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THE ANALYSIS OF URANIUM-ZIRCONIUM ALLOYS

AN A. E. R. E. REPORT

BY

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ABSTRACT

A satisfactory procedure is described for the analysis of uranium-zirconium alloys containing up to 25% zirconium. It is based on the separation of the zirconium from the uranium by dissolving the cupferron complex of the former element into chloroform. After the evaporation of the solvent from the combined organic extracts, the residue is ignited to zirconium oxide. The latter is then re-dissolved and zirconium is separated from other elements co-extracted in the solvent extraction procedure by precipitation with mandelic acid. The zirconium mandelate is finally ignited to oxide at 960°C. The uranium is separated from the aqueous solution remaining from the cupferron extraction by precipitating with tannin at a pH of 8; the precipitate being removed by filtration and then ignited at 800°C. The residue is dissolved in nitric acid and the uranium is finally determined by precipitating as ammonium diuranate and then igniting to U_3O_8. (auth)

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HARWELL.

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1. INTRODUCTION

Bricker(1) proposed a method for the analysis of this type of alloy without studying the behaviour of the method in routine application to alloy samples. This procedure consisted of precipitating the zirconium with cupferron, igniting the precipitate to the oxide after filtration, dissolving the zirconium oxide by fusion with potassium bisulphate and then precipitating the zirconium with phenylarsonic acid. The zirconium phenylarsonate precipitate was finally ignited to zirconium oxide after filtration and the zirconium content of the alloy calculated from the resulting weight of zirconium oxide. There are objections however to the use of phenylarsonic acid as a precipitant for zirconium, since the final zirconium oxide residue may be contaminated with arsenic unless the ignition is continued for a long time at a high temperature. Also several elements including uranium can be co-precipitated with the zirconium phenylarsonate in a single precipitation. In recent years however several new precipitating reagents have been developed for zirconium and the replacement of the phenylarsonic acid by certain members of this group of reagents should result in a considerable improvement in Bricker's method. Also Sandell(2) recently suggested that zirconium cupferrate might be soluble in chloroform and in this event the replacement of the cupferron precipitation technique by a chloroform extraction procedure should result in a cleaner separation of the zirconium from the uranium.

2. EXPERIMENTAL

(1) Determination of Zirconium

The preliminary experimental work was directed towards studying the recoveries of macro amounts of zirconium by the solvent extraction procedure with chloroform. Suitable zirconium solutions were prepared by dissolving amounts of zirconium oxide up to a maximum of 0.135 mg. in 10 ml. of nitric acid (sp. gr. 1.42) and 1-2 ml. of hydrofluoric acid in platinum basins. Then 10 ml. of 50% sulphuric acid were added to each basin and the solution evaporated to fumes of this acid. After cooling, the solution was diluted with about 50 ml. of water and cooled to a temperature of 5°C. It was then transferred to a suitable separating funnel, washing in with water to give a total volume of about 100 ml. The zirconium cupferrate was next precipitated by the addition of 25 ml. of 6% aqueous cupferron solution and the extractions carried out with suitable quantities of chloroform. Full recoveries for these amounts of zirconium were obtained in adopting the procedure of extracting the initial zirconium cupferrate precipitate with two separate 25 ml. portions of chloroform, followed by the addition of a further 10 ml. of cupferron solution and two further extractions with 10 ml. portions of chloroform.

On extending this technique to solutions containing zirconium and uranium, only very small amounts of uranium contaminated the final zirconium oxide residue produced by evaporating the chloroform from the combined extracts and igniting at a temperature of about 750°C. This behaviour is caused by the failure of hexavalent uranium to form a cupferrate precipitate under these conditions. However, several elements form cupferrate precipitates extractable from acid solutions (Fe, V, Nb, etc.) and these elements would contaminate the final zirconium oxide residue if they occurred in the original alloy samples. It was therefore considered desirable to include a step which separated the zirconium oxide from the small amounts of uranium and from the group of elements forming cupferrate precipitate.

