114

11/13/80

I.S

Lh. 1982

ornl

ORNL/TM-7449

OAK
RIDGE
NATIONAL
LABORATORY

UNION
CARBIDE

MASTER

Determination of Iodine-129 in Mixed Fission Products by Neutron Activation Analysis

L. C. Bate
J. R. Stokely

CONSOLIDATED FUEL REPROCESSING PROGRAM

OPERATED BY
UNION CARBIDE CORPORATION
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A02; Microfiche A01

ORNL/TM-7449
Dist. Category UC-86

Contract No. W-7405-eng-26

Consolidated Fuel Reprocessing Program

DETERMINATION OF IODINE-129 IN MIXED FISSION PRODUCTS BY NEUTRON ACTIVATION ANALYSIS

L. C. Bate and J. R. Stokely
Analytical Chemistry Division

Date Published: October 1980

NOTICE: This document contains information of a preliminary nature. It is subject to revision or correction and therefore does not represent a final report.

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

CONTENTS

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

ABSTRACT

This report describes an improved method for analyzing ^{129}I in fission product mixtures originating from fuel reprocessing studies. The method utilizes conventional iodine valence adjustment and solvent extraction techniques to chemically separate ^{129}I from most fission products. The ^{129}I is then determined by neutron irradiation and measurement of the 12.4-h ^{130}I produced by the neutron capture reaction.

Special techniques were devised for neutron irradiation of ^{129}I samples in the pneumatic tube irradiation facilities at the High Flux Isotope (HFIR) and Oak Ridge Research (ORR) reactors. Chemically separated ^{129}I is adsorbed on an anion exchange resin column made from an irradiation container. The loaded resin is then irradiated in either of the pneumatic facilities to produce ^{130}I. Sensitivity of the analysis with the HFIR facility (flux: 5×10^{14} neutrons cm^{-2} s^{-1}) and a 100-s irradiation time is approximately 2 ng. Samples up to 250 mL in volume can be easily processed. The method has been in routine use for about two years and has given good results on samples of reactor fuel solutions and off-gas traps.

1. INTRODUCTION

Iodine-129 is the predominant radioactive isotope of iodine in irradiated reactor fuels that have decayed for more than a few months. In addition, because of the long half-life (1.6×10^7 years) and high fission yield (0.7%), ^{129}I is a major fission product in old fission product mixtures from high burn-up fuels. The fate of ^{129}I in the chemical reprocessing of reactor fuels is therefore of considerable importance in relation to fission product inventory, eventual disposal or recovery of the isotope, and environmental release. The behavior of ^{129}I in chemical reprocessing operations is complicated by the volatility of iodine under some conditions and the presence of iodine in multiple oxidation states or organo-iodine compounds. Chemical analyses are often required to establish or verify the behavior and/or fate of ^{129}I in reprocessing operations.

Accurate analysis of ^{129}I in fission product mixtures by direct counting is not possible because ^{129}I decays by emission of low energy (0.15 MeV) beta particles, and there are no high energy gamma rays associated with the decay. Also, as a result of its long half-life, ^{129}I has a very low specific activity (6.4 Bq μg^{-1}). Both of these conditions make direct radioactivity measurements to determine ^{129}I difficult and insensitive.

Neutron activation analysis (NAA) is usually the preferred method for analysis of iodine-129[1–6]: submicrogram quantities can be determined by measuring ^{130}I produced by n, γ reaction. The thermal neutron cross section for the capture reaction is 27 barns, and the half-life of the ^{130}I product is 12.4 h.[7] Iodine-130 has four prominent gamma rays [418, 526, 668, and 734 keV][7] which can be easily measured by gamma ray spectrometry. When analyzing highly radioactive fission product mixtures, a chemical separation of ^{129}I is required prior to NAA to eliminate gamma ray-emitting fission products which cause interference in the analysis.

