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THE ANALYSIS OF URANIUM-NIOBIUM ALLOYS

by

G. W. C. MILNER

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ABSTRACT

A satisfactory procedure is described for the analysis of uranium-niobium alloys containing up to 25% niobium. It is based on the separation of the niobium from uranium by dissolving the cupferron complex of the former element into chloroform. After the evaporation of the solvent from the combined organic extracts, the niobium is ignited to the pentoxide. The uranium is afterwards precipitated from the remaining aqueous solution by the addition of ammonium hydroxide after the wet oxidation of organic matter. Absorptiometric procedures are included for the determination of the small amounts of uranium co-extracted with the niobium and the trace amounts of unextracted niobium.

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1. INTRODUCTION

In a recommended method[1] for the analysis of uranium-niobium alloys, the separation of the niobium from the uranium is accomplished by dehydration with fuming perchloric acid. Although this method also includes a long digestion of the solution after the fuming process, the recoveries of niobium may be low by as much as 5 mg. Results accurate to 0.5 mg. are claimed, however, by making a correction for the solubility of the niobium. This method was considered unsatisfactory and investigations were started to develop a procedure suitable for the accurate analysis of uranium-niobium alloys containing percentages of niobium up to a maximum of approximately 25%.

It is possible to determine macro amounts of niobium by titration with a standard potassium permanganate solution after reducing the niobium in a Jones reductor[2]. This type of procedure could not be satisfactorily applied to the direct determination of niobium in these alloys, however, because of the simultaneous reduction of the uranium in the reductor. Gravimetric methods of determination generally consist of the precipitation of the niobium as the cupferron or tannin complex followed by ignition to the oxide after filtration. Moreover, cupferron is particularly useful for the separation of niobium from uranium, since uranium does not form a precipitate with this reagent unless it is present in solution in the quadrivalent state[3]. In developing a new procedure for these alloys, therefore, the preliminary experiments were confined to an investigation of the applicability of this reagent.

2. EXPERIMENTAL

Suitable synthetic alloy solutions were prepared by fusing weighed quantities of niobium pentoxide with potassium bisulphate, extracting the melts with oxalic acid and then mixing each solution with a suitable uranyl solution. After making the solution 5% in sulphuric acid, they were cooled down to 5°C in an ice bath and then a quantity of a freshly prepared 6% solution of cupferron was added to precipitate the niobium. The resulting precipitates were filtered onto suitable filter papers and ignited at about 750°C after washing with a cupferron wash solution. In general, however, this procedure produced high recoveries for the niobium due to the serious contamination of the niobium pentoxide with uranium oxide (U_3O_8). In a recent report Furman and Mason[4] recommend that the contamination difficulty arising in the separation of certain elements from uranium with cupferron can be considerably minimised by extracting the cupferrate precipitate with chloroform or any other suitable organic solvent. Niobium cupferrate is however said to be insoluble in chloroform[5], but if chloroform plus hydrogen cupferrate is agitated with an aqueous niobium solution appreciable amounts of this element can be transferred to the chloroform layer. This type of extraction procedure was therefore investigated in an effort to improve the separation of the niobium from uranium.

Extraction of Niobium from Uranium-Niobium Mixture

In the initial experiments synthetic alloy solutions were prepared as before. Each solution was then made 5% in sulphuric acid, diluted to about 100 ml. with water and cooled down to about 5°C. in an ice bath. After

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transference to a suitable separating funnel, 25 ml. of a 6% aqueous cupferron solution were added and the niobium cupferrate extracted into chloroform by shaking with separate and decreasing amounts (25, 20, 15 and 10 ml.) of this solvent. The extracts were combined together, the solvent evaporated and the residue finally ignited at 750°C in a platinum dish.

Results showed that four extracts contained the majority of the niobium which appeared moreover almost free from uranium. A few typical recoveries obtained by this method are as follows:-

Wt. of Nb_2O_5 in solution with 0.5g. U_3O_8	Wt. of Nb_2O_5 recovered
0.0208 g.	0.0210 g.
0.0168 g.	0.0160 g.