According to the recent literature on the determination of zirconium there are now several reagents capable of selectively separating zirconium from many other elements. These reagents include phthalic acid(3), fumaric acid(4), m-cresoxyacetic acid(5) and mandelic acid(6). Phthalic acid and fumaric acid are not very attractive, since the former requires two hours for complete precipitation whereas the latter produces a gelatinous type of precipitate. M-cresoxyacetic acid does not suffer from the disadvantages of phthalic and fumaric acids, but unfortunately it was not readily available when this investigation was started. However, a small quantity of this reagent was prepared by the Organic Chemistry Group and a limited number of tests produced excellent results. Mandelic acid on the other hand is readily available and produces a zirconium salt of definite composition which is stable to heat over the range 60° - 188°C. Kumins(6) introduced this reagent for separating macro amounts of zirconium from Ti, Fe, V, Al, Cr, Th, Ce, Sn, Ba, Ca, Cu, Bi, Sb and Cd. Subsequently Hahn(7) showed that mandelic acid could be used for separating 1-15 mg. of zirconium from Mg, Hg, Ni, U and Zn in addition to the elements quoted by Kumins. Both workers filtered off the precipitate and ignited it to zirconium oxide. More recently Duval(8) indicated that the precipitate given by zirconium with mandelic acid, Zr $(C_6H_4.CHOH.COO)_4$, could be dried at any temperature between 60° - 188°C without undergoing decomposition. According to this observation it should be possible to replace the technique of igniting the final precipitate to the oxide by the more satisfactory procedure of filtering on to a sintered glass crucible and weighing after drying at a temperature of about 100°C.

Kumin's procedure briefly consists of taking a sample of zirconyl chloride in 20 ml. of concentrated hydrochloric acid, adding 50 ml. of 16% mandelic acid solution and diluting to a volume of 100 ml. with water. After digesting the solution at a temperature of 85°C for about 20 minutes, the precipitate is filtered off, washed with a hot solution of 2% HCl + 5% mandelic acid and finally ignited to the oxide. Unfortunately the presence of sulphate ions in solution leads to slightly low zirconium results by this procedure. This behaviour obviously rules out the application of the bisulphate fusion technique for redissolving the zirconium oxide residue resulting from the cupferron extraction, followed by the extraction of the melt with hydrochloric acid and the precipitation of the zirconium from this solution with mandelic acid. The most convenient technique for overcoming this difficulty was found to consist of precipitating the zirconium with ammonium hydroxide from the hydrochloric acid solution of the bisulphate melt. This precipitate was filtered off after a suitable digestion in the cold, washed with a 2% NH_4NO_3 solution, dissolved in concentrated hydrochloric acid and then the zirconium was precipitated with mandelic acid as above and finally ignited to the oxide. Excellent recoveries were obtained by this procedure for varying amounts of zirconium covering the range from 20 to 125 mg.

In subsequent experiments attempts were made to improve the zirconium determination by filtering the zirconium mandelate precipitate on to a sintered glass crucible and obtaining the weight of the precipitate after drying at about 100°C for a suitable period of time. Difficulties were immediately encountered, however, due to the appreciable solubility of zirconium mandelate in water and hence the need to include mandelic acid in the aqueous wash solution. After the completion of the washing of the zirconium mandelate precipitate it was hoped that this difficulty could be overcome by washing the precipitate once or twice with some suitable organic solvent. This assumes of course that organic solvents exist in which mandelic acid is readily soluble whereas zirconium mandelate is completely insoluble. Experiments were carried out with most of the common organic solvents, i.e. alcohol, ether, acetone, etc., but none of these solvents produced the desired results. In spite of Duval's suggestion, therefore, it proved necessary to complete the zirconium determination by igniting the zirconium mandelate precipitate to zirconium oxide.

(2) Determination of traces of Uranium Co-extracted with the Zirconium

As already indicated above, a small amount of uranium is co-extracted with the zirconium when the cupferron procedure is applied to solutions containing uranium and zirconium. In the complete analysis of alloy samples therefore it proved necessary to recover the uranium traces from the filtrate after removing the precipitate of zirconium mandelate. From previous experience with other uranium alloy systems it was considered that tannic acid might precipitate these small quantitites of uranium after adjusting the pH of the filtrate to a value of 8 and digesting for a suitable period of time. Experimental evidence was needed however to confirm this supposition and in addition the digestion time needed to give complete precipitation of the uranium tannate had to be determined experimentally. After filtration of the uranium tannate precipitate it was decided to ignite the precipitate in a silica crucible to a temperature of about 750°C and then determine the uranium content of any residue by an absorptiometric procedure. The uranium-thiocyanate colour was chosen for this latter procedure since previous experience with the uranium peroxide colour in sample analysis had not been very satisfactory. In some instances, for example, rapid fading of the uranium colour was encountered due to the presence of traces of other elements in solution resulting in the rapid decomposition of the hydrogen peroxide. Moreover this decomposition produced bubbles in solution which often caused erroneous results to be obtained for the absorbancy measurements.

