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DETERMINATION OF ^{95}Zr AND ^{95}Nb IN MIXTURES OF THE TWO NUCLIDES

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ABSTRACT

A method based on decay measurements was developed to determine the relative amounts of zirconium-95 and niobium-95 in mixtures of the two nuclides. The method was tested on synthetic and process solutions; plutonium and ruthenium did not interfere.

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DETERMINATION OF ^{95}Zr AND ^{95}Nb IN MIXTURES OF THE TWO NUCLIDES

INTRODUCTION

Zirconium-95 and niobium-95 are fission products that frequently limit decontamination in separations processes for the recovery of uranium and plutonium from irradiated nuclear fuels. Although the chemistry of zirconium and niobium are quite different, analysis of mixtures is often difficult, particularly in process solutions. The similarity of the gamma energies (0.724 and 0.757 Mev for ^{95}Zr, 0.768 Mev for ^{95}Nb) precludes the use of simple gamma-ray spectrometric techniques. A further difficulty is that in some process streams, particularly organic streams, both zirconium and niobium behave anomalously, and unless rigorous pretreatment of the samples is employed, there is no assurance that conventional wet chemical methods will actually achieve the desired separation. These nuclides are therefore usually determined together by gamma-ray spectrometry, and results are reported as activity due to a mixture of zirconium and niobium.

In studies of methods for improving the decontamination of separations processes, knowledge of the relative amounts of ^{95}Zr and ^{95}Nb in various process streams is mandatory. Some success was achieved with coincidence counting for such determinations,(1) but the presence of other nuclides that emit soft beta particles or gamma rays often interfered severely. On the other hand, these soft radiations do not interfere with measurement of the rates of growth and decay of the 0.75-Mev gamma peak, and these rates appeared to offer a convenient method for determining the relative amounts of ^{95}Zr and ^{95}Nb.

The present study was undertaken to develop such a method and to determine its applicability to process solutions. During the final stages of the work a similar method was reported in the literature.(2) The method described in the present report, however, was found to be more precise, less complicated, and more readily applicable to process solutions than that reported previously.

SUMMARY

A method was developed for determining ^{95}Zr and ^{95}Nb in mixtures of the two nuclides. The method consists of counting a sample and a standard composed of an equilibrium mixture of ^{95}Zr-^{95}Nb on a gamma-ray spectrometer both initially and after some specified interval. The fractions of ^{95}Zr and ^{95}Nb in the original ^{95}Zr-^{95}Nb mixture are then calculated from equations derived in this report.

Tests with synthetic mixtures of ^{95}Zr and ^{95}Nb at decay times of 7, 15, 22, and 29 days showed the absolute accuracy of the method to be about ±2% when adequate counting statistics (10^5 counts) were obtained. The accuracy after 7 days was about the same as that after 29 days. ^{106}Ru activity present in amounts three times that of ^{95}Zr-^{95}Nb did not interfere.

Tests with process solutions containing small amounts of ^{95}Zr-^{95}Nb [$4\text{-}12 \times 10^3$ c/(min)(ml)] and ruthenium, and larger amounts of ^{239}Pu [10^8 d/(min)(ml)] gave an average relative standard deviation of ±3.5% with a maximum of ±5.2%.

DISCUSSION

Method and Calculations

Samples were counted for ^{95}Zr-^{95}Nb gamma activity immediately after reception and periodically for thirty days thereafter. A standard consisting of an equilibrium mixture of ^{95}Zr and ^{95}Nb was counted on the same instrument under identical conditions immediately prior to counting the samples. This procedure was used to minimize the effects of fluctuations in counting efficiencies over long periods of time. The fraction of the total ^{95}Zr-^{95}Nb gamma counts due to ^{95}Zr was then calculated from the following equation:

$$f_{Zr} = \frac{1}{3.17}\left(\frac{Y - X}{1 - X}\right) \qquad (1)$$

Equation 2 was used to calculate the fraction of gamma counts due to ^{95}Nb.

$$f_{Nb} = 1 - f_{Zr} \qquad (2)$$

The terms of the equations are defined as follows:

f_{Zr}, f_{Nb} = the fractions of the ^{95}Zr-^{95}Nb gamma activity in the original sample due to ^{95}Zr and ^{95}Nb, respectively

$X = e^{-0.0091t}$

t = days after the original count was made

$Y = \frac{A(t)}{A(0)} \Big/ \frac{A_{std}(t)}{A_{std}(0)}$

$A(t)$ = the activity of the sample at time t

$A(0)$ = the initial activity of the sample

$A_{std}(t)$ = the activity of the standard at time t

$A_{std}(0)$ = the initial activity of the standard

The constant 0.0091 is the difference of the decay constants for niobium and zirconium, $\lambda_{Nb} = 1.98 \times 10^{-2}$ days^{-1} and $\lambda_{Zr} = 1.07 \times 10^{-2}$ days^{-1}.