Although these recoveries justified a more detailed study of this separation technique, it was considered desirable at this stage to investigate possible methods for dissolving actual alloy samples, as the method used for preparing synthetic alloys solutions would not be applicable. After sampling each alloy by carefully drilling so as to prevent the spontaneous ignition of the uranium, the best technique was found to consist of digesting the drillings in a platinum dish with repeated quantities of an acid mixture consisting of 2 to 3 ml. of hydrofluoric acid mixed with 25 ml. of nitric acid (sp. gr. 1.42). On obtaining the alloy completely in solution a quantity of sulphuric acid was added and the solution evaporated to fumes of this acid to remove the nitric and hydrofluoric acids. The above extraction procedure should then be directly applicable to this solution after diluting with water to adjust the acidity to 5% in sulphuric acid.

The investigation of a satisfactory procedure for purifying the separated niobium pentoxide from traces of co-extracted elements (especially uranium) was next considered desirable. A suitable procedure was eventually developed consisting of the fusion of the final oxide residue from the chloroform extracts with about 2 g. of potassium bisulphate, extraction of the melt with water to dissolve the uranium and precipitation of any soluble niobium with tannic acid. After digesting for about one hour the tannate precipitate was filtered off, washed with 1% ammonium sulphate and finally ignited to niobium pentoxide. The recovery of the uranium from the filtrate was easily accomplished by making the solution ammoniacal, removing the uranium tannate precipitate by filtration and finally igniting to U_3O_8.

The detailed study of the extractability of niobium cupferrate into chloroform was now carried out using a synthetic alloy of the 10% niobium type prepared from 0.106 g. of specpure niobium metal (99.99% purity) and 1.066 g. of U_3O_8. After the addition of the cupferron reagent, the niobium cupferrate was extracted into several separate portions of chloroform. The residue from each chloroform extract was analysed for niobium and uranium by the above tannic acid procedure with the results shown in Table I.

TABLE I

THE CONCENTRATIONS OF NIOBIUM AND URANIUM IN EACH CHLOROFORM EXTRACT

No. of Extract	Vol. of $CHCl_3$ used	Wt. of Nb extracted in g.	Wt. of U extracted
1	25 ml.	0.1029	trace
2	20 ml.	0.00196	nil
3	15 ml.	nil	nil
4	10 ml.	nil	nil

This investigation showed that two extractions removed the majority of the niobium cupferrate and only a small quantity of uranium contaminated the final niobium pentoxide residue. However, since a total of 0.1049 g. of niobium was recovered from the alloy, a small quantity of this metal appeared to be unextracted, which moreover resisted extraction on shaking with further portions of solvent. Further evidence confirming this behaviour was produced by extending the procedure to other synthetic alloys covering a wide range of niobium percentages. In preparing these alloy solutions, a sample weight was taken depending upon the niobium content, according to the following scheme:-

Niobium content	Approximate sample weight taken
Up to 5%	2.0 g.
5 to 10%	1.0 g.
Greater than 10%	0.5 g.

The total niobium recoveries obtained for these various synthetic alloys are shown in Table II.

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TABLE II

RESULTS FOR THE RECOVERY OF NIOBIUM IN THE ANALYSIS OF URANIUM-NIOBIUM MIXTURES

No.	Nominal Nb Content	Composition of mixture in g.		Wt. of Nb_2O_5 recovered	$\%Nb_2O_5$ in original mixture	$\%Nb_2O_5$ recovered
		U_3O_8	Nb_2O_5			
1	1%	1.9838	0.0210	0.0210	1.05	1.05
2	2%	1.9606	0.0405	0.0407	2.03	2.04
3	5%	0.9506	0.0500	0.0499	5.0	4.99
4	10%	0.4510	0.0528	0.0514	10.41	10.20
5	20%	0.5241	0.1430	0.1413	21.43	21.17

