IODINE-129 SEPARATION AND DETERMINATION BY NEUTRON ACTIVATION ANALYSIS[*]

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Abstract

This paper describes a method for analysis of iodine-129 in fission product mixtures originating from fuel reprocessing studies and low-level wastes. The method utilizes conventional iodine valence adjustment and solvent extraction techniques to chemically separate iodine-129 from most fission products. The iodine-129 is determined by neutron irradiation and measurement of the 12.4 hour iodine-130 produced by the neutron capture reaction.

Special techniques were devised for neutron irradiation of iodine-129 samples in the pneumatic tube irradiation facilities at the High Flux Isotope (HFIR) and Oak Ridge Research (ORR) Reactors. Chemically separated iodine-129 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 iodine-130. Sensitivity of the analysis with the HFIR facility (flux: 5×10^{14} n/cm^2/sec) and a 100 second irradiation time is approximately 0.03 nanograms. Samples up to 250 ml in volume can be easily processed.

Introduction

Iodine-129 is the predominant radioactive isotope of iodine in irradiated reactor fuels which have decayed for more than a few months. Also, due to the long half-live (1.6 x 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.

Analysis of ^{129}I in fission product mixtures by direct counting is not possible due to unfavorable nuclear decay characteristics. Iodine-129 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, iodine-129 has a very low specific activity (6.4 Bq μgm^{-1}). Both of these conditions make direct radioactivity measurements to determine iodine-129 difficult and insensitive.

Neutron activation analysis (NAA) is usually the preferred method for analysis of ^{129}I[1-6]; submicrogram quantities can be determined by measurement of ^{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 hours.[7] Iodine-130 has four prominent gamma rays [418, 526,

668, and 734 keV][7] which can be easily measured by gamma-ray spectrometry. In the analysis of highly radioactive fision 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.

Experimental

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 that contains the insert during irradiation. Approximately 20 holes of 0.4 mm diameter 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 was constructed to aid in loading of ^{129}I on the column. This apparatus is shown on Figure 2. 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 AGlx4 resin, 100-200 mesh, (Bio-Rad Laboratories, 32nd and Griffin Avenue, Richmond, CA 94804) is used in the nitrate form. The resin is pretreated in 20-30 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 g ^{129}I/ml 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 utilized in this work to determine ^{130}I and ^{131}I after neutron irradiation. One system used in development of the method 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. The comparator method[9] for NAA is used.

Recommended Procedure

The procedure for separation of ^{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.

Ten milliliters of 2 $\underline{M}$ 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. The solution is acidified by slowly adding 3-4 ml of concentrated HNO_3 with mixing. Five minutes is allowed for complete oxidation. Ten milliliters of CCl_4 and 3-5 ml of 1 $\underline{M}$ $NH_2OH\cdot HCl$ are then added to reduce

periodate to iodine which is extracted into the CCl_4 layer by shaking for 2 minutes. 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 that contains 3-5 drops of 1 $\underline{M}$ $K_2S_2O_5$ until both phases are colorless. The carbon tetrachloride phase is discarded, and the aqueous phase is retained for ion exchange chromatography.

Mount the insert on the suction flask (Figure 2), and fill the column 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 at least five minutes. A cap is placed on the insert, and the insert is removed from the suction flask and placed in a plastic rabbit for irradiation. Samples are either irradiated for 100 seconds in the HFIR or 5 minutes in the ORR and allowed to decay for at least 6 hours. 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 $\underline{N}$ NaOH and 3-5 drops of 1 $\underline{M}$ $K_2S_2O_5$. 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, 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 one-inch 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 $\underline{M}$ $NaNO_3$ 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. The resultant gamma-ray spectral data is processed by either an absolute or comparative NAA method.

Results and discussion

For analysis of ^{129}I in samples containing large quantities of mixed fission products, a chemical separation is required to remove fission products from the ^{129}I prior to NAA. The initial step in this separation involves oxidation of iodine to periodate with sodium hypochlorite. Oxidation insures 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 hydroxy-lamine hydrochloride. The iodine is extracted into carbon tetrachloride, and then stripped by reduction to iodide with potassium metabisulfite. 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-ray spectrometric determination of ^{130}I and ^{131}I. A decay period of at least 4 hours is effective in reducing the interference due to 37 minute ^{38}Cl. (The delay also allows 8.9 minute ^{130m}I produced in the irradiation to decay to ^{130}I.) Bromine-82 has a longer half-life (35 hours) and is therefore present when gamma spectral measurements are made to determine 12.4 hour ^{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 0.1 nanograms 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,[6,11] 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 (0.03 nanogram). 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-Chalmer reaction.[12] Therefore, an additional step was added to the method to selectively elute [82]Br from the resin column prior to measurement of the [130]I gamma rays. rays.