The following factors are important in the application of the thiocyanate procedure to the absorptiometric determination of uranium:-

1. The pH of the final solution (50 ml.) must be in the pH range 0.2 to 1.0

2. The thiocyanate ion concentration must be carefully controlled; a new calibration graph being needed for each new thiocyanate reagent solution.

3. Sulphate ions must be absent from the final solution.

On assuming that any amount of uranium less than about 4 mg. might be recovered from these solutions, a standard uranium solution was prepared containing 0.297 g. of U_3O_8 per 500 ml. This weight of U_3O_8 was dissolved in 17 ml. of concentrated nitric acid before diluting to 500 ml. with water, thereby producing a solution containing 0.5 mg. of uranium per ml. in 0.5N nitric acid. For the preparation of the calibration graph different suitable aliquots (x ml.) of the standard uranium solution were transferred to 50 ml. graduation flasks, followed by the addition of 0.2 ml. of a stannous chloride solution (10 g. in 20 ml. of concentrated hydrochloric acid diluted to 100 ml. with water) and 10 ml. of 8 M. ammonium thiocyanate to each flask. The requisite volume (y ml.) of a 0.5N nitric acid solution was next added to each flask to bring the value of x + y in all cases to 15 ml. After dilution with water to 50 ml. absorbancy measurements were taken on suitable aliquots of solution; the remaining solution being used for confirming the pH value to be in the requisite range. For the absorbancy meansurements a Spekker absorptiometer was used with H 556 filters and 1 or 2 cm. cells; typical results for the calibration being summarised in the following table:-

TABLE I

ABSORBANCY VALUES FOR THE URANIUM COLOURS FORMED WITH THIOCYANATE

Concentration of U in mg.	Absorbancy values for different cells	
	1 cm. cell	2 cm. cell
0	0	0
0.5	0.117	0.243
1.0	0.239	0.494
1.5	0.367	0.751
2.0	0.486	-
3.0	0.727	-

On plotting the results in Table I graphically a linear relationship was found to represent the measurements with both 1 and 2 cm. cells. The technique finally adopted for determining the uranium content of the oxide residues from the tannate precipitates consisted of the following:- Treat the residue in the silica crucible with about 2 ml. of aqua regia and gradually evaporate the solution almost to dryness. Treat with 15 ml. of 0.5N nitric acid and filter the resulting solution directly into a 50 ml. graduated flask, washing with water. Then add 0.2 to 0.3 ml. of freshly prepared stannous chloride solution (10%), 10 ml. of the 8M ammonium thiocyanate solution and complete the determination as above.

The length of the digestion time needed to give the complete precipitation of milligram amounts of uranium was next investigated. Several synthetic solutions were prepared corresponding in composition and volume with the filtrates from the zirconium mandelate precipitations and amounts of uranium covering the range up to 4 mg. were added to these solutions. After the addition of 20 ml. of a freshly prepared 5% tannin solution, each solution was heated to boiling and a (1:1) ammonium hydroxide solution was then added dropwise to increase the pH of each solution to a value of 8 as indicated by B.D.H. wide range indicator papers, followed by a small amount of filter paper pulp to collect the small precipitate. After standing at room temperature for varying periods of time each solution was filtered through a Whatman filter paper and after ignition the uranium content of the final oxide residue was determined by the thiocyanate procedure. Recovery results for different time intervals are included in the following table:-

TABLE II

RESULTS FOR THE RECOVERY OF SMALL AMOUNTS OF URANIUM AGAINST TIME OF PRECIPITATION

Time interval in hours	Weight of uranium recovered from 2.0 mg.	Weight of uranium recovered from 4.0 mg.
1.0 hr.	1.10 mg.	3.5 mg.
2.0 hr.	1.85	3.88
3.0	1.85	4.05
18	1.95	4.10

From the results in Table II it is obviously necessary to stand the solutions overnight to obtain the complete precipitation of the uranium tannate. But if an overnight standing is inconvenient in sample analysis, a period of from 3 to 4 hours should give fairly satisfactory results.

(3) Determination of Major Uranium

The determination of the concentration of uranium in the solution after the cupferron extraction was not expected to give much difficulty after the removal of chloroform by evaporation. This solution is then essentially a uranyl sulphate solution containing a small amount of cupferron. However, since the presence of this organic matter could lead to the incomplete precipitation of the uranium as ammonium diurante, it was considered safer to apply the tannic acid technique developed for the determination of uranium in tungsten-uranium alloys(9). (C/R.1045.) Full details of the final procedure are given in the Appendix.