Although very satisfactory recoveries were obtained for the niobium from the low percentage alloys, the recoveries from alloys containing more than 5% niobium tended to be slightly low. Confirmatory evidence for the existence of unextracted niobium was produced by recovering the uranium from the remaining solutions and examining the final U_3O_8 residues. Small amounts of material insoluble in nitric acid were found in some of the residues and this was accepted at this stage as satisfactory supporting evidence. In another series of experiments with synthetic alloys, the traces of unextracted niobium pentoxide were recovered by the above treatment of the U_3O_8 residues with nitric acid. In all cases the insoluble matter was filtered off, ignited at 750°C, weighed and combined with the weight of niobium pentoxide from the chloroform extractions. The uranium contents were also determined in the filtrates by rendering them alkaline with carbonate-free ammonium hydroxide after wet oxidising any organic matter and igniting the precipitate to U_3O_8 after filtration. The recoveries of the niobium and uranium from these alloys are shown in Table III.

TABLE III

RESULTS FOR THE COMPLETE ANALYSIS OF SYNTHETIC ALLOYS

No.	Nominal Alloy Composition	Sample Wt. taken in g.	Original composition		Nb_2O_5 recovered		Total Nb recovered in g.	Total U_3O_8 recovered in g.	% U determined
			Nb in g.	U_3O_8 in g.	Major portion in g.	Traces in g.			
1	25% Nb 75%U	0.5	0.1250	0.4422	0.1772	.0016	0.1252	0.4410	74.8
2	10% Nb 90%U	1.0	0.100	1.061	0.1419	.0008	0.0999	1.0595	89.84
3	5% Nb 95%U	2.0	0.100	2.241	0.1412	.0008	0.0994	2.238	94.9

The Determination of trace amounts of Niobium

In the analysis of actual alloy samples, it was considered preferable to examine the acid insoluble residues for niobium content, instead of assuming all residues to consist essentially of niobium pentoxide. This necessitated the development of a sensitive and selective procedure for determining trace amounts of this element. The method of activation analysis was considered for this purpose but experiments showed that other elements present (e.g. uranium) gave rise to such a variety and amount of activity after a short irradiation, that it was not possible readily to pick off the 6.6 minute decay due to niobium from the gross decay curve. The possibility of developing an absorptiometric method for this determination was therefore considered. On reducing niobium in a hydrochloric acid solution to the trivalent state with tin amalgam, Gentry and Sherrington[6] reported a strong yellow colour produced by the addition of potassium thiocyanate. Alimarin et al[7] used this colour complex in a method for the determination of niobium in minerals and ores after reducing the niobium with stannous chloride. Interference was encountered from many elements in this method, however, including Mo, W, U, V, Fe, Cr, Co, Cu, etc. Experiments showed that the reduction of the niobium is in fact unnecessary for the production of the colour complex and this observation immediately improved the selectivity of the thiocyanate method for niobium since several of the interfering elements mentioned react only in their lower valence forms. A satisfactory procedure was eventually developed along these lines which also included the extraction of the yellow niobium complex before taking the absorbancy measurements. Details of this procedure as applied to oxide residues are as follows:-

Fuse the residue with 1.0 g. of potassium bisulphate and extract the melt with a solution containing 2 g. of tartaric acid and dilute to a convenient volume with water. Transfer 20 ml. of hydrochloric acid (sp. gr. 1.16) to a 50 ml. stoppered measuring cylinder, add 15 ml. of water followed by 5 ml. of a potassium thiocyanate solution (75%). Then add a suitable volume of the niobium solution and dilute the final solution to the 50 ml. graduation mark. Extract the niobium colour by shaking with two separate 10 ml. portions of amyl alcohol, combine the extracts in a 25 ml. volumetric flask and dilute to volume with amyl alcohol. Mix thoroughly and measure the absorbancy using 601 filters and 1 cm. cell.

Although this procedure considerably reduced the interference from some elements including tungsten and molybdenum, the interference from iron was considerably intensified due to the absence of a reducing agent to prevent the formation of the ferric thiocyanate colour. Moreover, since the spectrographic method showed iron to be a usual constituent of these alloys; it was decided to investigate other possible absorptiometric methods.

