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A TEST FOR SOLVENT QUALITY

by

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Analytical Chemistry Division

August 1957

**E. I. du Pont de Nemours & Co.
Explosives Department - Atomic Energy Division
Technical Division - Savannah River Laboratory**

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ABSTRACT

A method was devised for determining the quality, or extent of degradation, of the solvent used in the extraction process for the recovery of uranium and plutonium from irradiated materials. The degradation products irreversibly complex zirconium, and the amount of degraded materials in the solvent is determined by equilibrating the solvent with a zirconium tracer solution of known activity and concentration. The amount of zirconium retained by the solvent is proportional to the amount of degraded materials and is determined by counting techniques.

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A TEST FOR SOLVENT QUALITY

INTRODUCTION

In the tributyl phosphate-kerosene extraction process for the recovery of uranium and plutonium from irradiated fuel, the solvent may be degraded to form materials that limit the extent to which certain fission products can be removed. Some of these degradation products arise from the kerosene diluent used in the solvent, are not removed from the solvent by caustic washing, and form very strong complexes with zirconium. Hence, a practical way to test for solvent quality would be to measure the essentially irreversible extraction of zirconium. An analytical test of this type is desirable since it would give warning of the accumulation of degradation materials and allow appropriate action to be taken before undesirable effects occur in the process.

SUMMARY

A method was devised to give a measure of the degradation products that appear in the solvent used in the extraction process for the recovery of uranium and plutonium from irradiated material. The method is referred to as the Zirconium Index Test. The value or "Z" number obtained from the test makes it possible to predict the performance of the solvent in the extraction process.

The method involves the equilibration of a portion of the solvent with a zirconium tracer solution of known concentration and activity. The equilibrated solvent is washed three times with nitric acid and an aliquot is mounted and counted. The activity remaining in the solvent and the known concentration and activity of the tracer are used to calculate the amount of zirconium retained by the solvent in moles per billion liters. This value is the "Z" number. *(cont.)*

DISCUSSION

BACKGROUND

In the earlier studies of the quality of tributyl phosphate-kerosene solvent, it was found that zirconium tracer that was extracted by degraded solvent was only partially removed by subsequent scrubbing with 3M nitric acid. The zirconium activity in the solvent decreased with the first two scrubs but remained essentially constant after the third.

It was found by an isotopic dilution technique that the total number of moles of zirconium retained per unit volume of solvent was dependent only on the previous history of the solvent; the greater the degree of degradation, the greater was the amount of zirconium retained. A measurement of the total concentration of zirconium retained by the degraded solvent after three scrubblings with nitric acid promised to be a satisfactory measure of the degree of degradation. Therefore, the Zirconium Index Test was devised for

determining the total concentration of retained zirconium.

OUTLINE OF METHOD

In the Zirconium Index Test, a zirconium tracer solution is adjusted to a specified concentration of inactive zirconium and is equilibrated with the tributyl phosphate-kerosene solvent. The solvent is then scrubbed three times with 3M nitric acid, and a sample of the solvent is counted for zirconium beta activity. The concentration of zirconium retained in the solvent is calculated from the known ratio in the tracer of radioactive zirconium to total zirconium. The "Z" number is then defined as the concentration of zirconium retained by the solvent in moles per billion liters.

The detailed procedure for the Zirconium Index Test, including the preparation of the tracer solution and the method used to analyze the zirconium tracer solution, is described in the Appendix.

PRELIMINARY TREATMENT OF SOLVENT

The residual activity in the solvent must be reduced to a minimum before proceeding with the Zirconium Index Test. This cleanup is done by washing the solvent with 1M sodium hydroxide. To minimize the time required for a determination of the "Z" number, the time and number of sodium hydroxide washings must be kept at a minimum.