(4) Determination of trace amounts of unextracted Zirconium

In the event of the extraction of zirconium by the cupferron procedure being incomplete, the residue resulting from the ignition of the uranium tannate precipitate in (3) will also contain small amounts of zirconium. On treating these residues with nitric acid, however, the uranium is readily dissolved whereas the zirconium oxide is completely insoluble and can be removed by filtration. It proved necessary therefore to develop a procedure suitable for determining these small amounts of zirconium oxide. The absorptiometric method appeared to be most suitable for this determination since alizarin forms a strongly coloured lake with zirconium which is stable in acid solution. The lakes formed by alizarin with other cations are unstable in acid solutions (with the exception of hafnium), thereby making this reagent almost specific for the determination of small amounts of zirconium. The most recent publication on the use of alizarin for the determination of zirconium is by Mayer and Bradshaw(10), dealing with the direct determination of zirconium in magnesium base alloys. These workers recommend that the zirconium alizarin red lake is best prepared in a 1.5N acid (hydrochloric acid) solution by heating for 2 minutes above 85°C. Details of their optimum conditions for colour development are as follows:-

Add 10 ml. of the zirconyl chloride solution to a 100 ml. graduated flask, followed by 3 ml. of 11.3N hydrochloric acid and 10 ml. of 0.15% aqueous alizarin S solution. Develop the colour by heating in a boiling water bath for 2½ minutes. Then cool, dilute to 100 ml. with water and measure the absorbancy on the Spekker absorptiometer using Ilford No. 605 filters.

This technique proved readily applicable to the magnesium-zirconium type of alloys due to the ready solubility of these alloys in hydrochloric acid. However, its application to the analysis of small residues of zirconium oxide presented difficulties because the most convenient methods of getting small amounts of zirconium oxide into solution involve the introduction of sulphate ions into solution either from a potassium bisulphate fusion or from a sulphuric acid-hydrofluoric acid treatment. Unfortunately sulphate ions seriously interfere in this determination by complexing the zirconium ions and thereby bleaching the zirconium-alizarin lake. After the solution of the zirconium oxide by either of the above procedures therefore it proved essential to remove the zirconium ions from the sulphate ions. It was considered that this separation might best be accomplished by precipitating the zirconium with ammonium hydroxide using aluminium hydroxide as a carrier for the zirconium hydroxide precipitate. Aluminium was chosen as the carrier because of its reputed negligible interference in the absorptiometric method for zirconium; 20 mg. amounts of this element being chosen in the first instance so as to produce a convenient amount of precipitate. In the development of such a scheme, however, two points needed clarification:-

(1) the influence of 20 mg. of aluminium on the intensity of the zirconium-alizarin colour;

and

(2) the efficiency of this amount of aluminium in coprecipitation of small amounts of zirconium.

To test the first point, increasing amounts (0, 2, 4, 6, 8 ml.) of a standard 0.10 mg. per ml. zirconium solution were added to 125 ml. conical beakers with graduation marks at the 10 ml. level. Then 20 ml. aliquots of an aluminium chloride solution (1 mg. per ml.) were added to each beaker and the resulting solutions evaporated to volumes of about 5 ml. Ammonium hydroxide (1:1) was next added to each solution to the change point of bromocresol purple, followed by water to the 10 ml. graduation mark. After the addition of 3 ml. of concentrated hydrochloric acid, the beakers were immersed in a water bath and the zirconium-alizarin colour developed as above. The absorbancies of these solutions were compared with the values produced by the same amounts of zirconium in the absence of aluminium. The results reported in Table III indicate that the aluminium has negligible interference in the zirconium-alizarin colour.