Thanheiser[8] reported a stable yellow colour produced by adding hydrogen peroxide to concentrated sulphuric acid solutions containing niobium and used it for the determination of niobium in steels. Preliminary experiments showed the colours to be rather insensitive and it was therefore not given an early consideration for this particular problem. However, after the failure of the thiocyanate colour, a fuller investigation was considered worthwhile. By keeping the volume of solutions as small as possible and by using micro cells for the absorbancy measurements, it was hoped to make this colour sufficiently sensitive for this particular requirement. Interference from other elements was also expected to be less troublesome, since titanium, vanadium and molybdenum are the only elements mentioned as forming colours under these strongly acid conditions. Moreover, molybdenum interference can be ruled out in this particular application, since this element should be volatilised off in the ignition of the residues at 750°C.

The longest micro-cell available for use with the Spekker Absorptiometer has a length of 3 cm. and a total capacity of less than 5 ml. For maximum sensitivity the volume of the final niobium coloured solution should therefore be adjusted to 5 ml., but a final solution volume of 10 ml. was found to be the smallest convenient working volume with concentrated sulphuric acid solutions. On assuming that any amount of niobium pentoxide less than 10 mg. might be encountered in the residues, a standard niobium solution containing 1 mg. of NB_2O_5 per ml. was chosen for the preparation of the calibration graphs. This solution was prepared by fusing 100 mg. of specpure niobium pentoxide with 1 g. of potassium bisulphate, extracting the melt with concentrated acid and diluting to 100 ml. in a volumetric flask with this acid. Different suitable aliquots were taken for the preparation of the calibration graphs and after diluting each solution to 10 ml. with concentrated sulphuric acid, the niobium colour was formed by the addition of 0.1 ml of 100 volume hydrogen peroxide. The absorbancy of each solution was then measured with the Spekker Absorptiometer using a mercury vapour lamp and Ilford 601 filter; the results being summarised in Table IV. On plotting these results graphically a linear relationship was found to represent the measurements with both 3 cm. and 1 cm. cells, but the graph for the 0.5 cm. cell was slightly curved. This latter graph was perfectly reproducible, however, and suitable for this determination.

An investigation of other elements producing colours under these conditions showed that the presence of either titanium or vanadium caused serious interference in the niobium determination. Attempts to eliminate the titanium colour by the use of sodium fluoride or phosphoric acid proved unsuccessful, since these reagents also suppressed the intensity of the niobium colour. Further investigations were abandoned after spectrographic analysis of actual alloys had shown the non-occurrence of these elements.

On now examining the residue produced in the analysis of alloys requiring the determination of niobium, the most convenient solution procedure was found to consist of fusing each residue with a small amount of potassium bisulphate followed by solution of the melt in concentrated sulphuric acid. After diluting each resultant solution to 25 ml. with concentrated sulphuric acid, a 10 ml. aliquot was taken for the formation of the niobium colour and another similar aliquot for determining the blank absorbancy due to other ions in solution. The niobium content of each residue was then determined by relating the absorbancy difference reading for these two solutions to the appropriate niobium calibration graph.

TABLE IV

ABSORBANCY VALUES FOR THE NIOBIUM COLOURS FORMED WITH HYDROGEN PEROXIDE

Concentration of Nb_2O_5 in mg.	Absorbancy values for different cells		
0	3 cm.	1 cm.	0.5 cm.
0	0	0	0
0.5	0.175	-	-
1.0	0.3575	0.13	0.0675
1.5	0.55	-	-
2.0	-	0.26	0.1375
3.0	-	0.375	0.1975
4.0	-	0.49	0.255
5.0	-	0.61	0.32
6.0	-	-	-
7.0	-	-	0.4175
8.0	-	-	0.4725
9.0	-	-	0.5125
10.0	-	-	0.5475

Interfering Elements

The spectrographic examination of several alloy samples, showed that iron and silicon were the only important contaminating elements. Silicon presented no difficulties in the complete scheme of analysis, since it is removed by volatilisation in the initial attack of alloys with the nitric-hydrofluoric acid solvent mixture. Iron, however, forms a cupferrate soluble in chloroform and is consequently separated from the uranium with the major niobium portion. The small amounts of iron are separated from the niobium in the reprecipitation of this element with tannic acid, and remain in the filtrate. They are easily recovered, however, by making the solution ammoniacal and igniting the precipitate at 750°C. after filtration. The residue produced at this stage contains a small amount of U_3O_8 in addition to the iron oxide (Fe_2O_3). The concentrations of both these elements can be readily determined by absorptiometric methods, using thioglycollic acid for the iron and hydrogen peroxide for the uranium determination.