For solvent having a "Z" number less than 200, one 5-minute washing is sufficient. Solvent having a "Z" number between 200 and 300 requires three 15-minute washings. Solvent that is more highly degraded ("Z" numbers greater than 300) requires a more drastic treatment. It is necessary to heat this solvent in a steel container with 1M sodium hydroxide for one hour at 100°C under reflux. The steel container is used because of the corrosive action of the alkali on glass at the elevated temperature.

EQUILIBRATION OF SOLVENT AND TRACER

The following experiments were performed to establish the time required for the washed solvent and tracer solution to reach equilibrium. Two ml of the solvent and 2 ml of the tracer solution were stirred for periods ranging from 2 to 35 minutes. After the phases were allowed to separate for five minutes, aliquots of the organic layer were counted. Equilibrium was reached in less than ten minutes. In the Zirconium Index Test, a stirring time of 15 minutes was recommended.

SOLVENT-TRACER EQUILIBRATION MEASUREMENTS

Equilibration Time, min.	Beta c/m in Solvent			
	Run #1	Run #2	Run #3	Run #4
0	0	0	0	0
2	2970	3190	--	--
5	3180	3250	--	--
10	3230	3480	980	12,700
15	--	3440	--	11,100
18	--	--	--	12,800
20	3590	3550	--	11,100
30	3300	--	1020	12,700
35	--	--	990	--

ACID SCRUB OF EQUILIBRATED SOLVENT

The equilibrated solvent is scrubbed with 3M nitric acid to remove the zirconium that is reversibly held by the tributyl phosphate. The only zirconium then remaining is that retained by the degradation products of the solvent. To keep the time required for a "Z" number determination at a minimum, it is necessary to use the smallest number of acid scrubs with the shortest possible time per scrub.

It was shown in the earlier stages of the investigation that the activity in 2 ml of solvent was reduced to a constant value after three 15-minute scrubs with 5 ml of 3M nitric acid. In the table below, the results of this treatment are compared to those obtained after two five-minute scrubs.

The more extensive acid scrub was recommended in the Zirconium Index Test. The results of the shorter scrub agreed essentially with the longer acid scrub method for solvent with high "Z" numbers ("Z" about 250), but the results from solvent with low "Z" numbers ("Z" about 40) were approximately 50 per cent high. In one series of experiments, virgin solvent was used. After this solvent was equilibrated with tracer the longer scrub time did not completely remove the activity but did reduce it to such an extent that the "Z" numbers ranged from three to six.

ACID SCRUB OF EQUILIBRATED SOLVENT

Solvent	Two 5-min. Scrubs,	Three 15-min. Scrubs,
	"Z" Number	"Z" Number
High "Z"	261	252
Low "Z"	62	43
Virgin	18	6
Virgin	16	3

PRECISION OF THE ZIRCONIUM INDEX TEST

The precision of the Zirconium Index Test was determined from four results on solvent of low "Z" number and from ten results on solvent of high "Z" number. The low "Z" values gave an average of 44 and a standard deviation of 1.5 (3.4 per cent). The high "Z" values gave an average of 261 and a standard deviation of 3.5 (1.3 per cent).

PRECISION OF ZIRCONIUM INDEX TEST

<u>Low "Z" Solvent, "Z" Number</u>	<u>High "Z" Solvent, "Z" Number</u>	
43	261	259
43	254	260
43	267	262
46	264	263
	260	259
Average 44	261	
Std. Deviation 1.5 (3.4%)	3.5 (1.3%)	

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APPENDIX A

ZIRCONIUM INDEX TEST

Section I - Preparation and Standardization of Zirconium Tracer Solution

Place 200 microliters of Zr-Nb tracer in a "Dri-Filmed*" 50-ml Erlenmeyer flask and add 20 ml of concentrated nitric acid. Heat this solution below boiling until approximately 50 per cent is evaporated. While continuing to heat, add slowly ten 1-ml aliquots of 30 per cent hydrogen peroxide over a period of about 15 minutes. Wait until the reaction has subsided before adding the next aliquot. Evaporate the solution to near dryness and repeat the operation three times. Do not evaporate to dryness at any time. Dilute with 25 ml of 3M nitric acid and analyze for total zirconium by the Chloranilic Acid Method as described in Appendix B. Finally dilute with 3M nitric acid to make the zirconium concentration $0.4 \mu\text{g} \pm 0.1 \mu\text{g}$ per ml and store in a "Dri-Filmed" container. The pipets and extraction vessels used throughout the remainder of the determination must also be "Dri-Filmed". Calculate the reciprocal specific activity of the zirconium tracer by the following procedure:

