to prevent the retention of biologically significant fission products other than tellurium and iodine, because it is desirable to determine these other fission products after the removal of tellurium and iodine. The retention of very young fission products was also studied to determine its effect on the accurate measurement of tellurium and iodine, but no further modifications in the procedure were necessary.

Retention of biologically significant fission products. Tracer solutions containing Ce-144, Sr-85, Cs-137, ZrNb-95, BaLa-140, and Ru-106 were processed according to the procedure to determine the extent to which other biologically significant fission products are retained along with tellurium and iodine. As shown in Table III, Ce-141, Ce-144, Sr-89, Sr-90, Cs-137, ZrNb-95, and BaLa-140 are not retained to any significant extent by either the tellurium precipitate or the silver chloride column. The retention of barium, strontium, and cesium was never significant enough to require precautions other than washing, but special measures were necessary to prevent the retention of zirconium, niobium, cerium, and lanthanum.

TABLE III

PER CENT OF BIOLOGICALLY SIGNIFICANT ISOTOPES
FOUND IN EFFLUENT SOLUTION

<u>Sample No.</u>	<u>Ce-144</u>	<u>Sr-85</u>	<u>Cs-137</u>	<u>ZrNb-95</u>	<u>BaLa-140</u>	<u>Ru-106</u>
1	98.7	101.0	98.2	98.2	97.0	71.1
2	97.0	99.9	100.5	95.9	96.1	77.4
3	99.4	99.4	100.5	94.2	96.8	69.8
4	96.2	101.0	100.9	99.4	96.1	75.6
5	97.9	101.0	98.6	98.1	99.6	72.7
6	87.9(a)	98.4	100.5	91.7	97.6	54.6
7	97.9	99.4	100.5	102.3	98.1	50.0
8	99.8	100.0	99.5	101.0	97.6	55.2
9	99.2	100.0	99.5	92.2	97.8	50.6
10	97.2	101.0	98.6	94.0	97.4	64.6
Avg	98.1	100.1	99.7	96.7	97.4	64.2
Std Dev	1.2	0.8	0.9	3.4	1.1	8.9

(a) A significant outlier not included in average or standard deviation.

In the beginning of the development of this procedure, silver chloride adsorbed on silica gel was used for absorbing iodine, as suggested by the work of Hild and Lieser.⁽²⁾ Because the silica gel irreversibly sorbed a significant amount of ZrNb-95, unsupported silver chloride was substituted. The sorption of ZrNb-95 on the silver chloride was reduced to near background by adding zirconium carrier and by complexing with hydrofluoric acid. Plastic apparatus, required in the presence of hydrofluoric acid, also sorbed less ZrNb-95 than glass.

In the presence of hydrofluoric acid, cerium and other lanthanides are retained on the walls of the sample beaker and on the tellurium precipitate unless the hydrochloric acid concentration is at least 3M. A hydrochloric acid concentration of 1M is sufficient to prevent retention of these elements by the silver chloride column, however.

As shown in Table III, ruthenium was the only biologically significant fission product element not satisfactorily recovered in the column effluent. As shown in Table IV, most of the nonrecovered ruthenium was carried on the tellurium metal precipitate. This is not surprising because ruthenium is easily reducible to the metal. The smaller amount of ruthenium sorbed on the silver chloride is probably removable by additional washing. However, the carrying of ruthenium on both the tellurium precipitate and the silver chloride is inconsequential because ruthenium, especially at the low levels expected in LOFT samples, does not interfere with the gamma-ray spectrometric analysis of either tellurium or iodine.

As shown in Table IV, varying amounts of the initial ruthenium were lost, that is, were not found in the tellurium precipitate, on the silver chloride, or in the effluent. Probable causes for this loss are volatilization as the tetroxide during the hypochlorite oxidation and plating on the surfaces of the apparatus. Such losses, as well as the carrying of ruthenium on the tellurium and silver chloride, are not reproducible, as is evident from Table IV. For these reasons, a separate aliquot of the initial sample will be used for the separation and determination of ruthenium. A well-established, rapid distillation procedure is available for this.

Retention of young fission products. A 1 mg sample of U-235 was irradiated for 30 sec in the VP-7 position in the Materials Testing Reactor. The irradiated uranium was dissolved under reflux in aqua regia, aliquots were taken at four different times, and tellurium was separated from these aliquots. Iodine was also separated from three of them. The resulting tellurium and iodine solutions were gamma counted in a NaI(Tl) well crystal, using a 512-channel analyzer. Only iodine isotopes were found in the iodine fractions. Tellurium isotopes contributed most of the activity in the tellurium fractions, but Se-81m and possibly some Sb-128 were also observed in the earliest separation. To confirm the identity of these isotopes, a second 1 mg sample of U-235 was irradiated and treated as before, one tellurium separation