Neutron activation analysis has been used for several years at ORNL for determination of ^{129}I in dissolved reactor fuels and gas trapping systems.[8] Several features of the method used for the analysis caused recurring problems. Samples for irradiation were large (10 mL), and only a few samples could be irradiated at a time, often resulting in delays in reporting of analysis results. There were appreciable flux gradients (~20%) in the irradiation facility which caused poor precision. Sensitivity of the analysis was inadequate for some samples because of insufficient neutron flux in the irradiation facility.

This report describes an improved method for analyzing ^{129}I which was made possible by the development of techniques for irradiation of samples in pneumatically operated irradiation facilities at the Oak Ridge Research (ORR) and the High Flux Isotope (HFIR) reactors. Both of these facilities have high and stable neutron fluxes (ORR: 4×10^{13}, HFIR: 5×10^{14} neutrons $cm^{-2} s^{-1}$). However, irradiation of aqueous samples at the ORR requires special care to avoid overheating and rupture of the polyethylene rabbits. Note that liquid samples cannot be irradiated in the HFIR and sample size is restricted to less than 0.5 cm^3 in both facilities. These limitations were overcome by preconcentration of ^{129}I on an anion exchange resin and direct NAA of the ^{129}I-loaded resin.

The improved method has been in routine use for about two years. It has been tested on several sample types and has increased the precision and accuracy of analysis results. Sensitivity of the analysis has been increased because of the higher neutron flux levels in the HFIR and ORR facilities. Shorter irradiation times and separation procedure modifications have resulted in a reduction in the time required for analysis. The new method is applicable, with slight modifications, to most high-flux pneumatically operated NAA facilities.

2. EXPERIMENTAL

2.1 Equipment and Reagents

A modified polyethylene irradiation insert is used as an ion-exchange column for preconcentration of ^{129}I prior to NAA. Figure 1 shows the modified insert and a polyethylene rabbit containing the insert during irradiation. Approximately 20 holes of 0.4-mm diam are drilled through the bottom of the insert to allow passage of solution through the resin bed. Because of the small size of the column, special apparatus (Fig. 2) was constructed to

ORNL-DWG 78-12432

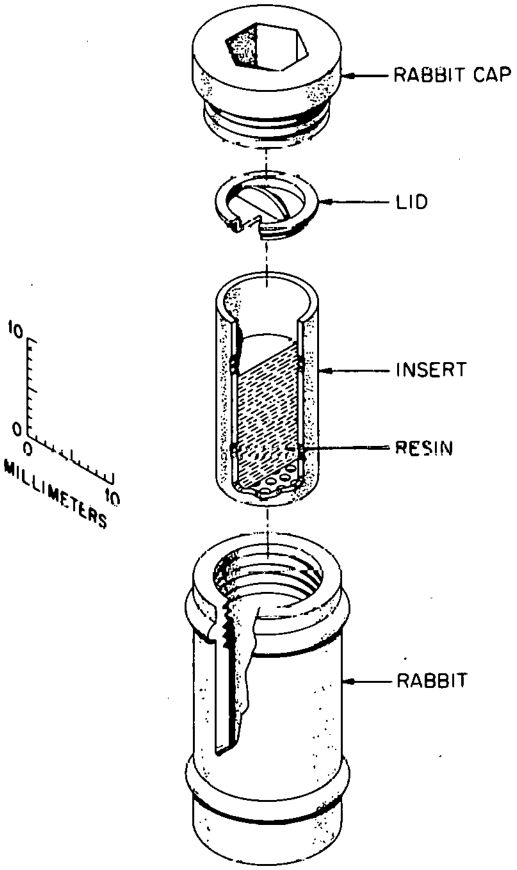

Fig. 1. Insert modified for ion exchange preconcentration of ^{129}I.

