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THE DETERMINATION OF RADIOACTIVE
ZIRCONIUM IN FISSION PRODUCTS

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Introduction

The method commonly used for the determination of radioactive zirconium (Zr^{95}) in fission products is the Barium Fluozirconate Method devised by Hume.¹ In this procedure zirconium is separated from other activities by precipitation as insoluble barium fluozirconate followed by a final precipitation with cupferron. This precipitate is ignited to zirconium dioxide which is then weighed and counted. This method gives excellent separations from other activities. The only disadvantage of the method lies in the use of cupferron. Cupferron² (the ammonium salt of nitroso phenyl hydroxylamine) is unstable in water, hence solutions must be prepared freshly before use, or must be stored under refrigeration. The cupferron-zirconium precipitate is bulky and spatters badly upon ignition. Because of these disadvantages other reagents were considered. Those which seemed most promising were mandelic acid and its derivatives.

Kumins³ showed that mandelic acid was a specific precipitant for zirconium and devised a procedure for the determination of zirconium in the presence of various interfering

¹ Hume, D. N., "Determination of Zirconium Activity in Fission by the Barium Fluozirconate Method," Paper 245, ed. by Coryell and Sugarman in "Radiochemical Studies: The Fission Products," Book 3, National Nuclear Energy Series, McGraw-Hill, New York, 1951, p. 1499.

² Smith, G. F., "Cupferron and Neo-Cupferron" G. F. Smith Chemical Co., Columbus, Ohio, 1938, page 12.

³ Kumins, C. A., Anal. Chem., 19, 376 (1947).

elements. Hahn,⁴ who used mandelic acid in the determination of small amounts of zirconium, showed that hafnium was likewise precipitated by mandelic acid. Astanina and Ostroumov⁵ also found that under controlled conditions the zirconium mandelate could be weighed directly without an ignition to the oxide.

Since Krumins³ showed that the zirconium was precipitated by mandelic acid as the tetramandelate, it was deemed unnecessary to carry out an extensive investigation as to the nature of the complex precipitate, and, therefore, the work was mostly confined to the application of mandelic acid to the determination of radioactive zirconium.

Solutions. A standard zirconium solution containing 9.36 mg. of zirconium per ml. was prepared by dissolving 15 g. of zirconyl nitrate (Eimer and Amend, C. P., molecular weight 267.268) in 500 ml. of distilled water and then standardizing by the cupferron method described by Hume.¹

A lanthanum carrier solution containing approximately 10 mg. of lanthanum per ml. was prepared by dissolving 7.8 g. of lanthanum nitrate (Fisher Scientific, C. P., molecular weight 433.04) in 250 ml. of distilled water.

A barium carrier solution containing 50 mg. of barium per ml. was prepared by dissolving 23.8 g. of barium nitrate

⁴ Hahn, R. B., Anal. Chem., 21, 1579 (1949).

⁵ Astanina, A. A., and Ostroumov, E. A., Zhur. Anal. Khim., 6, 27 (1951) in CA, 45, 6121 (1951).

(Merck, reagent, molecular weight 261.38) in 250 ml. of distilled water.

A 5% boric acid solution was prepared by dissolving 5 g. of boric acid (Baker's Analyzed, C. P., molecular weight 61.84) in 100 ml. of distilled water.

A 6% solution of cupferron was prepared by dissolving 6 g. of cupferron (Eastman Kodak Company, molecular weight 156.16) in 100 ml. of distilled water. This solution was stored in a refrigerator to prevent decomposition.

A 16% mandelic acid solution was prepared by dissolving 16 g. of mandelic acid (Eastman Kodak Company, molecular weight 152.14) per 100 ml. of distilled water. A 5% mandelic acid-2% hydrochloric acid wash solution was prepared by dissolving 50 g. of the solid acid and 48.5 ml. of concentrated hydrochloric acid in distilled water and diluting to one liter.

A Zr^{95} - Nb^{95} solution was obtained from the Oak Ridge National Laboratory. A solution was prepared by diluting 0.3 ml. of the isotopic mixture to 50 ml. with a mixture of hydrochloric acid and oxalic acid. The total beta activity was found to be 584,000 counts per minute per ml.