1. Mount a suitable aliquot of the $0.4 \mu\text{g}/\text{ml}$ zirconium tracer solution in a stainless steel dish and cover with "Scotch" tape.
2. Count on the gamma scintillation counter and record the net gamma c/m.
3. Count through 20 and 110 mg/cm^2 aluminum absorbers on the GM counter. Record the net c/m through the two absorbers.

The net zirconium beta activity is

$$A, \text{ c}/(\text{m-ml}) = \frac{(\text{c/m through } 20 \text{ mg}/\text{cm}^2) - (\text{c/m through } 110 \text{ mg}/\text{cm}^2)}{\text{sample size, ml}}$$

*Treated with "Dri-Film", a silicone product manufactured by General Electric Company.

Reciprocal specific activity of Zr (mmoles/beta c/m)* =

$$\frac{\text{Zr concentration**}, \text{ mmoles/ml}}{\text{A, c/(m-ml)}}$$

A factor B that is the ratio of the Zr-Nb gamma contribution on the GM counter to the Zr-Nb gamma counting rate on the scintillation counter is calculated for the tracer sample,

$$B = \frac{(\text{c/m through } 110 \text{ mg/cm}^2 \text{ on the GM counter})}{(\text{gamma c/m on the scintillation counter})}$$

This factor is used later in the calculation of "Z" to correct the beta counting rate of any sample for the contribution of the gamma activity in order to obtain the net zirconium beta count. The factor is constant with constant counting conditions so that once a good value for B is established, this calculation may be discontinued.

Section II - Preparation of Sample

Place 10 ml of the solvent in an extraction vessel and wash for five minutes with 15 ml of 1M sodium hydroxide. Allow the phases to separate and remove the aqueous phase. Wash the solvent for five minutes with 15 ml of water and allow to stand for five minutes. Equilibrate for five minutes with 10 ml of 3M nitric acid and discard the aqueous phase (Note 1).

Section III - Correction for Ruthenium Beta Activity

Ruthenium retained in the solvent contributes to the beta counting rate. In the analysis of a sample it is necessary to correct the beta counting rate for the ruthenium contribution in order to determine the net zirconium beta count. It is essential that all of the zirconium be washed from the solvent before data are obtained for the correction factor. Otherwise, the factor is not valid. If the washing described in Section II does not completely remove zirconium, then the more drastic treatment given in Note 1 is necessary.

*The reciprocal specific activity of the tracer solution changes with time due to the decay of Zr-95. Corrections for the decay of Zr-95 must be applied or the activity must be redetermined at intervals of about seven days.

**The Zr concentration is the molar concentration of the Zr in the final dilution of the tracer solution. That is,

$$\frac{0.4 \pm 0.1 \text{ } \mu\text{g/ml}}{9.5 \times 10^4 \text{ } \mu\text{g Zr/mole}} = \text{Zr, mmoles/ml}$$

The ruthenium beta correction involves the ratio of the ruthenium beta counts through the two aluminum absorbers. This ratio C is a constant for constant Ru-103/Ru-106 ratios and should be determined on typical solvent over a period of time to establish any variation in the ratio. If the results show insignificant variations, a constant value for C should be used and this calculation should be discontinued.

Determine C as follows:

1. Mount a 500-microliter sample of the washed solvent from Section II in a stainless steel counting dish and cover with "Scotch" tape.
2. Count on the gamma scintillation counter and record the net gamma c/m.
3. Count through 20 and 110 mg/cm² aluminum absorbers on the GM counter. Record the net c/m through the two absorbers.