ORNL-DWG 78-12433

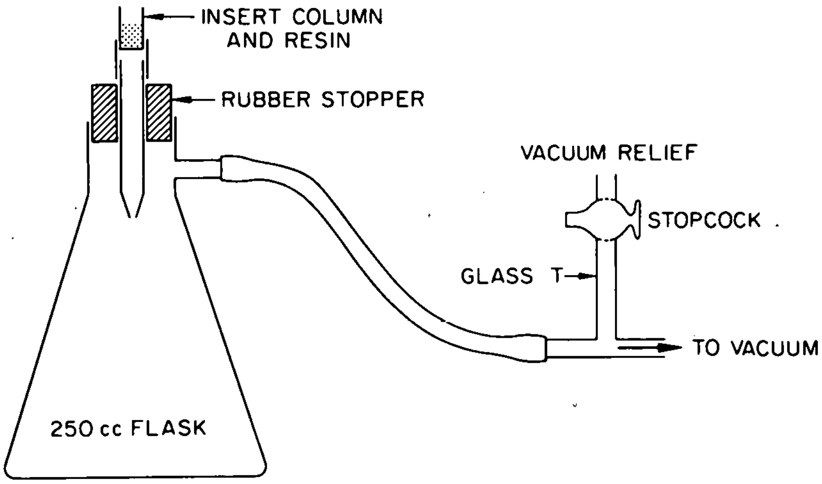

Fig. 2. Apparatus for loading ^{129}I on resin column.

aid in loading the ^{129}I on the column. Vacuum is applied to the bottom of the insert from a 250-mL filtering flask. Vacuum is controlled by a stopcock allowing adjustment of the flow rate of sample through the column.

Bio-Rad AG1x4 resin*, 100–200 mesh, is used in the nitrate form. The resin is pretreated in 20- to 30-g batches by thoroughly flushing with distilled water to remove excess nitrate. The resin is stored as a slurry in distilled water.

Iodine isotopes used in this work were obtained from the ORNL Operations Division. An ^{129}I secondary standard containing 0.256 μg/mL of ^{129}I was prepared and standardized against NBS SRM 4949 using NAA. All other reagents were of reagent-grade quality.

Two computer-based gamma-ray spectrometer systems were used to determine ^{130}I and ^{131}I after neutron irradiation. One system consisted of a Ge(Li) detector of 10% efficiency coupled to a Nuclear Data Analyzer, 50/50 series. Data from this system were stored and processed using the computer program, MONSTR.[8] A Nuclear Data 6620 spectrometer system and 20% Ge(Li) detector are presently used for routine application of the method. Irradiations are performed in the NAA facilities at the HFIR or the ORR.

2.2 Recommended Procedure

The procedure for separating ^{129}I from other fission products is given below along with information on the irradiation and radioactivity measurements. A post-irradiation removal of ^{82}Br is included in the procedure but is used only on samples where ^{82}Br interferes with the ^{130}I radioactivity measurement. Standard ^{129}I samples are treated in the same manner as the samples.

---

*Registered trademark.

Ten milliliters of 2 *M* Na_2CO_3, 1 mL of ^{131}I internal standard for yield determination, and 1 mL of 2 mg/mL iodide carrier are mixed in a 60-mL separatory funnel. A predetermined volume of sample solution is added to the funnel followed by 2 mL of 5% NaClO solution, and the contents of the funnel are mixed. Complete oxidation takes 5 min. The solution is acidified by slowly adding 3 to 4 mL of concentrated HNO_3 with mixing. Ten milliliters of CCl_4 and 3 to 5 mL of 1 *M* $NH_2OH{\cdot}HCl$ are then added to reduce periodate to iodine which is extracted into the CCl_4 layer by shaking for 2 min. The carbon tetrachloride layer is then transferred into a new separatory funnel, and the aqueous solution is discarded. The carbon tetrachloride solution is shaken with 5 mL of H_2O containing 3 to 5 drops of 1 *M* $K_2S_2O_5$ until both phases are colorless. The carbon tetrachloride phase is discarded, and the aqueous phase is retained for ion exchange chromatography.