Preliminary Study of the Use of Mandelic Acid in the Determination of Radioactive Zirconium. A preliminary study was made to determine if the zirconium would be satisfactorily precipitated by mandelic acid under the conditions which would be present according to the planned modifications in the barium fluozirconate method. In this determination,

2 ml. of barium carrier solution was well mixed in a luster-
oid tube with 4 ml. of standard zirconium solution, and the
mixture was treated with 2 ml. of concentrated hydrofluoric
acid and mixed again. After standing for one minute, the
precipitate was centrifuged and the supernate was discarded.
The precipitated barium fluozirconate was suspended in 10 ml.
of water and 4 ml. of 5% boric acid and dissolved with 6 ml.
of concentrated hydrochloric acid. Two drops of concentrated
sulphuric acid was added to remove the excess barium, the
mixture was centrifuged and the supernate was decanted into
a glass centrifuge tube. Two normal sodium hydroxide was
added until a permanent precipitate was formed, the solution
was centrifuged, the supernate discarded, and the precipi-
tated zirconium hydroxide washed by decantation with a
dilute solution of sodium hydroxide. The zirconium hydroxide
was then dissolved in 10 ml. of concentrated hydrochloric
acid, the solution treated with 25 ml. of 16% mandelic acid,
and then diluted with water to a total volume of 50 ml.
This solution was gradually heated to about 85°C. and kept
at that temperature for 20 minutes. The precipitate was then
filtered through a Hirsch funnel on a previously weighed
filter paper, washed successively with hot 5% mandelic acid-
2% hydrochloric acid wash solution, absolute ethyl alcohol,
and ethyl ether. The precipitate and filter paper were
transferred to a weighed 25 mm. watch glass, dried under a
heat lamp for 5 minutes, and weighed. The weight of the

zirconium tetramandelate was 238.1 mg., equivalent to a yield of 83.4%, which was considered satisfactory since the loss of zirconium could be attributed to the slight solubility of the barium fluozirconate formed in the step prior to the final precipitation. The precipitate was then ignited to the oxide to check the purity of the zirconium tetramandelate. The theoretical weight of zirconium oxide calculated from the tetramandelate was 42.2 mg., while the actual weight of zirconium oxide obtained was 42.3 mg. The conclusion drawn was that reliable results were possible with the modified procedure, and that further investigation of the method would be worthwhile.

Determination of the Amount of Carrier Suitable for Radiochemical Study. It was shown⁶ that the best results were obtained in a radiochemical separation if the amount of carrier element was such that the final precipitate to be mounted weighed from 4 to 40 mg.; optimum results being obtained if the weight was about 20 mg. The preferred mounting area was established as 2 square centimeters, thus yielding a source that weighed 2 to 20 mg. per square centimeter. With these facts in mind, a series of tests were run to determine the amount of zirconium carrier that would best fulfill the requirements. The results of the study, Table IX, indicated that 5 mg. of zirconium carrier gave a final

⁶ Engelkemeir, D. W., Seiler, J. A., Steinberg, E. P., and Winsberg, L., "Investigation of the Effects on Beta Counting of Self-Scattering Due to Source Weight," Paper 4, ed. by Coryell and Sugarman in "Radiochemical Studies: The Fission Products," Book 1, National Nuclear Energy Series, McGraw-Hill, New York, 1951, p. 56.

precipitate weighing about 25 mg., a weight which was well within the recommended limits.

TABLE IX

Determination of the Suitable Amount of Zirconium Carrier
Applicable in the Modified Barium Fluozirconate Method
for Radiochemical Zirconium

Sample	mg. of zirconium carrier	mg. of final precipitate	Per cent yield of zirconium	Equivalence in mg. ZrO ₂	mg. ZrO ₂ obtained on ignition
1*	18.72	100.6	70.50	17.8	17.6
2	18.72	109.0	76.38	19.3	19.6
3	9.36	51.9	72.75	9.2	9.4
4	4.68	26.4	73.86	4.6	4.5

*One drop of concentrated sulphuric acid was added to this sample to remove excess barium just prior to final precipitation. No acid added to other samples.