TABLE III

ABSORBANCY RESULTS FOR THE ZIRCONIUM-ALIZARIN COLOUR IN THE ABSENCE AND PRESENCE OF ALUMINIUM

Wt. of zirconium taken	No aluminium present Absorbancy	20 mg. of aluminium Absorbancy
0	0	0
0.203	0.20	0.205
0.407	0.45	0.4475
0.509	0.5625	0.5725

Experiments were next carried out to cover the second point. To suitable measured aliquots of the standard zirconyl chloride solution, 20 mg. amounts of aluminium were added and after the dilution of each solution to about 100 ml. with water, ammonium hydroxide was added to the change point of bromo-cresol purple indicator. All solutions were then allowed to digest for 1 hour in the cold to assist the precipitation; cold digestion being used to ensure the re-solution of the zirconium hydroxide in hydrochloric acid after filtration. The hydroxide precipitates were next filtered on to suitable Whatman papers, redissolved in hydrochloric acid and the resultant solutions, evaporated to volumes less than 10 ml. The zirconium alizarin colours were then formed as above and the absorbancy measurements used to determine the amounts of zirconium recovered by this procedure. From the results in Table IV it is clear that the bulk of the zirconium is recovered by this technique.

TABLE IV

RESULTS FOR THE RECOVERY OF ZIRCONIUM FROM SOLUTION USING ALUMINIUM AS CARRIER

Wt. of zirconium taken	Absorbancy due to recovered zirconium	Wt. of zirconium recovered
0	0	0
0.10 mg	0.0725	0.07
0.203	0.1875	0.17
0.407	0.4475	0.407
0.509	0.5425	0.48
0.61	0.665	0.585

Experiments were next designed to correspond as closely as possible to the conditions arising in the analysis of uranium-zirconium alloys. Under these circumstances the zirconium is in the form of its oxide after separation from the major uranium. The above experiments were therefore repeated but this time the aliquots of the zirconyl chloride solution were placed in platinum dishes and evaporated to dryness to convert the zirconium to the oxide. On redissolving these oxide residues by fusing with potassium bisulphate, low zirconium recoveries often resulted and in some cases it was possible to see the zirconium oxide out of solution. However, on dissolving the zirconium oxide in a small amount of hydrofluoric acid, then adding sulphuric acid and evaporating to fumes of this acid to remove the excess hydrofluoric acid, similar zirconium recovery results to those in Table IV were obtained. This latter technique was therefore incorporated in the final procedure.

(5) The Analysis of Alloy Samples

(a) Synthetic Alloys

Synthetic oxide mixtures to correspond to alloys containing from approximately 1% to 25% of zirconium were prepared from specpure samples of U_3O_8 and zirconium oxide using sample weights of 0.5 g. for the high zirconium percentages, 1.0 g. for percentages from 5 to 10% and 2.0 g. for the low percentages. These alloys were then analysed according to the full procedure outlined in the Appendix with the results shown in Table V.

TABLE V

RESULTS FOR THE ANALYSIS OF OXIDE MIXTURES CORRESPONDING TO SYNTHETIC ZIRCONIUM-URANIUM ALLOYS

No.	Percentage Composition of Alloys		Percentage Composition by Analysis		
	Zirconium	Uranium	Zirconium	Uranium	Total
1	24.87	75.13	24.84	74.82	99.66
2	10.10	89.89	10.11	89.82	99.93
3	5.00	95.00	5.01	94.75	99.76
4	1.07	98.93	1.10	98.59	99.69

(b) Alloy Samples

The spectrographic analysis of several typical alloys samples showed that copper was a contaminating element, being apparently picked up from a copper hearth in the smelting process. Since the copper percentage varied from trace amounts up to about 0.5% in exceptional cases it proved desirable to investigate the behaviour of this element in the final procedure in some detail. Copper forms an insoluble cupferrate from weakly acid solutions which is extractable into chloroform. However, under the strongly acid conditions used for the separation of the zirconium cupferrate, the copper is only partially extracted with the zirconium. Experiments with synthetic alloys showed that approximately 50% of the copper contaminated the zirconium; the remaining 50% staying in the aqueous phase with the major uranium. In the zirconium determination, an ammonia precipitation is included to remove sulphate ions and to get the zirconium in a hydrochloric acid solution suitable for the precipitation with mandelic acid. In this step most of the copper remains in the filtrate, but it is impossible to completely wash the last traces of copper from the zirconium hydroxide precipitate. However, the mandelic acid precipitation completely removed the zirconium from these trace amounts of copper. A similar state of affairs existed in the uranium determination. The copper is precipitated as tannate with the uranium, but the ammonia precipitation step prior to the ignition of the uranium to U_3O_8 served for separating the uranium from the copper. In the exceptional samples containing large amounts of copper, a double precipitation of the uranium with ammonia should be incorporated for safety.

The only other contaminating element proved to be silicon. However, this element presented no interference in the complete scheme for the analysis of these alloys since it is removed by volatilisation in the initial attack with the nitric-hydrofluoric acid mixture. The spectrographic method proved to be the most satisfactory procedure for determining the silicon content of alloy samples. In addition this technique was used for determining the very small percentages of the remaining contaminating elements.