A table of values of X vs. t and the derivation of Equations 1 and 2 are in the Appendix.

Analysis of Errors

Errors in the computation of f_{Zr} and f_{Nb} will arise from counting fluctuation, failure to count the sample and standard simultaneously, and uncertainties in the decay constants of ^{95}Zr and ^{95}Nb. Emphasis is placed on errors in the ^{95}Zr determination because ^{95}Nb is determined by difference.

Cork et al.(3) reported values for the half-lives of ^{95}Zr and ^{95}Nb as 65 ±1 days and 35 ±0.5 days, respectively. Propagation of these errors in the computation of f_{Zr} causes an uncertainty of about ±0.02 in f_{Zr}. This error is a bias in the method and can be reduced if more precise values of the half-lives become available.

Errors in f_{Zr} due to counting fluctuation are represented by the following equation:

$$\sigma_{f_{Zr}} = \frac{1}{3.17}\left(\frac{\sigma_Y}{1 - X}\right)$$

The relative error in Y, σ_Y/Y, is twice the relative counting error of any one of the measured quantities used to calculate Y providing all measurements are made to about the same total number of counts. Since the relative counting error, σ_A/A, is the reciprocal of the square root of the total number of counts, C, the error in f_{Zr} can be expressed as follows:

$$\sigma_{f_{Zr}} = \frac{2}{\sqrt{C}}\left[f_{Zr} + \frac{1}{3.17}\left(\frac{X}{1 - X}\right)\right]$$

Although this equation shows that the error decreases as the counting interval increases, fairly reliable estimates of f_{Zr} or f_{Nb} can be obtained in reasonably short times if adequate counting statistics are obtained. For example, if the mixture contains equal amounts of ^{95}Zr and ^{95}Nb, and the total number of counts is 10^5 in each measurement, the errors in f_{Zr} or f_{Nb} would be only 0.033, 0.018, 0.012, and 0.009 after 7, 15, 22, and 30 days, respectively.

Errors in f_{Zr} due to uncertainty in time could arise from the fact that samples and standards must be counted over a finite time interval and from the fact that the sample and standard cannot be counted at precisely the same time. The first of these can be shown to be completely insignificant, compared to other sources of error, for counting times normally employed (up to several hours). The second can be eliminated if careful records of time are kept and suitable corrections are made, but it is worth considering just how precisely the time need be known to obtain adequate results with a minimum of effort.

If the sample is counted before and after an interval t, and the standard is counted after an interval t ±Δt, the error in f_{Zr} due to the difference in the time interval Δt, expressed in hours, is given by the following equation:

$$\sigma_{f_{Zr}} = \left[f_{Zr} + \frac{1}{3.17}\left(\frac{X}{1 - X}\right)\right] 0.26\ \Delta t$$

The factor 0.26 is the decay constant of ^{95}Zr in hours^{-1}. The interval Δt that will give rise to an error of any arbitrary size can readily be calculated from the above equation. For example, if $\sigma_{f_{Zr}}$ is set at ±0.01 (an error smaller than that caused by other sources) and f_{Zr} is one, Δt will be approximately 4, 8, 10, and 12 hours for total time intervals t of 7, 15, 22, and 30 days, respectively. Since samples and standards are counted both at the beginning and end of the interval t, the time difference Δt will be the sum of differences occurring at each end of the interval. The allowable interval between counting the sample and standard will therefore be just half of Δt.

Evaluation of the Method

The method was tested with synthetic mixtures of ^{95}Zr and ^{95}Nb that contained no other radionuclides, with equilibrium mixtures of ^{95}Zr and ^{95}Nb to which ^{106}Ru was added, and with a series of organic extracts from a miniature mixer-settler test of the Purex process.

The tracers ^{95}Nb, ^{106}Ru, and an equilibrium mixture of ^{95}Zr and ^{95}Nb were obtained from Oak Ridge National Laboratory. When pure ^{95}Zr was desired, it was separated from ^{95}Nb in the equilibrium mixture by extraction into thenoyltrifluoroacetone immediately before use. Synthetic mixtures were prepared by mixing known amounts of pure ^{95}Zr, ^{95}Nb, and ^{106}Ru activities. In the test made to determine the effect of ruthenium on the method, the ^{106}Ru activity was three times that of the ^{95}Zr-^{95}Nb activity.