The zirconium tetramandellate precipitates in each of the determinations were then ignited to the oxide and the weights obtained were compared to the weight theoretically obtainable from the complex mandelate. The results, which are also shown in Table IX, revealed that the determinations with 5 mg. of zirconium carrier not only gave the desired weight of precipitate, but also gave results which were just as reliable as those obtained with 10 and 20 mg. of carrier.

Therefore it was concluded that the use of 5 mg. of zirconium carrier would not introduce any serious errors in regard to the accuracy of the determination.

The requirement of mounting area was easily solved by punching 17 mm. discs from Whatman #42 filter paper with a #9 cork borer.

Procedure Adopted for the Determination of Radioactive Zirconium. From the results of the preliminary experiments, a procedure was devised for the application of mandelic acid in the determination of radioactive zirconium, and it was followed in all the mandelic acid determinations. The procedure devised was:

Step 1. Add 5 mg. of Zirconium carrier to 1 ml. of 6 normal nitric acid in a lusteroid tube and mix. Add a known volume of the $\text{Zr}^{95}\text{-Nb}^{95}$ tracer with a lambda pipet and 0.5 ml. of concentrated hydrofluoric acid and mix.

Step 2. Add 2.5 mg. of lanthanum carrier, stir thoroughly, centrifuge, add second 2.5 mg. of lanthanum carrier, and centrifuge the precipitate on top of the first precipitate. The solution is decanted thoroughly into a lusteroid tube, and the precipitate is discarded.

Step 3. Add 0.25 ml. of barium carrier, mix, centrifuge, and discard the supernatant solution.

Step 4. Suspend the precipitate in 1.5 ml. water and 0.5 ml. boric acid, and dissolve by adding 0.25 ml. concentrated nitric acid. After a clear solution is obtained, add

0.25 ml. barium carrier and 0.25 ml. concentrated hydrofluoric acid.

Step 5. Repeat step 4.

Step 6. Suspend the precipitate in 1.5 ml. of water and 0.5 ml. of boric acid, and dissolve by adding 1 ml. of concentrated hydrochloric acid. Add sufficient 6 normal sodium hydroxide to ensure complete precipitation of the zirconium as the hydroxide. Centrifuge and discard the supernatant solution.

Step 7. Dissolve the precipitate in 1.5 ml. of concentrated hydrochloric acid and 3 ml. of water and transfer the solution to a glass centrifuge tube. Rinse the lusteroid tube with two 1 ml. portions of water, adding each rinse solution to the solution in the glass tube. Add 5 ml. of a 16% mandelic acid solution and heat in a water bath at about 85°C. for 20 minutes.

Step 8. While the solutions are being heated, weigh the required number of watch glasses and filter papers. After the 20 minutes have elapsed, filter the hot solution through the previously weighed filter paper in a Hirsch funnel, wash with hot wash solution (5% mandelic acid-2% hydrochloric acid), and then follow with successive portions of ethyl alcohol and ethyl ether. Transfer precipitate and filter paper to the watch glass and dry under a heat lamp for 5 minutes. Weigh and mount for counting.

Steps 1 through 5 are essentially the same as the steps in Hume's barium fluozirconate method with the exception that the volumes and weights of reagents used above are only one-fourth as large.

Mounting of Precipitate for Counting. After the watch glass containing the precipitate and the filter paper was weighed, it was mounted for counting. The components of the mount were a rectangular piece of 3-ply paper, 3 1/4" by 2 1/2" in size, with a 1 inch hole in the center, a 2 1/2 inch square of cellophane, 1/2 inch scotch tape, and the 1 inch watch glass bearing the precipitate. The procedure of mounting was to place the watch glass on a flat surface, cover it with the cellophane, and force the watch glass through the hole in the rectangular card. The watch glass was secured in place with two strips of scotch tape which were fastened across the underside of the card. The sample was now ready for counting.