The ratio C of the ruthenium beta count through the 20 mg/cm² absorber to the ruthenium beta count through the 110 mg/cm² absorber is calculated as follows:

$$C = \frac{(c/m \text{ through } 20 \text{ mg/cm}^2) - (B)(\text{gamma c/m})}{(c/m \text{ through } 110 \text{ mg/cm}^2) - (B)(\text{gamma c/m})}$$

where B is the ratio from Section I.

Section IV - Determination of "Z" Number

1. Place 2 ml of zirconium tracer solution in the extraction vessel (see figure) and add 2 ml of washed solvent from Section II. The extraction vessel, pipets, and other equipment that contacts the zirconium solution must be thoroughly "Dri-Filmed".
2. Stir the solution for 15 minutes.
3. Lower the extraction vessel until the stirrer is above the liquid.
4. Turn off the stirrer and allow to stand undisturbed for five minutes.
5. Drain off and discard the aqueous layer.
6. Add 5 ml of 3M nitric acid and stir for 15 minutes.
7. Repeat Steps 3, 4, and 5.
8. Wash the organic phase for a total of three times with 5 ml of 3M nitric acid as in Steps 6 and 7.

9. Allow phases to separate for 15 minutes and mount a 500-microliter aliquot of the organic phase in a stainless steel dish for counting.
10. Count through a 20 mg/cm² aluminum absorber on the GM counter.
11. Count through a 110 mg/cm² aluminum absorber on the GM counter.
12. Count on the gamma scintillation counter and record as net gamma c/m.
13. Calculate the net zirconium beta c/(m-ml) as follows:

$$\text{net Zr beta c/(m-ml) =}$$

$$\frac{(\text{c/m through } 20 \text{ mg/cm}^2) - (C)(\text{c/m through } 110 \text{ mg/cm}^2) - (B)(1-C)(\text{gamma c/m})}{\text{volume sample mount, ml}}$$

where B is taken from Section I and
C is taken from Section III.

14. Calculate the "Z" number as follows:

$$\text{Zr retained, moles/liter (E) =}$$

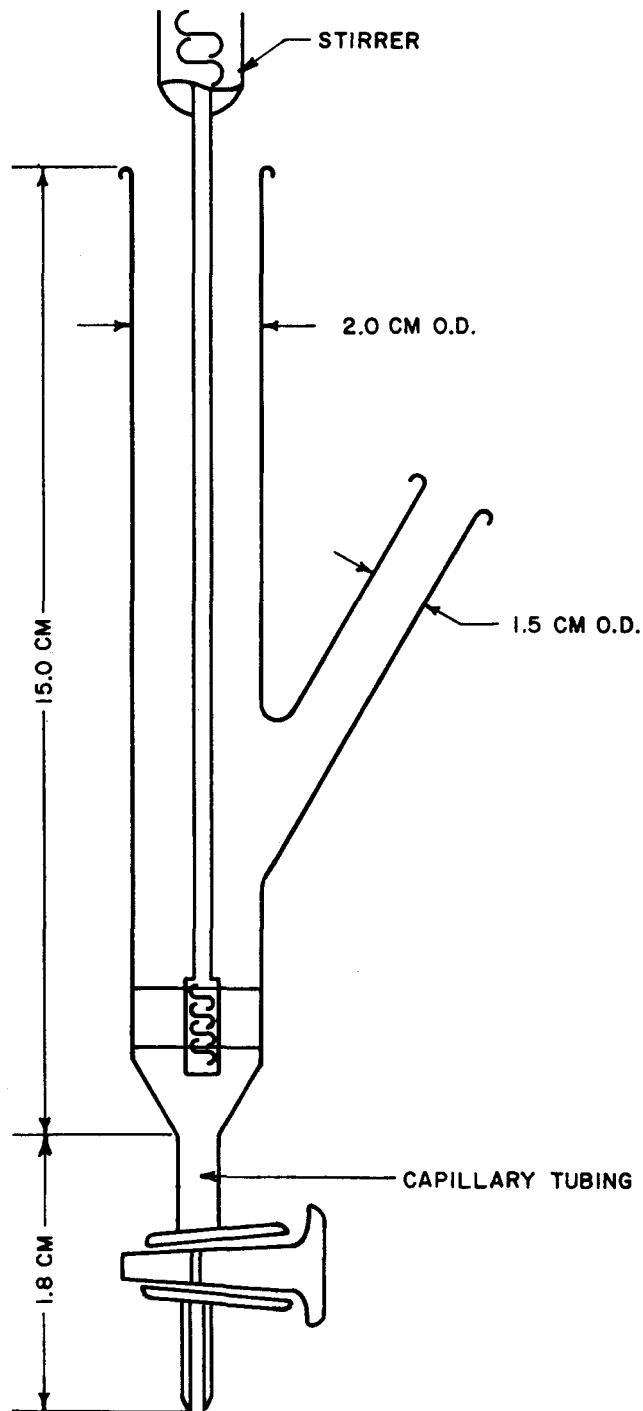
$$\frac{\text{net Zr beta c/(m-ml)} \times \text{reciprocal specific activity of tracer Zr, mmoles/beta c/m}}{\text{"Z" number} = (E)(10^9)}$$