TABLE IV

PER CENT DISTRIBUTION OF RU-106

<u>Sample No.</u>	<u>Effluent Soln</u>	<u>Te ppt</u>	<u>AgCl-AgI</u>	<u>Not Recovered</u>
1	71.1	16.3	1.2	11.4
2	77.4	15.1	2.9	4.6
3	69.8	16.9	2.9	10.4
4	75.6	12.8	5.2	6.4
5	72.7	18.7	5.8	2.8
6	54.6	18.7	5.2	21.5
7	50.0	24.4	6.4	19.2
8	55.2	17.4	2.9	24.5
9	50.6	14.5	7.0	27.9
10	64.6	12.8	10.5	12.1
Avg	64.2	16.8	5.0	14.1
Std Dev	8.9	3.8	3.0	8.7

was made, and the tellurium fraction was counted one hour after irradiation and at half-hour intervals for four more hours. The presence of Se-81m was confirmed, but no Sb-128 was observed. Two peaks appearing at 0.19 and 0.28 Mev were not identified with any isotopes whose half-lives were like those observed in this decay study. None of the isotopes observed will interfere in the accurate determination of tellurium.

V. SUBSEQUENT DETERMINATION OF OTHER ISOTOPES

The biologically significant isotopes of strontium, Sr-90 and Sr-89, cannot be determined by gamma-ray spectrometry because they emit beta particles only. A very complete separation of strontium from all other fission products is necessary to determine these isotopes, and even then the gamma-ray-emitting isotopes Sr-91 and Sr-92 will prevent the determination of Sr-89 and Sr-90 until about a week after blowdown. For these reasons, Sr-89 and Sr-90 will be determined on separate aliquots of the LOFT samples by established procedures.

With the full recovery shown in the previous section, gamma-emitting biologically significant isotopes except ruthenium may be determined in the effluent solution from the tellurium and iodine separation. Some can be determined without further separation by gamma-ray spectrometry, but in some cases further chemical separations will be necessary. The gamma energies of Ce-141 and Ce-144 are very nearly the same, and common procedures for resolving them require a clean separation of cerium from other fission products. The activity of long-lived Cs-137 is expected to be very low, especially in early LOFT samples; and its separation will probably be necessary. Fast procedures, especially adapted to the effluent solution from the tellurium and iodine separation, for the separation of cerium and cesium are being developed.

The procedure being developed for the separation of cerium is based on an extraction with di(2-ethylhexyl)phosphoric acid. Hydrofluoric acid, added to prevent the carrying of ZrNb-95 on the tellurium precipitate and silver chloride column, prevents the extraction of cerium. Masking the fluoride with aluminum may eliminate this interference.

Two other potential interferences are eliminated by diluting the sample to 1M hydrochloric acid after the reduction of tellurium to the metal and before transferring it to the silver chloride column. If the sample passed through the silver chloride is 3M in hydrochloric acid, considerable amounts of silver chloride dissolve and later precipitate when the sample is neutralized. The dilution also decreases the concentration of hydrazine hydrate in the solution to a sufficiently low level that silver chloride is not reduced to free silver. Precipitates of either free silver or silver chloride carry significant amounts of ZrNb-95, BaLa-140, and Ce-144.

VI. ADAPTABILITY TO VARIOUS TYPES OF LOFT SAMPLES

The procedure for separating tellurium and iodine from other fission products is very versatile. Of the reagents usually used to dissolve samples such as LOFT containment samples, the only probable interference is large amounts of sulfate, which may cause retention of barium and other elements whose sulfates are slightly soluble. Nitrate, chloride, fluoride, and perchlorate do not interfere. Because provisions are made for the dilution of the final tellurium and iodine solutions, no problems are expected to result from variations in the relative amounts of isotopes unless the activity levels of ruthenium are much larger than the tellurium activity levels. Large amounts of ruthenium will not interfere in the determination of iodine. The procedure as written is designed for small sample volumes, but reagent volumes can easily be adjusted for any volume of sample.

In some of the later samples, tellurium may have decayed enough that a tellurium separation is no longer necessary. When this is the case, considerable time can be saved by following the procedure given in Appendix B, in which only iodine is separated from other fission products.

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APPENDIX A

SEPARATION OF TELLURIUM AND IODINE FROM OTHER FISSION PRODUCTS

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APPENDIX A

SEPARATION OF TELLURIUM AND IODINE FROM OTHER FISSION PRODUCTS

SAFETY PRECAUTIONS

Hydrazine hydrate is potentially explosive. The reagent should be stored away from heat, and only one drop at a time should be added to the sample solution.

Cyanide solutions must never be made acidic because extremely volatile and toxic hydrocyanic acid forms under these conditions. Ammonia added to the cyanide solution will neutralize any acid in the silver chloride column.