The results obtained by applying the final procedure to the analysis of typical alloys are shown in Table VI. The suitability of this procedure is confirmed by the satisfactory results produced for the total percentage composition in all cases.

TABLE VI

RESULTS FOR THE COMPLETE ANALYSIS OF ZIRCONIUM-URANIUM ALLOYS

No.	Percentage Composition by Analysis			Total
	Zr	U	Impurities	
1	2.20	97.5	0.2	99.95
2	2.85	96.3	0.67	99.82
3	4.65	95.1	0.30	100.05
4	4.80	94.5	0.21	99.51
5	6.40	93.4	0.2	100.0

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APPENDIX

RECOMMENDED PROCEDURE FOR THE ANALYSIS OF ZIRCONIUM-URANIUM ALLOYS

A. OUTLINE OF METHOD

After dissolving the alloy in a nitric acid-hydrofluoric acid mixture, a quantity of sulphuric acid is added and the solution is evaporated to fumes of this acid. The solution is then suitably diluted with water, cupferron is added to precipitate the zirconium and the precipitate is separated by extracting with chloroform. After the removal of the chloroform from the combined extracts, the zirconium is ignited to the oxide. The zirconium is next separated from small amounts of uranium and other elements co-extracted with it by precipitation with mandelic acid. The small amount of uranium is recovered from the filtrate with tannin and finally determined absorptiometrically using the uranium-thiocyanate colour complex. The major uranium is also precipitated with tannin and after filtration the uranium tannate is ignited to the oxide. The resulting oxide is dissolved in nitric acid, and the uranium content of this solution is determined by precipitating as ammonium diuranate followed by ignition to U_3O_8. Any insoluble residue is examined for the presence of zirconium by an absorptiometric method using the coloured zirconium-alizarin lake.

B. APPLICABILITY

The procedure is suitable for the determination of zirconium contents up to 25% with an error less than ± 1% of the zirconium present.

C. REAGENTS REQUIRED

(a) Mandelic acid, manufactured by Thomas Marson and Son Ltd., London.

(b) Alizarin Red S, B.D.H. reagent.

(c) All other reagents of analar quality.

D. PROCEDURE

Take a 2 gm. sample weight for Zr.% ages < 5%.

Take a 1 gm. sample weight for Zr.% ages from 5% - 10%.

Take a 0.5 gm. sample weight for Zr.% ages > 10%.

Transfer to a 100 ml. platinum dish and digest with repeated quantities of 25 ml. of HNO_3 (SG.1.42) together with 2-3 ml. HF until complete solution of the alloy is obtained, then add 10 ml. of H_2SO_4 (1:1) and evaporate to fumes of this acid - fume strongly for a short period to completely remove the hydrofluoric acid. Cool, dissolve in about 50 ml. of water and transfer to a 250 ml. squat type beaker. Adjust the volume to about 100 ml. with water and cool to a temperature less than 5°C in an ice bath. At the same time cool a freshly prepared 6% aqueous solution of cupferron to the same temperature. Transfer the alloy solution to a 300 ml. separating funnel and add 25 ml. of the cupferron reagent with gentle agitation. Then shake vigorously for a few minutes to cause the coagulation of the cupferron precipitate.

Extract the precipitate by shaking with two separate 25 ml. portions of chloroform. Separate the organic layer after each extraction and wash through with about 5 ml. of pure chloroform. Combine the extracts and washings together in either a 150 ml. fused silica beaker or a platinum dish. Add about another 25 ml. of the cupferron reagent and extract with two separate 10 ml. portions of chloroform, combining these extracts and washings in the same silica or platinum vessel. Reserve the aqueous solution for the determination of uranium.