Section V - Additional Steps Required for Samples of High "Z" Number

If the "Z" number is greater than 100, determine the zirconium beta activity of the washed solvent by counting a 500 microliter sample on the GM counter and on the gamma scintillation counter. Calculate the net zirconium beta c/m-ml from the equation given in Step 13 of Section IV. The value used for C in this calculation is the "normal" value that was previously established for typical solvent free of zirconium activity. If the zirconium beta counts in the washed solvent are above ten per cent of the net zirconium beta counts found in Step 13 of Section IV, rewash the solvent until the value is below ten per cent and repeat the determination of "Z".

Note 1

High "Z" number solvent ("Z" number greater than 300) that is contaminated with process zirconium may require a more drastic caustic treatment to remove zirconium. Zirconium is removed from these solvents by heating with 1M sodium hydroxide for one hour at 100°C. The solvent-caustic mixture is heated under reflux in a steel container. A glass container is not recommended because of the corrosive action of the caustic solution on glass at the elevated temperature.



EXTRACTION VESSEL

APPENDIX B

CHLORANILIC ACID METHOD FOR THE DETERMINATION OF ZIRCONIUM IN TRACER SOLUTIONS

The Chloranilic Acid Method, developed by Menis* for the determination of zirconium, was modified to tolerate the presence of nitric acid. This method is especially sensitive to the concentration of nitric acid. A relative error of one per cent in acidity causes 0.8 per cent error in the zirconium analysis. Therefore, the acidity must be carefully controlled. The zirconium-chloranilic acid complex is stabilized by the addition of sulfamic acid which renders the complex stable for several days. Without the stabilizing agent, nitric acid at the concentration required by the Zirconium Index Test destroys both the complex and the chloranilic acid almost immediately.

The Chloranilic Acid Method is also sensitive to the concentration of oxalic acid. Since the tracer as received from Oak Ridge is in 0.5M oxalic acid, the oxalate must be destroyed as described in Section I of the Zirconium Index Test. The maximum permissible oxalate to zirconium concentration ratio is about 20/1; at this value the error is six per cent.

A standard curve is prepared by plotting the log of the transmission at 340 m μ versus the concentration for solutions of known zirconium content. The unknown samples should contain exactly the same reagent concentrations as the standard solutions. After the transmission of the unknown is measured, the concentration is read directly from the standard curve.