Determination of Background Count. During the time that the precipitates were being digested, filtered, weighed, and mounted, a count was being made of the background and of the standard. The extent of background count per minute was determined by obtaining the number of counts for a period of ten minutes and then taking one-tenth of the value as a representative background count per minute. The background was determined immediately before the sample were counted and again after the sample were counted. If the counts

differed, the average was determined and used in the calculations.

Determination and Use of Standard Count. Since the high voltage setting was manually operated, it was impossible to exactly duplicate operating conditions of the scaler. This factor along with the factors of life decay of the geiger tube and the electronic tubes in the circuit of the scaler necessitated the determination of the count of an absolute radioactive standard every time that a sample or a series of samples was to be counted. By means of the standard it was then possible to make all values relative to some initially selected value which in this study was the value obtained during the first radiochemical determination. The corrected values were obtained by means of the following expression:

$$\text{Sample count}_1 \times \frac{\text{Standard count}_0}{\text{Standard count}_1} = \text{Corrected count}$$

where Sample count_1 = actual count for sample.

Standard count_1 = count recorded by standard at time when Sample count_1 was made.

Standard count_0 = count recorded by standard at time of initial sample determination.

Corrected count = value of sample count relative to count of initial sample.

The beta standard used was a sample of $\text{UX}_2\text{-234}$, and the gamma standard was a sample of cobalt 60.

Determination of Sample Count. After the determinations of the background and standard counts were made, the mounted sample was placed on the second level of the lucite holder

of the vertical shield and counted for two or three ten minute periods, and the average count per minute was calculated and recorded. To this value was added a coincidence correction which amounted to 5% of the observed count. This coincidence count correction was necessary in order to take into account the events that occurred during the dead time of the scaler and geiger tube. The value of 5% was chosen since that was the value commonly used at the Oak Ridge National Laboratory. The background count was then subtracted, and the remaining count was corrected for the losses that occurred during the chemical operations. The value thus obtained was then corrected to standard operating conditions by means of the standard count method described previously.

These steps are best illustrated by an actual example in which all the calculations are shown.

Example: A 50 lambda sample of the isotope was treated according to the adopted procedure. The per cent yield of zirconium carrier was 62.67%. The precipitate of zirconium tetramandelate was mounted and a ten minute count of the beta activity was made. The background was 50 c/m (counts per minute), and the standard count was 3359 c/m. The corrected standard count was then 3309 c/m (3359 - 50).

1. Actual count registered by scaler
in 10 minutes 106,340
2. Actual count per minute (item 1 ÷ 10) . . . 10,634

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3. Coincidence correction (item 2 x 0.05) ...	532
4. Corrected actual count (item 2 + item 3) .	11,166
5. Background correction	50
6. True count (item 4 minus item 5).	11,116
7. Count for 100% yield (item 6 $\div$ 0.6267). . .	17,737
8. Standard corrected count (item 7 x $\frac{3247}{3309}$) . .	17,405
9. Counts per minute per ml., c/m/ml. (item 8 x $\frac{1.0}{0.050}$)	348,100

Determination of Radioactive Zirconium by Beta Count.

An evaluation of the mandelic acid method for the determination of the radioactive zirconium was obtained by means of a comparison of the radiochemical yields obtained by the barium fluozirconate-mandelic acid method and Hume's quantitative barium fluozirconate-cupferron method. Determinations in duplicate were run by both methods either simultaneously or within a period of 24 hours. The results of the study are recorded in Table X.

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TABLE X

Analysis of Radioactive Zirconium by Cupferron and
Mandelic Acid Methods. Beta Count.

Beta activity of zirconium for 100% chemical yield, c/m/ml.

Sample	Cupferron procedure	Mandelic acid procedure
1	699 772	748 761
2	791 788	766 779
3	3.63×10^5 (?)*	3.50×10^5 3.87×10^5
4	4.05×10^5 4.02×10^5	3.48×10^5 3.68×10^5
5	2.74×10^5 2.73×10^5	2.61×10^5 2.71×10^5
6	2.40×10^5 2.44×10^5	2.39×10^5 2.40×10^5

*Insufficient removal of barium with sulphuric acid
resulted in an uncorrected yield of zirconium oxide
which was over 150%.