The Determination of Uranium

Although good recoveries were obtained for the uranium in synthetic alloys after the wet oxidation of organic matter, this procedure proved rather time consuming and a quicker procedure was considered desirable. The direct precipitation of ammonium diuranate in the presence of cupferron and other organic material remaining from the extraction of niobium always resulted in low uranium recoveries. However, it was thought that the addition of tannic acid to the ammoniacal solution after precipitating the ammonium diuranate would result in the complete precipitation of the uranium. Experiments were therefore carried out to test the behaviour of tannic acid in synthetic alloys prepared from 2.0 and 1.0 g. sample weights. In all cases the solutions remaining after the extraction of the niobium cupferrates were boiled to remove chloroform, cooled and then diluted to 250 ml. with water. Separate 50 ml. aliquots were taken, diluted with 100 ml. of water and rendered alkaline with ammonium hydroxide. A one gram quantity of tannic acid dissolved in 10 ml. of water was then added to each solution and digestion of the solution allowed to take place for a definite period of time. After filtration on to No. 541 Whatman filter papers and washing with 2% ammonium nitrate, all precipitates were ignited to uranium oxide (U_3O_8). The results obtained for the recovery of uranium in these experiments are shown in Table V and prove conclusively that the tannic acid method is definitely inferior to the wet oxidation method. It proved impossible therefore to replace the lengthy wet oxidation procedure by a quicker method for the determination of uranium.

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TABLE V

RECOVERIES OF URANIUM UNDER VARIOUS EXPERIMENTAL CONDITIONS

Composition of Alloy	Wt. of U_3O_8 50 ml. aliquot	*Wt. of U_3O_8 recovered		
		1. After wet oxidation	2. Digesting tannate for 1 hour.	3. Digesting tannate for 12 hours.
1. 0.10gNb,2.2494g.U_3O_8	0.4499	0.4471	0.4053	0.3509
2. 0.10gNb,1.0684g.U_3O_8	0.2137	0.2112	0.2066	0.1921

*These weights do not take into account any small amounts extracted with the niobium.

Results of the Analysis of Alloys

The results obtained by applying the final procedure to the analysis of typical alloys are shown in Table VI. The total percentage for the trace impurities present in each alloy are based on the results of spectrographic analysis. The suitability of the procedure is confirmed by the satisfactory results produced for the total percentage composition in all cases.

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TABLE VI

RESULTS FOR THE COMPLETE ANALYSIS OF ALLOYS

No.	Nominal Nb Content	Nb	Percentage Composition		Total
			Uranium	Impurities	
1.	25%	20.40	79.53	0.06	99.99
2.	10%	10.82	88.75	0.20	99.77
3.	5%	4.47	95.10	0.05	99.62
4.	1%	0.96	98.66	0.05	99.67

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APPENDIX

COMPOSITE SCHEME FOR THE ANALYSIS OF URANIUM-NIOBIUM ALLOYS

RECOMMENDED PROCEDURE

A. Outline of Method

After dissolving the alloy in a nitric-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 niobium and the precipitate is separated by extracting with chloroform. Small amounts of iron and uranium are separated from the resulting niobium pentoxide residue and their concentrations are determined by absorptiometric methods. Organic matter remaining in the aqueous solution after the extraction procedure is decomposed by wet oxidation and the uranium is determined by precipitating as ammonium diuranate followed by ignition to U_3O_8. This residue is examined for the presence of matter insoluble in nitric acid; any such material being examined for the presence of niobium by an absoptiometric method.

B. Applicability

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

C. Reagents Required

Cupferron (6%) - dissolve 6 g. of Analar reagent in 100 ml. of cold water and filter before use.

Tannic acid (5%) - dissolve 5 g. of B.P. quality reagent in 100 ml. of water.

Oxalic acid (4%) - dissolve 4 g. of Analar reagent in 100 ml. of water.