All samples were counted in a well-type gamma scintillation counter in conjunction with a 256-channel pulse height analyzer. Photopeak boundaries were selected as 0.68 and 0.90 Mev. When ^{106}Ru was present, corrections were made for the slight interference of ruthenium on the

^{95}Zr-^{95}Nb peak. In the series of experiments with synthetic mixtures, the counting error was held to only 0.3% by accumulating 10^5 counts within the photopeak boundaries. The process samples were counted to only about 10^4 counts, so a counting error of about 1% resulted. All samples were counted at intervals over a period of 30 days. The standard ^{95}Zr-^{95}Nb equilibrium mixture was counted similarly and always within two hours of the samples. Values of f_{Zr} were calculated from Equation 1 and are reported as % Zr (100 x f_{Zr}) in the tables. The % Nb is merely the difference between % Zr and 100.

RESULTS

The results of tests with synthetic mixtures are summarized in Table I. Each of the values in columns 2, 3, 4, and 5 (% Zr found) is the average of two measurements. The standard deviations at the bottom of the table are the root mean squares of the deviations of these measured values from the appropriate average, and give the measure of the precision after the number of days indicated at the top of each column. The quantities labeled "RMS Bias" are the root mean squares of the biases of the quantities in each column and give a measure of the absolute accuracy of the method after the designated time intervals.

Table I

Determination of ^{95}Zr in Synthetic Mixtures

Zr Added, %	Zr Found, %					Std Dev	Bias
	7 Days	15 Days	22 Days	29 Days	Avg		
0.0	0.1	0.9	0.1	1.3	0.6	0.5	+0.6
4.5	7.0	7.8	6.5	5.9	6.8	0.7	+2.3
9.3	11.4	11.8	9.3	9.6	10.5	1.1	+1.2
14.4	13.7	16.4	14.5	14.9	14.9	1.0	+0.5
31.6	31.8	32.4	31.2	32.6	32.0	0.6	+0.4
31.6(a)	32.9	30.5	33.0	34.9	32.8	1.6	+1.2
100.0	100.6	94.9	96.3	99.8	97.9	2.4	-2.1
Std Dev:	0.6	0.8	0.8	0.7			
RMS Bias:	1.4	2.7	1.7	1.5			

(a) Contained three times as much ^{106}Ru activity as ^{95}Zr-^{95}Nb activity.

Examination of these quantities reveals that the RMS bias is about twice that of the standard deviation and that neither quantity changes greatly with time, so the precision and accuracy are as good after 7 days as they are after 29 days. However, the precision after 7 days is somewhat better than predicted.

The standard deviations and biases at the right of the table are those calculated from averages of results over the different time intervals. The biases are all positive except for the one at 100% Zr; therefore, a small error in the constants used in Equation 1 might be involved, but since the standard deviations are of the same size as the biases, modification of the constants is not worthwhile. The over-all standard deviation and RMS bias were 1.3 and 1.4, respectively, and are in good agreement with calculated values based on counting statistics for 10^5 counts. The results obtained on solutions containing ^{106}Ru showed ^{106}Ru had little if any effect on the precision or accuracy. Generally, the experimental data indicate the determination of ^{95}Zr and ^{95}Nb will be accurate to ±2%.

Table II contains the results of measurements made on organic streams from a miniature mixer-settler test of the Purex process. These samples contained between 4×10^3 and 12×10^3 c/(min)(ml) of

Table II

Determination of ^{95}Zr in Process Solutions

	Zr Found, %					
Sample	7 Days	15 Days	22 Days	29 Days	Avg	Std Dev
1	-	66	72	69	69	2.5
2	69	59	69	-	66	4.6
3	72	73	69	62	69	4.2
4	-	75	74	72	74	1.3
5	76	68	70	74	72	3.2
6	85	85	82	81	83	1.8
7	84	70	78	77	77	5.0
8	-	81	83	82	82	1.0
9	-	88	93	91	90	2.2
10	72	67	68	-	69	2.2
11	-	68	75	73	72	3.0
12	81	68	78	71	75	5.2
					Mean	3.5

^{95}Zr-^{95}Nb activity and approximately 10^8 c/(min)(ml) of ^{239}Pu alpha activity. The samples also contained ^{106}Ru and ^{103}Ru of activities between 4 and 0.2 times that of the ^{95}Zr-^{95}Nb. The precision of these results, which varies between 1 and 5%, is about that predicted on the basis of the number of counts used in each measurement. The results demonstrate that good precision can be obtained with rather small amounts of ^{95}Zr-^{95}Nb in the presence of large quantities of ^{239}Pu and significant amounts of ^{103}Ru and ^{106}Ru gamma activities.