The results show that in all the samples, except sample four, the beta activity yields obtained by the two methods were in close agreement. The variation in the two methods for sample four could not be satisfactorily explained, although one possible explanation was that the self-absorption of the beta activity by the zirconium oxide was low because of the low weights of the oxide obtained

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(17.5 and 16.6 mg. respectively) for these particular cupferron determinations, as compared to the usual final weight of about 20 mg. which was obtained in all the other determinations.

Effect of Carrier Weight on the Self-absorption of Beta Activity. A series of determinations were made in which only the amount of zirconium carrier was varied. The results, tabulated in Table XI, show that an increase of self-absorption occurred with an increase in the weight of precipitate mounted, that is with an increase in the amount of zirconium carrier used.

TABLE XI

Effect of Carrier Weight on the Self-absorption of Beta Activity

Beta activity of zirconium for 100% chemical yield, c/m/ml.

mg. Zirconium carrier	mg. Zirconium tetramandrelate	Yield of zirconium, %	Activity c/m/ml.
4.68	22.4	62.67	3.27×10^5
4.68	21.1	59.04	3.43×10^5
9.36	43.2	60.53	2.68×10^5
9.36	37.2	52.12	2.75×10^5
18.72	96.2	67.41	1.60×10^5
18.72	96.3	67.48	1.59×10^5

The results further reveal that in each pair of analyses the sample with the lower chemical yield gave a final corrected count which was higher than the final count of the

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sample with the higher chemical yield. This difference in count can be attributed to instrumental and operational errors, but it also can just as well be the result of a lower self-absorption by the lower weight of the precipitate mounted.

Determination of Radioactive Zirconium by Gamma Count. It was decided to run a series of determinations by the two methods in order to make a comparative study of the gamma activity yields of the two methods. One ml. samples of the zirconium tracer solution were used so that an appreciable count could be obtained. The following results were obtained,

TABLE XII

Analysis of Radioactive Zirconium by Cupferron and Mandelic Acid Methods, Gamma Count.

Gamma activity of zirconium for 100% chemical yield, c/m/ml.

Sample	Cupferron Procedure	Mandelic Acid Procedure
1	8432 8296	7327 7385
2	7641 7517	6900 6625
3	8609 8332	7829 7782
4	7671 7532	7119 6703

The gamma activities obtained by the mandelic acid method were from 6 to 14 per cent lower than the activities of samples which were run simultaneously by the cupferron method. Because of the nonuniformity in the self-absorption of the gamma activity by the zirconium tetramandelate, mandelic acid could not be successfully applied in a radiochemical zirconium determination which would depend on the measurement of gamma activity.

Separation from Foreign Activities. A series of determinations were performed to study the effectiveness of the separation of the zirconium activity from the activities of some of the other fission products. The separation from cerium was tested first. The samples, which were analyzed according to the developed mandelic acid procedure, contained 11,500 counts per minute (c/m) of beta radiations of carrier-free cerium tracer. The final precipitates of zirconium tetramandelate gave counts that were from 9 to 213 c/m of beta radiation above counter background, indicating a 0.08 to 1.8 per cent contamination by cerium.

The separation from strontium activity was tested next. Samples containing 45,900 c/m of beta radiations of carrier-free strontium tracer were analyzed by the mandelic acid procedure. The counts given by the final precipitates ranged between 102 and 1,035 above background, or between 0.22 and 2.25 per cent of initial strontium activity.

Niobium decontamination was tested by running through

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the mandelic acid procedure in the presence of 10,650 c/m of beta activity of niobium. The final precipitates gave counts that varied from 7 to 28 c/m above background, indicating a 0.07 to 0.27 per cent contamination by niobium. The results of all the decontamination experiments are compiled in Table XIII.