With the resin column insert on the suction flask (Fig. 2), the column is filled approximately one-half full with slurried resin. Excess liquid is removed by adjusting the stopcock on the vacuum line to maintain a flow rate of one drop per second through the column. The resin is then washed with 2 mL of distilled water. The sample is filtered to remove any solids and transferred to the resin column. After sample loading, the resin is washed with 5 mL of H_2O to remove all cations. The resin is then dried by pulling air through the resin for 1 min. A cap is placed on the insert, and the insert is removed from the suction flask and placed in a plastic vial for irradiation. Samples are either irradiated for 100 s in the HFIR or 5 min in the ORR and allowed to decay for at least 6 h. Irradiated inserts are removed from the rabbits and transferred to counting vials. Samples are normally counted at a source-to-detector distance of 10 cm.

The chemical yield of iodine in the separation procedure is determined by adding a 1-mL aliquot of ^{131}I internal standard iodide solution into a centrifuge cone with 1 mL of 1 *N* NaOH and 3 to 5 drops of 1 *M* $K_2S_2O_5$. The solution is mixed and transferred to a resin column. Iodine-131 is quantitatively retained as iodide ion by the resin column. The column is dried, capped, and placed in a counting vial for gamma ray spectrometry measurements at the same geometry that samples are counted. (This method was developed for aged fission product solutions where the ^{131}I has decayed. In samples containing ^{131}I, ^{125}I can be used as an internal standard for yield determination.)

Samples normally need no further treatment except those very low in ^{129}I where ^{82}Br interferes. Bromine-82 radioactivity in the resin is removed by washing the irradiated resin with $NaNO_3$ solution. The insert is placed on the suction flask, and a 1-in piece of rubber tubing is attached to the upper part of the insert to act as a reservoir for solution. The resin column is washed with 10 mL of 0.1 *M* $NaNO_3$ at a flow rate of one drop per second. Suction is applied to the column to remove excess solution, and the column is placed in a clean plastic vial for radioactivity measurements. Resultant gamma ray spectral data are processed by either an absolute or comparative NAA method.[9]

3. RESULTS AND DISCUSSION

A chemical separation is required to remove fission products from the ^{129}I prior to NAA in samples containing large quantities of mixed fission products. The initial step in this separation involves oxidation of iodine to periodate with sodium hypochlorite. Oxidation ensures that all reduced iodine species are transformed to a single valence state and that there is isotopic exchange of added tracer ^{131}I and ^{129}I from the sample. After the initial oxidation, periodate is reduced to iodine by hydroxylamine hydrochloride. The iodine is extracted into carbon tetrachloride, and then stripped by reduction to iodide with $K_2S_2O_5$. This procedure has been used previously[10] and is very effective in separating iodine from fission products. For samples containing very high levels of fission product activities, however, it may be necessary to repeat the chemical valence adjustment and solvent extraction procedure to obtain additional decontamination.

The ion exchange resin used in this work was Bio-Rad AG1x4 in the nitrate form. The purity of the resin was a critical factor because resin impurities can give radioactive products in the irradiation which would interfere in the activation analysis. Bio-Rad AG1x4 is a high purity resin, but still contains small quantities of bromine and chlorine. Extensive washing of the resin with sodium nitrate does not significantly reduce the halogen impurity content. It is suspected that chlorine and bromine are covalently bonded to the resin and therefore cannot be removed by anion exchange processes.

Chlorine and bromine impurities in the resin give ^{38}Cl and ^{82}Br products in the activation analysis. Both of these products have gamma rays in their decay which cause complications in the gamma spectrometric determination of ^{130}I and ^{131}I. A decay period of at least 4 h is effective in reducing the interference due to 37 min ^{38}Cl. (The delay also allows 8.9 min ^{130m}I produced in the irradiation to decay to ^{130}I.) Bromine-82 has a longer half-life (35 h) and is therefore present when gamma spectral measurements are made to determine 12.4 h ^{130}I. In this work, the bromine content of the resin has been of the order of 0.25 ppm which limits the sensitivity of the method to about 2 ng of ^{129}I.