Sulphuric acid (Sp.gr. 1.84); nitric acid (Sp.gr. 1.42); hydrofluoric acid (40%); thioglycollic acid; hydrogen peroxide.

D. Procedure

1. Preparation of solution of the alloy

Carefully drill the sample to produce very fine drillings and then take a suitable sample weight depending upon the niobium content, according to the following table:-

For samples with Nb percentages less than 5%, take a 2.0 g. sample weight.
For samples with Nb percentages between 5 and 10% take a 1.0 g. sample weight.
For samples with Nb percentages greater than 10% take a 0.5 g. sample weight.

Notes

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Transfer the alloy to a 100 ml. platinum dish and digest with repeated 25 ml. portions of nitric acid (Sp.gr. 1.42) together with 2 or 3 ml. of hydrofluoric acid (40%), until complete solution of the alloy is obtained. (a) Then add 10 ml. of sulphuric acid (50%) evaporate to fumes of this acid and fume strongly for a short period to completely remove the hydrofluoric acid. Cool, dissolve in 50 ml. of an aqueous solution containing 3 to 4 g. of ammonium oxalate (b) wash into a 250 ml. squat beaker and adjust the final volume to between 100 and 150 ml. with water. If necessary add more sulphuric acid (50%) to adjust the acidity of the solution to be approximately 5% in sulphuric acid.

2. Extraction Procedure

Cool the alloy solution down to less than 5°C in an ice bath and 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 cupferrate precipitate.

Extract the precipitate by shaking with successive and diminishing quantities (e.g. 25, 20, 15 and 10 ml.) of pure 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 a 150 ml. fused silica beaker. At this stage add a few drops of the cupferron solution to the aqueous layer, if there is an immediate formation of a white precipitate which does not persist but redissolves on gentle shaking of the funnel, the extraction of the niobium cupferrate may be regarded as complete as possible. Wash the aqueous solution into a 500 ml. squat beaker, evaporate to low bulk and reserve for the gravimetric determination of the uranium.

Notes

(a) If uranium fluoride precipitates during this procedure, dilute slightly with water to dissolve the precipitate.

(b) The ammonium oxalate prevents the niobium from precipitating from solution.

3. Determination of Niobium

Evaporate the combined solvent extracts to dryness in the silica beaker using a moderate hot plate and finally a bunsen flame. Then ignite the residue carefully at first and finally at 750°C for thirty minutes in a muffle furnace. Cool, fuse the residue with 2 g. of potassium bisulphate until a clear melt is obtained and then extract the cooled melt with about 100 ml. of hot water in the silica beaker (c). Bring the solution to the boil, stir and precipitate the soluble niobium by the dropwise addition of 10-15 ml. of a freshly prepared 5% tannic acid solution. Boil for one or two minutes after the addition of the reagent and digest hot for sixty minutes. Then filter through a small Whatman No. 40 filter paper, washing well with a hot 1% ammonium sulphate solution. Dry and ignite the precipitate at 750°C in a weighed platinum dish. Calculate the weight of niobium in the sample by multiplying the weight of the oxide residue by the factor 0.699.

Notes

(c) This solution is cloudy at this stage due to the hydrolysis of the niobium.

Make the filtrate ammoniacal to precipitate iron and uranium tannate and digest the solution hot for about one hour. Filter through a Whatman No. 40 filter paper, washing the precipitate with a hot 2% ammonium nitrate wash solution. Dry and ignite any precipitate in a platinum dish at 750°C. Transfer the residue to a small glass beaker and attack with a few mls. of aqua regia. Filter off any insoluble and combine its weight after ignition with the weight of the main niobium pentoxide residue. Dilute the filtrate to 50 ml. and reserve for the determination of iron and uranium.

4. Determination of Iron

Pipette 20 ml. of the filtrate from 3 into a conical beaker and add 3 ml. of a 25% thioglycollic acid solution. Then neutralise the solution by the addition of ammonium hydroxide (Sp.gr. 0.88) and add three drops in excess. Dilute to 50 ml. with water and mix thoroughly. Measure the absorbancy on the Spekker Absorptiometer using Ilford 604 filters and 2 cm. cells. Determine the iron concentration by reference to a calibration graph prepared by applying this method to a suitable standard iron solution (d). Multiply by 2.5 to obtain the total iron concentration of the sample.