Determination of Zirconium

Evaporate the combined solvent extracts to dryness in the silica beaker or platinum dish using a moderate hot plate and finally a bunsen flame. Then ignite the residue carefully, and finally at 750°C for 30 mins. in a muffle furnace(a). Cool, fuse the residue with about 2 gm. $KHSO_4$ to give a clear melt. Then take up the fused mass in 100 ml. (1:9) HCl and transfer the solution to a 400 ml. squat beaker. Dilute the solution to a volume of about 200 ml. with water. Precipitate the zirconium and uranium as hydroxides by the addition of FRESH ammonium hydroxide (1:1). Allow the precipitate to stand in the cold for 30 minutes, then filter through a No. 40 Whatman filter paper washing with 2% NH_4Cl solution and finally with water to remove all sulphate ions which interfere with the mandelic acid precipitation of zirconium. Transfer the filter paper and precipitate back to the 400 ml. squat beaker and add 40 ml. of hot (1:1) HCl solution. Carefully macerate the paper with a glass rod and wash the sides of the beaker with 10 ml. of distilled water. Then add 50 ml. of 16% mandelic acid solution and after mixing, maintain at a temperature of about 85°C for 60 minutes. Then filter off the resulting precipitate on a Whatman No. 40 paper, washing with a hot solution containing (1:49 v/v HCl + 5% mandelic acid and ignite to the oxide of zirconium at 960°C for 30 minutes.

(a) Make sure that there is no carbonaceous matter left behind.

Determination of Uranium Co-extracted with the Zirconium

Take the filtrate from the mandelic acid precipitation, add 3.5 gm. of ammonium acetate and heat the solution to boiling. Then add 2.5 gm. of tannic acid dissolved in a minimum of water and adjust the pH of the solution to pH 8 by the addition of ammonium hydroxide (1:1) using wide range pH papers. Add Whatman accelerators and allow to stand for at least 4 hours(b) in the cold. Filter through a Whatman No. 541 paper, wash with 2% ammonium nitrate solution and ignite at 800°C in a silica crucible for about 30 minutes. Dissolve the residue (U_3O_8) in about 2 ml. of aqua regia and evaporate the solution almost to dryness.

(b) When possible allow to stand overnight.

Add 15 ml. of approximately 0.5N HNO_3, and filter the solution through a Whatman No. 541 into a 50 ml. beaker washing with water. Combine the washings with the filtrate. Then add 0.2 to 0.3 ml. of freshly prepared $SnCl_2$ solution(c) and 10 ml. of 8 M NH_4CNS solution. Dilute the solution to a volume of 50 ml. in a volumetric flask with distilled water. Measure the absorbance with the Spekker absorptiometer using a 2,1 or 0.5 cm. cell, H.556 filters and a Hg vapour lamp. Determine the amount of uranium present by reference to a calibration graph prepared as described below.

(c) 10 g. $SnCl_2$ dissolved in 20 ml. conc. HCl diluted to 100 ml. with water.

Calibration Graph

Take a suitable aliquot, x ml. of standard uranium solution(d) in a 50 ml. standard flask, together with 0.2 ml. stannous chloride solution and 10 ml. 8M ammonium thiocyanate solution(e). Then to each flask add y ml. of 0.5N HNO_3 such that (x + y) ml. = 15 ml. Dilute the solution to 50 ml. with redistilled water. Measure the absorbance on the Spekker Absorptiometer using a 2,1 or 0.5 cm. cell, H.556 filters and Hg vapour lamp. Plot the results graphically.

(d) Dissolve 0.297 gm. U_3O_8 in 17 ml. conc. HNO_3 and dilute to 500 ml. with water. 1 ml. ≡ 0.5 mg. U in 0.5N HNO_3.

(e) Dissolve 608 gm. of ammonium thiocyanate in redistilled water and dilute to 1000 ml. with water.

Determination of Major Uranium

After evaporating chloroform from the aqueous phase, dilute this solution to a definite volume in a volumetric flask. (Omit this step if the total uranium content is less than 200 mg.) Take a suitable aliquot of this solution containing between 200 and 400 mg. of uranium and dilute to 150 ml. with water in a 400 ml. squat beaker. Dissolve 3.5 gm. of ammonium acetate in this solution, then add 50-60 ml. of 5% tannic acid solution with stirring. Bring the solution to pH 8 by the dropwise addition of (1:1) NH_4OH with constant stirring. Add one macerated Whatman accelerator and digest cold for one hour. Filter through a Whatman No. 40 or 541 paper using slight suction if necessary. Wash well with hot 2% NH_4NO_3 solution and finally ignite at about 800°C in a platinum dish. Dissolve the residual oxide in a quantity of 1:1 HNO_3, dilute and filter off any insoluble residue. Ignite the paper and residue, treat with a small quantity of HNO_3, refilter and combine this filtrate with the main uranium filtrate. Reserve the residue (R) for the determination of traces of zirconium. Make the main uranium filtrate slightly ammoniacal with fresh (i.e. carbonate-free) ammonium hydroxide, stirring during the addition. Digest warm for about 30 minutes after adding 6 macerated Whatman accelerators. Filter through a Whatman No. 40 filter paper and wash 6-8 times with hot 2% NH_4NO_3 solution. Ignite the precipitate to U_3O_8 at about 800°C in a tared platinum dish for about 30 minutes. Determine the weight of U_3O_8 and calculate the weight of uranium in the sample by applying the factor 0.848. Combine this weight of uranium with the small amount co-extracted with the zirconium.