The interference of ^{82}Br in the method can possibly be reduced or eliminated by use of coincidence counting of ^{130}I, but a chemical separation of the ^{82}Br from the ^{130}I is easily performed and was used in this work to obtain maximum sensitivity (0.1 ng).[6,11] Experiments showed that following neutron irradiation of the anion exchange resin, the ^{82}Br formed during the irradiation was present as an anion that could be readily eluted from the column. Since bromine is tightly held by the resin before the irradiation, it is apparent that ^{82}Br is released by the Szilard-Chalmers reaction.[12] Therefore, an additional step was added to the method to selectively elute ^{82}Br from the resin column prior to measurement of ^{130}I gamma rays.

Previous studies[13–15] have shown that halides are sequentially eluted from anion columns by nitrate in the order: chloride, bromide, and iodide. Experiments were performed to establish specific conditions for the ^{82}Br/^{130}I separation using the resin column. For these experiments, a 0.1 *M* $NaNO_3$ solution was used as the eluting solvent, and the flow rate through the resin was approximately one drop per second. As shown in Table 1,

Table 1. Elution of halides from resin column with 0.1 *M* sodium nitrate

Elution volume, mL	Percent eluted		
	Chloride	Bromide	Iodide
3	70	38	<2
6	88	58	<2
9	91	78	<2
12	90	89	<2
15	93	91	6

separation of ^{82}Br and ^{130}I is not quantitative but is adequate for most applications. An elution volume of 10 mL is recommended for samples containing small amounts of ^{130}I. Under these conditions, 80 to 85% of the ^{82}Br is eluted with no significant loss of ^{130}I. Iodine-130 elution starts when approximately 15 mL of 0.1 *M* $NaNO_3$ solution is passed through the resin. Small losses of ^{130}I cause no difficulties because chemical yields may be determined from the final yield of ^{131}I tracer in the counting sample; therefore, elution volumes up to 15 mL are satisfactory in most cases.

Because of the small quantity of resin (~0.3 g) and high flow rates used in this work, studies were made to determine the recovery of iodide by the anion exchange column. Incomplete retention by the column would result in low recovery and decreased sensitivity of the method. These studies were made using ^{131}I as a tracer for iodide, and showed that greater than 99.8% of the iodide is retained by the column with the conditions specified in the procedure.

In some cases, it may be desirable to load ^{129}I directly on the ion exchange resin without prior chemical separation. For this reason, additional studies of iodide adsorption were made from solutions of nitric acid and sodium hydroxide. Results of this study are shown in Table 2. High retention of iodide is obtained from all sodium hydroxide solutions from 0.1 to 5 *N*. Quantitative adsorption is not possible from nitric acid solutions greater than 0.1 *N*. Based on these studies, ^{129}I can be directly absorbed on the resin from weak nitric acid (<0.1 *N*) or sodium hydroxide solutions.

Iodine-129 is adsorbed on the anion resin column as iodide. Under some conditions, iodide could be oxidized to iodine and volatilized resulting in losses from the irradiation container, decreased sensitivity, and possible contamination of the irradiation rabbit and/or pneumatic tube. Experiments were performed to ensure that losses by volatilization were not occurring. Iodine-129 and stable iodide were adsorbed on the resin, and the load of resin was irradiated for 31 s at the HFIR. The resultant ^{130}I radioactivity was then measured, and the ^{129}I concentration in the resin was calculated. At 10-d intervals, the irradiation and ^{130}I measurement were repeated. For the three successive irradiations performed in this manner, 0.255, 0.256, and 0.258 μg of ^{129}I were found, indicating no significant losses due

Table 2. Retention of iodide on resin column from nitric acid and sodium hydroxide solutions

Concentration NaOH or HNO_3	Retention, %	
	Sodium hydroxide	Nitric acid
0.1	100	100
0.5	98	54
1	100	44
2		20
3		13
4	100	*a*
5	100	*a*

[a] At these nitric acid concentrations, iodine appeared in the solution and could not be kept in the iodide form.

to volatilization. Also, losses by volatilization could not be detected for samples containing from 0.001 to 1 mg of natural iodine carrier.