APPENDIX

DERIVATION OF EQUATION FOR CALCULATING THE ^{95}Zr FRACTION OF Zr-Nb GAMMA ACTIVITY

The equations for the activity due to ^{95}Zr and ^{95}Nb as a function of time, derivable from elementary principles of radioactive decay, are:

$$A_{Zr}(t) = A_{Zr}(0)\, e^{-\lambda_{Zr} t} \tag{1}$$

$$A_{Nb}(t) = A_{Zr}(0)\left(\frac{\lambda_{Nb}}{\lambda_{Nb} - \lambda_{Zr}}\right)\left(e^{-\lambda_{Zr} t} - e^{-\lambda_{Nb} t}\right) + A_{Nb}(0)\, e^{-\lambda_{Nb} t} \tag{2}$$

A(t) and A(0) are the activities in disintegrations per unit time at time t and time 0, respectively, and the λ's are the respective decay constants.

The total measured activity at time t, A(t), is the sum of that due to ^{95}Zr and ^{95}Nb

$$A(t) = A_{Zr}(t) + A_{Nb}(t) \tag{3}$$

and

$$A(0) = A_{Zr}(0) + A_{Nb}(0) \tag{3'}$$

The fractions of the total activity due to ^{95}Zr and ^{95}Nb are defined as follows:

$$f_{Zr} \equiv \frac{A_{Zr}(0)}{A(0)}$$

$$f_{Nb} \equiv \frac{A_{Nb}(0)}{A(0)}$$

From Equation 3' and the above definitions it follows that

$$f_{Zr} + f_{Nb} = 1 \tag{4}$$

If Equations 1, 2, 3, and 4 together with the definitions of f_{Zr} and f_{Nb} above are combined, the following is obtained:

$$\frac{A(t)}{A(0)} = f_{Zr}\left(1 + \frac{\lambda_{Nb}}{\lambda_{Nb} - \lambda_{Zr}}\right)\left(e^{-\lambda_{Zr}t} - e^{-\lambda_{Nb}t}\right) + e^{-\lambda_{Nb}t} \tag{5}$$

The decay expression for the standard as a parent nuclide with its daughter in transient equilibrium can be stated as:

$$\frac{A_{std}(t)}{A_{std}(0)} = e^{-\lambda_{Zr}t} \tag{6}$$

where A_{std} refers to the activity of the equilibrium mixture of ^{95}Zr and ^{95}Nb.

If Equation 5 is divided by Equation 6, the following results:

$$\frac{A(t)}{A(0)}\Big/\frac{A_{std}(t)}{A_{std}(0)} = f_{Zr}\left(1 + \frac{\lambda_{Nb}}{\lambda_{Nb} - \lambda_{Zr}}\right)\left(1 - e^{-(\lambda_{Nb} - \lambda_{Zr})t}\right) + e^{-(\lambda_{Nb} - \lambda_{Zr})t} \tag{7}$$

When the term on the left of Equation 7 is defined as Y, the values $\lambda_{Nb} = 1.98 \times 10^{-2}$ days^{-1} and $\lambda_{Zr} = 1.07 \times 10^{-2}$ days^{-1} are substituted, the term $e^{-0.0091t}$ is defined as X, and the equation is solved for f_{Zr}, the following results:

$$f_{Zr} = \frac{1}{3.17}\left(\frac{Y - X}{1 - X}\right) \tag{8}$$

Of course, f_{Nb} can be obtained from Equation 4 after f_{Zr} has been determined.

Values of X

Time, days	X	Time, days	X
1	0.991	16	0.864
2	0.982	17	0.856
3	0.973	18	0.849
4	0.964	19	0.841
5	0.956	20	0.834
6	0.947	21	0.826
7	0.938	22	0.819
8	0.930	23	0.811
9	0.921	24	0.804
10	0.913	25	0.796
11	0.905	26	0.789
12	0.895	27	0.782
13	0.889	28	0.775
14	0.881	29	0.768
15	0.872	30	0.761

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