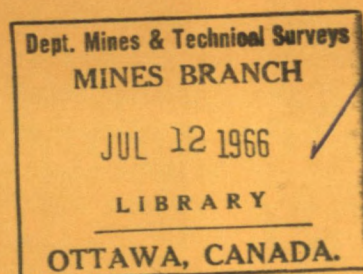




CANADA

ANALYTICAL PROCEDURES FOR A VANADIUM RECOVERY PROCESS



DEPARTMENT OF MINES AND
TECHNICAL SURVEYS, OTTAWA

R. J. GUEST AND J. C. INGLES

EXTRACTION METALLURGY DIVISION

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ANALYTICAL PROCEDURES FOR A VANADIUM RECOVERY PROCESS

by

R.J. Guest* and J.C. Ingles**

ABSTRACT

Analytical procedures are described for the determination of a number of elements in connection with a process for the recovery of high-purity vanadium compounds from vanadium-bearing boiler fly ash. Although the basic procedures used are standard ones, a number of modifications have been made where necessitated by the nature of the sample material. A discussion of the reason for these modifications is included and the experimental work carried out on several procedures is described.

RÉSUMÉ

Les auteurs décrivent des méthodes analytiques servant à doser un certain nombre d'éléments qui entrent en jeu dans la récupération de composés de vanadium de grande pureté provenant des cendres volantes de chaudière. Quoique les méthodes de base utilisées soient régulières, ils ont apporté un certain nombre de modifications à cause de la nature du matériau en cause. Ils étudient les raisons de ces modifications et décrivent les expériences faites avec diverses méthodes.

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INTRODUCTION

In the course of small-scale test work on processes for the production of commercial-grade vanadium pentoxide from boiler fly ash, carried out by the Hydrometallurgy Section of this Division on material submitted by Canadian Petrofina (ref. 1, under Vanadium), a need arose for suitable procedures for the analysis of sample materials from the various process stages. A number of different types of samples were received, representing products from treatments of the fly ash by processes employing soda ash, sulphuric acid and nitric acid for extraction of the vanadium. In addition, samples were received which had been obtained in the course of the preparation of various salts of vanadium by processes involving precipitation from the leach solution with sulphuric acid, ammonia, and ammonium chloride. The main analyses required were vanadium, iron, sodium, and nickel. On some samples, analyses for phosphate, titanium, aluminum, silica, sulphate, chloride, ammonia, carbon, total sulphur, free acid and loss on ignition were also requested. Chemical and spectrographic analyses of samples of boiler fly ash and chemical analyses on vanadium pentoxide products indicated a range of chemical composition for these materials as shown in Table 1. In the work carried out, standard analytical methods were used where possible but it was found that modifications were necessary in the case of some procedures and in the presence of certain contaminants. For the sake of completeness and to facilitate the use of the methods by analysts unfamiliar with the methods, discussion and detailed directions for all the methods, even the comparatively well-known ones, are included. Where modifications were made, a description is given of these modifications and of any experimental work found necessary.

TABLE 1

Chemical and Spectrographic Analyses of Typical Samples

Type of Sample	Type of Analysis	Indicated Concentration Ranges																
		V ₂ O ₅ %	Na %	Ni %	Al %	Si %	S total as SO ₄ %	Fe %	P %	S total %	C %	Ti %	Mg %	Ca %	Cr %	Mo %	Zr %	Cu %
Boiler fly ash	Chemical	9 to 15	0.1 - 0.4	0.5 - 1	-	-	-	1 to 2	-	4 to 5	50 - 60	-	-	-	-	-	-	-
	Spectrographic	-	-	-	1 to 3	1 to 3	-	-	-	-	-	0.1 0.2	0.01 0.1	0.3 0.5	0.01 0.02	0.005 0.05	0.01 0.1	0.03 0.1
Vanadium pentoxide product	Chemical	50 to 98	0.05 0.4	0.05 0.6	0.03 1.5	0.01 0.1	0.1 to 7.0	0.5 - 5.0	<0.03	-	-	-	-	-	-	-	-	-

Procedure 1

DETERMINATION OF VANADIUM

INTRODUCTION

Vanadium is determined by an amperometric titration using ferrous ammonium sulphate following oxidation of the vanadium to vanadate. The oxidation step is carried out by treatment of the sample with perchloric acid and/or potassium permanganate. The end point is detected using a rotating platinum wire electrode at an applied potential of + 1.0 volt versus the standard calomel electrode.