(d) A solution containing 1 mg. of iron per ml. is suitable. Prepare by dissolving 150 mg. of specpure iron in a small volume of aqua regia and diluting to 100 ml. with water.

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5. Determination of the Uranium Co-extracted with the Niobium

Pipette 20 ml. of the filtrate from 3 into a conical beaker. Add 0.5 ml. of 20 vols. hydrogen peroxide and a 10% sodium hydroxide solution to neutralise the acidity. Then add 5 ml. of 10% sodium hydroxide in excess, filter if necessary and dilute to 50 ml. with water. Measure the absorbancy of the solution on the Spekker using a mercury vapour lamp, H.556 filters and a 4 cm. cell. Determine the uranium concentration by reference to a calibration graph prepared by applying this method to a suitable standard uranium solution (e). Multiply this result by 2.5 and combine with the result from 6 to give the total uranium content of the sample.

6. Determination of Uranium

Transfer the aqueous solution reserved from 2 to a 300 ml. Kjeldahl flask and add 10 ml. of sulphuric acid (50%). Heat the flask on a sandbath to the formation of sulphuric acid fumes and then occasionally add nitric acid dropwise (Sp.gr. 1.42) to decompose organic matter. Cool slightly, wash the walls of the Kjeldahl flask with a minimum volume of water and refume.

Transfer the solution to a 400 ml. squat beaker and dilute to about 100 ml. with water. Then add carbonate-free ammonium hydroxide to make the solution slightly ammoniacal. Add about six macerated Whatman accelerators and digest warm for about thirty minutes to enable complete precipitation of the ammonium diuranate.

Filter through a No.40 Whatman filter paper, washing six to eight times with a hot 2% ammonium nitrate solution. Transfer the precipitate to a platinum dish, dry and ignite at 750°C for thirty minutes. After cooling, add a few mls. of nitric acid (Sp.gr. 1.42) to the platinum dish and digest, warm to dissolve the U_3O_8. Dilute the solution with a small volume of water and examine for the existence of insoluble matter. If present, filter through a small No. 40 Whatman filter paper, washing with 2% ammonium nitrate solution. Ignite the residue, but repeat the treatment with nitric acid to completely recover the uranium from the residue. Combine this filtrate with the main uranium filtrate and reserve the residue for the determination of niobium.

Notes

(e) A solution containing 1 mg. per ml. is suitable. Prepare by dissolving 0.5902 g. of specpure U_3O_8 in a small quantity of H_2SO_4 with the addition of a minimum of HNO_3. Dilute to 500 ml. with water.

Notes

Add carbonate-free ammonium hydroxide to the combined filtrates to precipitate the ammonium diuranate. Then add the filter paper pulp to collect the precipitate and filter through a Whatman No. 40 filter paper in the usual way, after digesting for about thirty minutes. Ignite the precipitate to U_3O_8 at 750°C in a weighed platinum dish for about thirty minutes and determine the weight of U_3O_8 from the increase in weight of the dish. Calculate the weight of uranium in the sample by using the factor 0.848.

7. Determination of trace amounts of unextracted Niobium

Fuse the small residue from 6 with about 0.25 g. of potassium bisulphate in a platinum dish. Extract the melt with a few mls. of sulphuric acid (Sp.gr. 1.84) and dilute to 25 ml. with this acid. Mix the solution thoroughly and pipette two separate 10 ml. portions into small beakers. To one portion add 0.1 ml. of hydrogen peroxide (100 volumes) to form the niobium colour and mix thoroughly. Measure the absorbancy of this solution using an appropriate micro cell, Ilford 601 filters and the mercury vapour lamp. Then transfer a portion of the other 10 ml. aliquot to the same cell and measure the absorbancy of the blank solution. Relate the difference reading to the calibration graphs (f) to obtain the niobium concentration. Multiply this result by 2.5 to give the total niobium content of the residue and combine with the niobium result obtained in 3.

(f) See Table IV.

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