Previous studies[13-15] have shown that halides are sequentially eluted from anion columns by nitrate in the order: chloride, bromide, 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 $\underline{M}$ NaNO$_3$ solution was used as the eluting solvent, and the flow rate through the resin was approximately 1 drop per second. As shown in Table I, 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 amount of [130]I. Under these conditions 80-85% of the [82]Br is eluted with no significant loss of iodine. Iodine elution starts when approximately 15 ml of 0.1 $\underline{M}$ NaNO$_3$ solution is passed through the resin. Small losses of iodine cause no difficulties because chemical yields are 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 on Table II. 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 insure that losses by volatilization were not occurring. Iodine-129 and stable iodide were adsorbed on the resin, and the loaded resin was irradiated for 31 sec at the HFIR. The resultant ^{130}I radioactivity was then measured, and the ^{129}I concentration in the resin was calculated. At 10-day 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 g of iodine-129 were found indicating no significant losses due to volatilization. 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 ^{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 III shows typical results for routine samples run by the method. The uncertainty of results shown on 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 1-4% 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 3 x 10^{-5} μg ^{129}I using either the ORR or HFIR reactor. Sample volumes up to 25 ml have been run routinely with lower limits of 10^{-6} μg ^{129}I/ml. Sample volumes up to 500 ml have been used in the separation of ^{129}I and irradiation time of 300 sec to obtain a sensitivity level of the order of 10^{-8} μg ^{129}I/ml.

Overall, this method has eliminated the deficiencies in the analysis of ^{129}I in samples originating from fuel reprocessing studies. Also, it is possible to determine the ^{129}I in low-level waste solutions that previously could not be measured or detected at our laboratory. This method has increased the sensitivity and accuracy of ^{129}I determinations in a wide variety of radioactive solutions.

Acknowledgments

References

1. G. BUZZELLI, Anal. Chem., 36 (1964) 1973.

2. B. C. PURHAYASTHA and G. R. MORLIN, Canadian J. Chem., 34 (1956) 293.

3. M. KAHN and J. KLEINBERG, NAS-NS Monograph 3062 (1977).

4. N. LAVI, J. Radioanal. Chem., 20 (1974) 41.

5. T. J. ANDERSON, ASTM Standard Test Procedure 698, J. J. Kelly, ed. 1980.

6. B. KEISCH, R. C. KOCH, and A. S. LEVINE, Proc. of Intern. Conf. Modern Trends in Activation Analysis, College Station, Texas (1965) 284.

7. F. F. DYER and L. C. BATE, RISC Data Library Collection, ORNL-DLC-19 (1973).

8. J. F. EMERY and F. F. DYER, Proc. 2nd Intern. Conf. on Nucl. Methods in Environmental Research, Columbia, MO., (1974) 123.

9. W. S. LYON, JR., ed., Guide to Activation Analysis, Robert E. Krieger Publishing Co., Huntington, N.Y. (1972).

10. ORNL Master Analytical Manual, Method No. 2 21391-1 (1965).

11. F. P. BRAUER and J. H. KAYE, Trans. Nucl. Sci., NS-21, No. 1 (1974) 496.

12. G. FRIEDLANDER, J. W. KENNEDY, and J. M. MILLER, Nuclear and Radiochemistry, Wiley, New York (1964) 209.

13. R. C. DeGEISO, et al., Anal. Chem. 26 (1954) 1840.

14. R. W. ATTEBERRY and G. E. BOYD, J. Am. Chem. Soc., 72 (1950) 4805.

15. W. RIEMANN III, Record of Chemical Progress, 15 (1954) 85.

Table I. Elution of halides from resin column
with 0.1 $\underline{M}$ sodium nitrate

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

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

Concentration NaOH or HNO$_3$, N	Retention, %	
	Sodium hydroxide	Nitric acid
0.1	100	100
0.5	98	54
1	100	44
2	--	20
3	--	13
4	100	*
5	100	*