Separations using CCl_4 often resulted in insoluble impurities containing sodium being occluded by the organic phase. The insoluble matter was stripped into the aqueous phase and was retained by the ion exchange resin. Sodium-24 was produced during the irradiation and interfered with gamma ray spectrometric analysis of the sample. This difficulty was circumvented by filtering the sample prior to adsorption of ^{129}I on the anion exchange resin as described in the recommended procedure.

The improved ^{129}I method has been in use for approximately two years. In routine analyses, duplicate sample aliquots are processed through the chemical separation and subsequent activation analysis procedures. Table 3 shows typical results for routine samples run by the new method. The uncertainty of results shown in the table is the average deviation for duplicate determinations. In most cases, samples contained large amounts of fission products which were separated prior to NAA. Typically, the average deviation of duplicate samples is of the order of 1 to 4% of the mean value, which is acceptable for most studies. Rechecks are presently being performed on analyses when the average deviation is greater than 10% of the mean values. Experience to date indicates that the need for recheck analysis is very infrequent (less than one sample in 100).

Sensitivity of the analysis is of the order of 2 ng of ^{129}I using either the ORR or HFIR reactor. Sample volumes up to 25 mL have been run routinely with lower limits of 10^{-4} μg ^{129}I/mL. Sample volumes could be increased to 250 mL, if necessary, to give a sensitivity limit of the order of 10^{-5} μg ^{129}I/mL.

Overall, the improved method has eliminated most deficiencies in the analysis of ^{129}I in samples originating from fuel reprocessing studies. The precision of the new method is at least a factor of 5 greater than could be obtained previously. This precision increase is

Table 3. Results for ^{129}I routine analyses

Sample No.	Irradiation site	^{129}I found, μg/mL	Average deviation/mean, %
1981	HFIR	$1.40 (\pm 0.01) \times 10^{-2}$	0.7
1983	HFIR	$1.96 (\pm 0.23) \times 10^{-2}$	11.7
2081	HFIR	1.39(±0.06)	4.3
2105	HFIR	3.17(±0.10)	3.2
2154	HFIR	40.9(±0.4)	1.0
2203	ORR	0.304(±0.012)	3.9
2231	ORR	0.154(±0.001)	0.7
2235	ORR	140(±4)	2.8
2265	ORR	0.344(±0.015)	4.4
2270	ORR	5.10(±0.08)	1.6
2336	ORR	23.8(±0.8)	3.4
2375	ORR	$\leqslant 5 \times 10^{-5}$	
2502	ORR	$\leqslant 1 \times 10^{-4}$	

primarily due to the reproducible irradiation of samples and standards in the pneumatically operated NAA facilities at the ORR and HFIR. In addition, sensitivity of the analysis has been improved by at least a factor of 100 because of the higher neutron flux in the ORR and HFIR. Improvements in the chemical separation procedure and elimination of the need for post-irradiation chemical purification have reduced the analysis time by approximately 50%.

4. ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance of H. A. Parker, L. M. Roseberry, J. H. Davidson, and L. R. Hall for their technical contributions to this work.

5. REFERENCES

1. G. Buzzelli, "Determination of Long-Lived Iodine-129 in Irradiated Graphite Fuel Systems," *Anal. Chem.* 36, 1973 (1964).

2. B. C. Purhayastha and G. R. Morlin, "The Yield of ^{129}I in Material and Neutron-Induced Fission of Uranium," *Canadian J. Chem.* 34, 293 (1956).