TABLE XIII

Separation of Zirconium from Cerium, Strontium
and Niobium by Mandelic Acid Procedure

Tracer Element	Initial Activity, counts per min.	Final Activity, counts per min.	Per Cent Contamination
Ce	11,500	213	1.85
	11,500	61	0.53
	11,500	11	0.10
	11,500	9	0.08
Sr	45,900	1,035	2.25
	45,900	556	1.21
	45,900	102	0.22
	45,900	324	0.71
Nb	10,650	18	0.17
	10,650	17	0.16
	10,650	7	0.07
	10,650	28	0.26

Insufficient mixing after the addition of the lanthanum carrier was responsible for some of the high contamination carry-over in the strontium and cerium studies. The lower results were obtained when the mixing at the lanthanum carrier step was more thoroughly performed. Nevertheless, the results in all three series indicate that the separations

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obtained by the mandelic acid procedure are satisfactory, and therefore the method can be applied in presence of foreign activities.

D. Study of the Use of p-Bromomandelic Acid in the Determination of Zirconium

Previous Work. Oesper and Klingenberg⁷ showed that p-bromomandelic acid possessed the same selectivity for zirconium as exhibited by mandelic acid, and they suggested that the determination of zirconium might be possible by the direct weighing of the zirconium tetra-p-bromomandelate. Because of the similarity of activity of these two acids, it was decided that a partial investigation of the possible use of p-bromomandelic acid as a substitute for mandelic acid should be carried out.

Solutions. A 0.1 molar solution of p-bromomandelic acid was prepared by dissolving 11.6 g. of p-bromomandelic acid (molecular weight 231.05, m.p. 115-118°) in 500 ml. of distilled water. The p-bromomandelic acid was prepared by the method suggested by Klingenberg.⁸

The standard zirconium, lanthanum carrier, barium carrier, and 5% boric acid solutions which were used in the mandelic acid study were also used in the p-bromomandelic acid study. The wash solution for the precipitated zirconium

⁷ Oesper, R. E., and Klingenberg, J. J., Anal. Chem. 21, 1509 (1949).

⁸ Klingenberg, J. J., private communication.

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tetra-p-bromomandelate was hot distilled water.

Application of p-Bromomandelic Acid in the Modified Barium Fluozirconate Method. Since a satisfactory procedure for the precipitation of zirconium with p-bromomandelic acid was already devised by Oesper and Klingenberg, it was not necessary to spend any time on this phase of the study. It was then only necessary to determine the weight and purity of the final precipitate that would be obtained with a given amount of carrier under the conditions of the entire procedure for radioactive zirconium. The weight of carrier selected for study was 5 mg. since this was the amount that gave satisfactory results with the mandelic acid procedure.

The weight range of the final precipitate was determined by means of a series of determinations which were performed according to the procedure devised for the mandelic acid method, with the exception that no radioactive tracer was added in the initial step. The purity was determined by ignition of the final precipitate to zirconium oxide. The results of these determinations are shown in Table XIV.

The weight of the final precipitate was slightly higher than desired, and the volume of precipitate obtained was about three times larger than that obtained for a corresponding weight of zirconium precipitated with mandelic acid. The large volume would make it difficult to mount the precipitate in the desired area and along with the higher weight would increase the amount of self-absorption. A logical

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decrease in the amount of carrier would bring the weight and volume of the final precipitate to the desired range, but the decrease would also introduce an adverse effect, since the volume of the intermediate precipitate of barium fluozirconate would be decreased to such an extent that the barium fluozirconate could no longer be conveniently handled.

TABLE XIV

Weight and Purity of the Zirconium Tetra-p-Bromomandelate
Obtained by the Modified Barium Fluozirconate Method

Sample	mg. of Final Precipitate	Per Cent Yield of Zirconium	Equivalence in mg. ZrO_2	mg. ZrO_2 Obtained on Ignition
1.	33.0	63.60	4.0	4.0
2.	31.8	61.28	3.9	3.9
3.	32.8	63.22	4.0	3.8
4.	29.8	57.44	3.6	3.5
5.	36.6	70.55	4.5	4.5
6.	35.3	68.04	4.3	4.3

4.68 mg. of zirconium carrier was used in all the determinations.

Because the disadvantages would outweigh any advantages that would be introduced by the use of p-bromomandelic acid as the precipitant, the study of its use was not pursued any further.

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