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

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

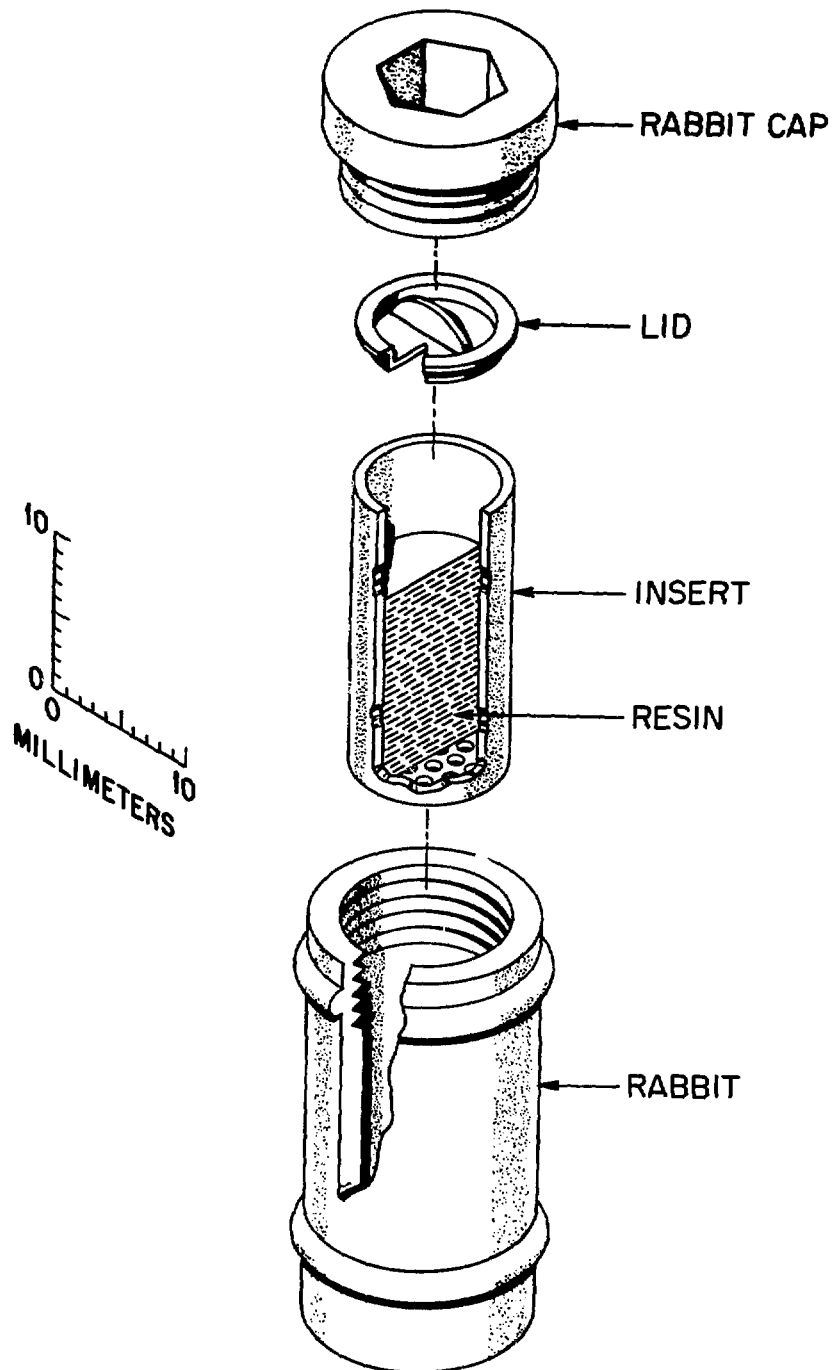| Sample No.	Irradiation site	^{129}I found, µgm/ml	Average deviation/mean, %
1981	HFIR	$1.40(\pm0.01)\times10^{-2}$	0.7
1983	HFIR	$1.96(\pm0.23)\times10^{-2}$	11.7
2081	HFIR	$1.39(\pm0.06)$	4.3
2105	HFIR	$3.17(\pm0.10)$	3,2
2154	HFIR	$40.9(\pm0.4)$	1.0
2203	ORR	$0.304(\pm0.012)$	3.9
2231	ORR	$0.154(\pm0.001)$	0.7
2234	ORR	$140(\pm4)$	2.8
2265	ORR	$0.344(\pm0.015)$	4.4
2270	ORR	$5.10(\pm0.08)$	1.6
2336	ORR	$23.8(\pm0.8)$	3.4
RSF*	HFIR	$8.28(\pm0.56)\times10^{-6}$	6.7
BG-5*	HFIR	$2.33(\pm0.46)\times10^{-6}$	19.7

*Average of four determinations.

FIGURES

Fig. 1. Polyethylene rabbit with resin column insert.

Fig. 2. Apparatus for loading iodine-129 on ion exchange column.

RABBIT CAP

LID

INSERT

RESIN

RABBIT

MILLIMETERS

INSERT COLUMN
AND RESIN

RUBBER STOPPER

VACUUM RELIEF

STOPCOCK

GLASS T

TO VACUUM

250 cc FLASK