Section I - Preparation of Reagents and Standard Curve

A. Chloranilic Acid (2,5-dichloro-3,6-dihydroxy-p-quinone)

1. Purification: The practical grade chloranilic acid is purified in the manner described by Menis*.
 - (a) Dissolve 8 g of the reagent in one liter of boiling water and filter while hot.
 - (b) Extract the filtrate at 50°C with two 200-ml portions of benzene in a two-liter separatory funnel. Discard the benzene phase.
 - (c) Cool the aqueous phase in an ice bath until crystallization is complete. Filter off the crystals of the reagent and wash the crystals with three 10-ml portions of distilled water.
 - (d) Dry the crystals at 115°C.

*Menis, O. The Determination of Zirconium by the Chloranilic Acid Method. Oak Ridge National Laboratory, ORNL-1626, April 7, 1954.

2. Preparation of Solution: Dissolve 900 mg of the reagent with distilled water in a one-liter volumetric flask and dilute to the mark (Note 1).

B. Standard Zirconium Stock Solution

1. Dissolve 0.2930 g of C.P. grade zirconyl nitrate, $ZrO(NO_3)_2 \cdot 2H_2O$, in 187 ml of concentrated nitric acid in a 250-ml beaker. It may be necessary to warm the acid.
2. After the zirconyl nitrate is completely dissolved, transfer the solution to a one-liter volumetric flask. Wash the beaker with three 25-ml portions of distilled water and add the washings to the flask. Allow the solution to cool to room temperature, then dilute to the mark with distilled water (Note 2).

C. Sulfamic Acid Solution

1. Dissolve 4.8 g of C.P. grade sulfamic acid with distilled water in a 100-ml volumetric flask.
2. Dilute to the mark with distilled water. This gives a 0.5M sulfamic acid solution.

D. Standard Curve

1. Prepare five zirconium solutions and a blank according to the table below. Use 10-ml volumetric flasks (Note 3). Add the reagents in the order given in the table, that is, concentrated nitric acid first, then sulfamic acid, chloranilic acid, and zirconium stock solution. Finally, dilute to the mark with distilled water, mix thoroughly, and let stand 15 to 30 minutes.

SOLUTIONS FOR STANDARD CURVE

<u>Reagents</u>	<u>Zr Concentration, $\mu\text{g}/\text{ml}$ in final 10-ml dilution</u>					
	<u>Blank</u>	<u>0.25</u>	<u>0.50</u>	<u>1.0</u>	<u>1.5</u>	<u>2.0</u>
Conc. HNO_3 , ml	1.88	1.87	1.87	1.86	1.85	1.84
Sulfamic Acid, ml	2.0	2.0	2.0	2.0	2.0	2.0
Chloranilic Acid, ml	4.0	4.0	4.0	4.0	4.0	4.0
Zr Stock Solution, μl	--	25	50	100	150	200

2. With the solutions in 1-cm quartz absorption cells, measure the transmission of the zirconium standards against the blank which contains all the reagents except zirconium. Measurements are made with a Beckman DU Quartz Spectrophotometer at a wavelength of 340 μ and a slit width of 0.7 mm.

3. Plot log per cent transmission versus concentration. The points should fall on a straight line which passes through the 100 per cent transmission point at zero concentration.

Section II - Analysis of Tracer Solutions

Pretreatment of the zirconium tracer solution with concentrated nitric acid and 30 per cent hydrogen peroxide is required as directed in the Zirconium Index Test. It is necessary that the final evaporation be carried as nearly to dryness as possible so that the resultant solution after the addition of the 25 ml of 3M nitric acid will still be very close to 3M.

- A. Prepare a blank solution identical to the one used in the preparation of the standard curve.
- B. Add to each of three 10-ml volumetric flasks the following reagents in the order given (Note 3):

Concentrated nitric acid	1.41 ml
Sulfamic acid	2.0 ml
Chloranilic acid	4.0 ml
Treated Zr tracer	2.5 ml

Dilute to the mark with distilled water, mix thoroughly, and let stand 15 to 30 minutes.