3. M. Kahn and J. Kleinberg, "Radiochemistry of Iodine," NAS-NS Monograph 3062, 1977.

4. N. Lavi, "A Fast Radiochemical Procedure for Separating Iodine from Fission Products," *J. Radioanal. Chem.* 20, 41 (1974).

5. T. J. Anderson, "Methodology for the Determination of Environmental ^{129}I and ^{99}Tc," p. 84 in ASTM Standard Test Procedure 698, ed. by J. J. Kelly, 1980.

6. B. Keisch, R. C. Koch, and A. S. Levine, "Determination of Biospheric Levels of ^{129}I by Neutron Activation Analysis," pp. 284–90 in *Proc. of Intern. Conf. Modern Trends in Activation Analysis*, College Station, Tex., (1965).

7. F. F. Dyer and L. C. Bate, "DECAYGAM, Radioactive Gamma-Ray Spectra Compilation, Nuclear Data Tables, RISC Data Libratory Collection," ORNL-DLC-19, 1973.

8. J. F. Emery and F. F. Dyer, "Multielement Determination in Environmental NAA Using MONSTR," p. 123 in *Proc. 2nd Intern. Conf. on Nucl. Methods in Environmental Research*, Columbia, Mo. (1974).

9. W. S. Lyon, Jr., ed., "Guide to Activation Analysis," Robert E. Krieger Publishing Co., Huntington, N.Y., 1972, p. 9.

10. *ORNL Master Analytical Manual*, Method No. 2 21391-1, "Iodine Radioactivity in Aqueous and Organic Solutions," 1965.

11. F. P. Brauer and J. H. Kaye, "Detection Systems for the Low-Level Radiochemical Analysis of Iodine-131, Iodine-129, and Natural Iodine in Environmental Samples," *Trans. Nucl. Sci.* 21 (1), 496 (1974).

12. G. Friedlander, J. W. Kennedy, and J. M. Miller, *Nuclear and Radiochemistry*, Wiley, New York, 1964, p. 209.

13. R. C. DeGeiso et al., "Analysis of Halide Mixtures by Ion-Exchange Chromatography," *Anal. Chem.* 26, 1840 (1954).

14. R. W. Atteberry and G. E. Boyd, "Separation of Seventh Group Anions by Ion-Exchange Chromatography," *J. Am. Chem. Soc.* 72, 4805 (1950).

15. W. Rieman III, "Quantitative Separations by Ion-Exchange Chromatography," *Record of Chemical Progress* 15, 85 (1954).

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

ORNL/TM-7449
Dist. Category UC-86

INTERNAL DISTRIBUTION

1. W. J. Armento
2. S. M. Babcock
3–7. L. C. Bate
8–12. W. D. Burch
13–14. D. A. Costanzo
15. J. S. Eldridge
16. J. F. Emery
17. M. J. Feldman
18. W. S. Groenier
19. B. A. Hannaford
20. R. T. Jubin
21. P. R. Kasten
22. L. J. King
23. C. E. Lamb
24. A. P. Malinauskas
25. J. L. Marley
26. R. L. Philippone, DOE
27–28. R. H. Powell
29. D. J. Pruett
30. R. R. Rickard
31. T. G. Scott
32. J. H. Shaffer
33–37. J. R. Stodely
38. L. M. Toth
39. W. E. Unger
40. O. O. Yarbro
41–42. Laboratory Records
43. Laboratory Records, ORNL-RC
44. ORNL Patent Office
45. Nuclear Safety Information Center

EXTERNAL DISTRIBUTION

46–47. W. W. Ballard, Nuclear Fuel Cycle Division, Office of Light-Water Reactors, DOE, Washington, DC 20545
48. Office of Assistant Manager for Energy Research and Development, DOE-ORO, Oak Ridge, TN 37830
49–159. Given distribution as shown in TID-4500 under UC-86, Consolidated Fuel Reprocessing Category (25 – NTIS)