APPARATUS AND REAGENTS

A. Apparatus

1. Plastic beakers and funnels must be used.
2. Silver chloride columns. Place a Teflon wool plug in the stem of a 2.5-in. plastic funnel. Pour a slurry of coagulated silver chloride and water into the funnel, and use suction and a glass rod to pack the silver chloride closely enough to prevent channeling. The length of the silver chloride in the funnel stem should be about 1 in., and the flow rate through the column when suction is applied should be 1-2 sec/drop. Before using the column, test it for channeling by passing a few ml of water containing a few drops of iodine carrier through the column. The location of the yellow silver iodide formed will show whether channeling will be a problem.
3. Suction apparatus. A convenient suction apparatus can be made from a flat glass plate and a 1-liter bottle whose bottom has been removed and which has an outlet tube connecting it with the vacuum line. The receiving vessel is placed on the glass plate, and the bottomless bottle is placed over it and sealed with silicone grease. The tip of the funnel passes through a rubber stopper in the top of the bottle, and must extend below the top of the receiving vessel.
4. Counting tubes, polystyrene vials having a capacity of 50 ml.

B. Reagents

NOTE: All reagents used are C.P. or Analytical Reagent grade stock. Use distilled water for the preparation of all reagents.

1. Silver chloride. Add 5 ml of concentrated nitric acid and 0.1M hydrochloric acid to 100 ml of 0.1M silver nitrate until precipitation is complete. Stir for 30 min to coagulate the precipitate. Decant the solution and rinse the precipitate with water. Store under water. The packing properties of silver chloride improve with storage, and the silver chloride should preferably be stored at least a week before use.
2. Zirconium carrier, 10 mg Zr/ml. Dissolve 29.3 g $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in 100 ml of concentrated hydrochloric acid and 900 ml of water.
3. Tellurium carrier. Dissolve 10 g of tellurium metal in a minimum amount of concentrated nitric acid and dilute to 100 ml with water. Standardization is not necessary.
4. Iodine carrier. Dissolve 13 g of sodium iodide in 1 liter of water. Standardization is not necessary.
5. Hydrazine hydrate, 85% solution.
6. 3M hydrochloric acid - 0.1M hydrofluoric acid - hydrazine hydrate. Dilute 250 ml of concentrated hydrochloric acid, 7 drops of concentrated hydrofluoric acid, and 1 ml of 85% hydrazine hydrate to 1 liter with water.
7. Basic cyanide solution. Add 10 ml of concentrated ammonium hydroxide to 1 liter of saturated potassium cyanide solution.

PROCEDURE

1. To the sample aliquot in a plastic beaker, add one drop of zirconium carrier, three drops of tellurium carrier, and ten drops of iodine carrier. Add two drops of phenolphthalein indicator and make basic with 6M sodium hydroxide. Add one or two drops of sodium hydroxide in excess.
2. Add 1 ml of 5% sodium hypochlorite. Dilute to a total volume of at least 4 ml with water. Heat under a heat lamp for 10 min.
3. Add 1.5 ml of concentrated hydrochloric acid and 4 drops of concentrated hydrofluoric acid. Heat in a boiling water bath for 10 min.
4. Add a few drops of saturated sodium bisulfite solution until the green color disappears.
5. While keeping the solution hot, add 85% hydrazine hydrate, one drop at a time, swirling after each addition, until no more precipitation is observed. Add 15 drops in excess. Dilute to 5 ml with water.

6. Heat in a boiling water bath or under a heat lamp until the precipitate coagulates. Let cool to room temperature.
- 7a. If no rare earths are present, dilute to 15 ml with water. Place a Whatman 41 filter paper in the funnel used for the silver chloride column, and pass the sample through the filter paper and column with suction. Thoroughly rinse the sample beaker, filter paper, and column with a solution 1M in hydrochloric acid, 0.1M in hydrofluoric acid, and containing a few drops of hydrazine hydrate.
- 7b. If rare earths are present, filter the sample through Whatman 41 filter paper. Rinse the sample beaker and filter paper thoroughly with about 15 ml of a solution 3M in hydrochloric acid, 0.1M in hydrofluoric acid, and containing a few drops of hydrazine hydrate. Dilute the combined filtrate and washings to three times their combined volume with water. Pass the filtrate and washings through the silver chloride column with suction. Rinse the column thoroughly with a solution 1M in hydrochloric acid and 0.1M in hydrofluoric acid.
8. Collect the effluent from the silver chloride column in a plastic beaker if further chemical separations of fission products are to be made; collect it in counting tubes if other fission products are to be determined by gamma-ray spectrometry only.
9. If Step 7a was followed, transfer the filter paper to another funnel. Dissolve the tellurium precipitate in the sample beaker and on the filter paper in 5% sodium hypochlorite containing a few drops of concentrated hydrochloric acid. Rinse the beaker and filter paper thoroughly with additional portions of the same solution. Collect the tellurium solution in a volumetric flask or a counting tube containing 10 ml of 6M sodium hydroxide. Dilute to volume with water, and count the tellurium solution or a dilution made from it in a NaI(Tl) well crystal. A multichannel analyzer is recommended.
10. Use tweezers to remove the Teflon wool plug from the silver chloride column. Place the Teflon wool plug in the mouth of the funnel, and use a metal rod to push the plug and the silver chloride through the funnel stem and into a counting tube or volumetric flask. Rinse the funnel into the counting tube or flask with basic cyanide solution. Add an additional 15 ml of basic cyanide solution and agitate in an ultrasonic bath until the silver precipitate is completely dissolved. Dilute to volume with water, and count the iodine solution or a dilution made from it in a NaI(Tl) well crystal. A multichannel analyzer is recommended.