- C. With the solutions in 1-cm quartz absorption cells, measure the transmission of the tracer solutions against the blank. Measurements are made with a Beckman DU Quartz Spectrophotometer at a wavelength setting of 340 m μ and a slit width of 0.7 mm. The concentration, in $\mu\text{g/ml}$, of the solutions from the 10-ml volumetric flasks is read directly from the standard curve. If this concentration is $n \mu\text{g/ml}$, then the concentration of the treated tracer solution is $4n \mu\text{g/ml}$ (Note 4).

Note 1

Since the chloranilic acid solution absorbs at the wavelength at which measurements are made, the reagent used to obtain data for the standard curve and that used in the analysis of the unknowns should come from the same stock solution. The solution is stable for two to four weeks, but after the first week, a sample of standard zirconium solution of known zirconium concentration should be run at the same time the unknown is analyzed to insure that the standard curve is still valid.

Note 2

This solution contains zirconium at a concentration of 100 $\mu\text{g/ml}$ in 3M nitric acid. The specified quality of the zirconyl nitrate is such that gravimetric standardization is not necessary. Any loss in concentration of zirconium due to deposition on the walls of the

container is negligible up to a period of one month. After that time a fresh stock solution should be prepared.

Note 3

The 10-ml volumetric flasks and the quartz absorption cells should not be "Dri-Filmed". Freshly "Dri-Filmed" surfaces react instantly with concentrated nitric acid to produce a yellow solution which may give an indicated zirconium concentration several hundred per cent high. The zirconium does not deposit on the walls of the 10-ml volumetric flasks or the absorption cells because of the formation of the zirconium-chloranilic acid complex.

Note 4

Considerable variations have been observed in the concentration of zirconium tracer solutions from different stock bottles. It is desirable that the concentration of the solutions in the 10-ml volumetric flasks be between 0.15 and 2.0 $\mu\text{g/ml}$, since at lower concentrations the standard curve is difficult to read accurately. At higher concentrations, the solutions do not obey Beer's law.

If the concentration is greater than 2.0 $\mu\text{g/ml}$, the volume of the tracer aliquot is reduced from 2.5 ml to a value that will bring the concentration within the desired range. Samples requiring such a reduction in aliquot size also require a correction to the amount of concentrated nitric acid added to the 10-ml volumetric flask in order to maintain the acidity of 3M. If v ml of treated tracer solution are used, then $1.88(1-0.1 v)$ ml of concentrated acid are substituted for the 1.41 ml in Step 2 of Section II. The concentration of the treated tracer solution is then $10 n/v$ ($\mu\text{g/ml}$), where n is the $\mu\text{g/ml}$ concentration in the 10-ml volumetric flask.

Although the minimum desirable concentration is 0.15 $\mu\text{g/ml}$, satisfactory analyses can be made down to about 0.1 $\mu\text{g/ml}$. Because the maximum volume of treated tracer solution which can be added to the 10-ml volumetric flask is 2.5 ml, only two alternatives are available in the low concentration range: (1) add sufficient inactive zirconium stock solution to the tracer solution to bring the total zirconium concentration to the desired level or (2) increase the volume of the tracer solution withdrawn from the stock bottle for treatment with nitric acid and peroxide.

The choice between (1) and (2) is based primarily on the activity of the tracer solution. If the activity is very high, resulting in a reciprocal specific activity of much less than 1×10^{-11} mmoles/beta c/m, the first alternative is the better one. If the activity of the tracer solution is low, resulting in a reciprocal specific activity larger than 2×10^{-10} mmoles/beta c/m, then the second alternative is preferred.

In any event, the final concentration adjustment for use in the "Z" number determination is to $0.4 \mu\text{g/ml} \pm 0.1 \mu\text{g/ml}$ with a reciprocal specific activity between 1×10^{-11} and 2×10^{-10} mmoles/beta c/m.