Determination of Zirconium remaining with the Uranium

Transfer the residue (R) from above to a small platinum basin, add 3-5 ml. hydrofluoric acid to dissolve the zirconium, then add 5 ml. (1:1) H_2SO_4 and evaporate to fumes of H_2SO_4. Fume strongly for about 10 minutes. Cool, wash with a maximum of 5 ml. of water. Refume and fume strongly for another 10 minutes. (Strong fuming is required to remove the fluoride ions.) Cool, transfer the solution to a 150 ml. squat beaker, or a suitable aliquot containing < 0.8 mg. Zirconium, washing with water. Add 20 ml. of an aluminium solution(f) and then add 1:1 ammonium hydroxide to the change point of bromocresol purple. Digest the solution cold for 1 hour. Filter off on a Whatman No. 54 filter paper washing with 2% NH_4NO_3 (3 or 4 washings required) and then jet the hydroxide precipitate from the paper into a 125 ml. conical beaker with a 10 ml. graduation mark on it. Add 20 ml. 1:1 HCl to the original precipitation beaker, warm and then pour over the filter paper and collect in the conical beaker. Wash the beaker and paper with water. Boil the final solution in the conical beaker down to a volume of about 5 ml.

(f) Dissolve 1 gm. of 99% Al powder in 60 ml. of 1:1 HCl and dilute to 1 litre with water.

Cool the solution, add 1:1 NH_4OH dropwise to just produce the purple colour of bromocresol purple indicator. Dilute the solution to the 10 ml. graduation mark by the addition of distilled water, then add 3 ml. of conc. HCl, allowing it to run over the beaker walls to dissolve any precipitate. Immerse the beaker in a boiling water bath for about 3-4 mins. to ensure the complete solution of the zirconium hydroxide. Then add 10 ml. of Alizarin Red S(g) and immerse the beaker again in the boiling water bath for not less than 2½ minutes and not more than 3½ minutes. Cool and dilute the solutions to 100 ml. with water. Measure the absorbance in a 2 cm. cell using the mercury vapour lamp and Ilford No. 605 filters. Carry out a blank determination on the reagents. Obtain the zirconium concentration by referring the difference reading to a calibration graph, multiplying by a factor (depending on the aliquot taken for the uranium determination) to give the total content of the zirconium with the major uranium.

(g) Dissolve 1.5 gm. of Alizarin Red S in 300 ml. of hot water, filter through a pulp pad and dilute to 1 litre with water.

Calibration Graph

Standard Zirconium Solution - Dissolve 8.85 gms. of zirconyl chloride octahydrate in 250 ml. of water and 50 ml. conc. HCl. Filter if necessary and dilute to 500 ml. Standardise this solution by taking an aliquot, precipitating the zirconium hydroxide with NH_4OH, ignite and weigh as ZrO_2. 1 ml. of this solution should contain about 5 mg. of zirconium. Dilute this solution so that 1 ml. ≡ 0.1 mg. of zirconium.

Calibration Procedure

Take 0, 2, 4, 6, 8 ml. of the standard zirconium solution (0.1 mg/ml.) in 125 ml. conical beakers with graduation marks at the 10 ml. level. Add 20 ml. of the aluminium solution to each beaker and evaporate each to a volume of about 5 ml. Then add 1:1 NH_4OH to the change point of bromocresol purple indicator, add water to give a volume of 10 ml. then add 3 ml. of conc. HCl, running over the beaker walls to dissolve any precipitate. Immerse the beaker in a boiling water bath for about 3-4 minutes to ensure the complete solution of the zirconium hydroxide. Then add 10 ml. of Alizarin Red S solution and immerse the beaker again in the boiling water bath for not less than 2½ minutes and not more than 3½ minutes, to produce the zirconium Alizarin Red S colour. Measure the absorbance on the Spekker Absorptiometer in a 2 cm. cell using the mercury vapour lamp and Ilford No. 605 filters. Carry out a blank determination on the reagents. Plot the results graphically.