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APPENDIX B

SEPARATION OF IODINE FROM OTHER FISSION PRODUCTS

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SEPARATION OF IODINE FROM OTHER FISSION PRODUCTS

SAFETY PRECAUTIONS

Cyanide solutions must never be made acidic because extremely volatile and toxic hydrocyanic acid forms under these conditions. Ammonia added to the cyanide solution will neutralize any acid in the silver chloride column.

APPARATUS AND REAGENTS

A. Apparatus

1. Plastic beakers and funnels must be used.
2. Silver chloride columns. Place a Teflon wool plug in the stem of a 2.5-in. plastic funnel. Pour a slurry of coagulated silver chloride and water into the funnel, and use suction and a glass rod to pack the silver chloride closely enough to prevent channeling. The length of silver chloride in the funnel stem should be about 1 in., and the flow rate through the column when suction is applied should be 1-2 sec/drop. Before using the column, test it for channeling by passing a few ml of water containing a few drops of iodine carrier through the column. The location of the yellow silver iodide formed will show whether channeling will be a problem.
3. Suction apparatus. A convenient suction apparatus can be made from a flat glass plate and a 1-liter bottle whose bottom has been removed and which has an outlet tube connecting it with the vacuum line. The receiving vessel is placed on the glass plate, and the bottomless bottle is placed over it and sealed with silicone grease. The tip of the funnel passes through a rubber stopper in the top of the bottle, and must extend below the top of the receiving vessel.
4. Counting tubes, polystyrene vials having a capacity of 50 ml.

B. Reagents

NOTE: All reagents used are C.P. or Analytical Reagent grade stock. Use distilled water for the preparation of all reagents.

1. Silver chloride. Add 5 ml of concentrated nitric acid and 0.1M hydrochloric acid to 100 ml of 0.1M silver nitrate until precipitation is complete. Stir for 30 min to coagulate the precipitate. Decant the solution and rinse the precipitate with water. Store under water. The packing properties of silver chloride improve with storage, and the silver chloride should preferably be stored at least a week before use.
2. Zirconium carrier, 10 mg Zr/ml. Dissolve 29.3 g $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in 100 ml of concentrated hydrochloric acid and 900 ml of water.
3. Iodine carrier. Dissolve 13 g of sodium iodide in 1 liter of water. Standardization is not necessary.
4. Basic cyanide solution. Add 10 ml of concentrated ammonium hydroxide to 1 liter of saturated potassium cyanide solution.

PROCEDURE

1. To the sample aliquot in a plastic beaker, add one drop of zirconium carrier and ten drops of iodine carrier. Add two drops of phenolphthalein indicator and make basic with 6M sodium hydroxide. Add one or two drops of sodium hydroxide in excess.
2. Add 1 ml of 5% sodium hypochlorite solution. Dilute to a total volume of at least 4 ml with water. Heat under an infrared lamp for 10 min.
3. Add 1 ml of concentrated hydrochloric acid and 4 drops of concentrated hydrofluoric acid. Heat in a boiling water bath for 30 sec.
4. Add a few drops of saturated sodium bisulfite solution until the green color disappears. Dilute to 10 ml with water.
5. Pass the solution through a silver chloride column with suction. Rinse the sample beaker and column with a 1M hydrochloric acid - 0.1M hydrofluoric acid solution, added in small portions. Collect the effluent in a counting tube if other fission products are to be determined by gamma-ray spectrometry only, or in a plastic beaker if further chemical separations are to be made.
6. Use tweezers to remove the Teflon wool plug from the silver chloride column. Place the Teflon wool plug in the mouth of the funnel and use a metal rod to push the plug and the silver chloride through the funnel stem and into a counting tube or volumetric flask. Rinse the funnel into the counting tube or volumetric flask with basic cyanide solution. Add about 15 ml

of basic cyanide solution, and agitate in an ultrasonic bath until the silver precipitate is completely dissolved. Dilute to volume with water, and count the iodine solution or a dilution made from it in a NaI(Tl) well crystal. A multi-channel analyzer is recommended.

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