This titration has been used for the determination of vanadium and/or chromium in steels, alloys, and some petroleum products (2, 3, 4), and has been used in this laboratory by Hitchen for the determination of vanadium in uranium ores (5). Amounts of vanadium from 0.01 to 100 mg of vanadium can be titrated readily by using different strengths of iron solution. The titration procedure described here is essentially that of Rulfs et al. (3), and Hitchen (5), applied to the specific types of sample material encountered during this project. Although the titration end-point can be detected visually, the same precision cannot be achieved using a visual indicator as would be found by using an amperometric titration.

APPARATUS AND REAGENTS

Apparatus

Sargent Manual Polarograph, Model III.

Synchronous Rotator, Sargent Cat. No. S-76485.

Platinum wire electrode, Sargent Cat. No. S-30421.

Saturated calomel electrode (S.C.E.) half-cell.

Burette, 25 ml, with an offset tip.

Reagents

Ferrous ammonium sulphate, 0.01 N or 0.001N. Dissolve the pure ferrous ammonium sulphate in 0.1N sulphuric acid. Standardize against standard potassium dichromate solution and against a known vanadium standard (1 ml 0.01N ferrous solution is equivalent to 0.5095 g V or 0.9095 mg V_2O_5).

Standard vanadium solution

Dissolve 0.161 g ammonium vanadate (NH_4VO_3) in 5% sulphuric acid and make up to 250 ml. 1 ml = 0.500 mg V_2O_5 .

Sodium nitrite solution, 2% (w/v)

Potassium permanganate solution, 1% (w/v)

PROCEDURE

Sample Dissolution

(a) Fly ash

Weigh 0.5 - 1.0 g sample (5-20 mg V_2O_5) into a 150-ml platinum dish. Add 2 ml of water to wet the sample, then add 10-12 drops concentrated hydrofluoric acid, 5 ml concentrated nitric acid, and about 10 drops concentrated sulphuric acid. Evaporate slowly on the hot plate, swirling the sample occasionally. When completely dry, place the dish on a hot plate and heat until fuming stops. Transfer the dish to a furnace at 600°C. Leave the furnace door partly open for 15 minutes, then close the door and raise the temperature to 700°C and give the samples an extra 20 minutes at this temperature. Remove from the furnace and fuse over a (Meker) burner with potassium pyrosulphate. Dissolve the melt in 10 ml of 1:1 sulphuric acid and 100 ml of water. Transfer to a volumetric flask or beaker, depending on whether or not aliquots are to be taken.

Fly ash may also be treated as described in section (b), "Precipitates", but the presence of large amounts of carbon then makes it difficult to determine whether or not complete solution of vanadium has been obtained.

(b) Precipitates

Weigh 0.5 g of the sample into a 250-ml beaker, and add 75 ml of 5% sulphuric acid and 75 ml of 10% hydrochloric acid. Heat until the sample dissolves, then transfer to a volumetric flask and dilute to the mark.

(c) Solutions

Pipette an aliquot containing 0.5-5.0 mg V_2O_5 into a 250-ml beaker and proceed as in "Titration Procedure".

Titration Procedure

Place an aliquot containing 0.5 - 10 mg V_2O_5 into a 250-ml beaker and dilute to about 100 ml. Adjust the acidity to about 5% in sulphuric acid. Add 2-5 g of urea, then enough 1% $KMnO_4$ (w/v) to obtain a permanent pink colour, and allow sample to stand for 5 minutes. Add enough 2% sodium nitrite solution to decolorize the permanganate (about 2 drops), then add at once 1-2 g more of urea. Allow to stand for five minutes.

Titrate with standard ferrous solution, using an H type polarographic cell and a Sargent polarograph with a rotating platinum indicator electrode and a saturated calomel reference electrode. Connect the electrodes to the polarograph, making sure the platinum wire electrode is the anode. Adjust the polarizing potential of the platinum wire electrode to + 1.0 v vs the S.C.E. Check the applied potential switch and make sure it reads zero. Set the galvanometer at a reading between 10 and 20 by varying the scale-adjusting switch. Start the rotator and titrate the vanadate with standard ferrous ammonium sulphate solution. Samples which contain 1 - 50 mg of vanadium should be titrated with 0.01N or 0.1N ferrous solution, while samples which contain 0.05 to 1 mg of vanadium should be titrated with 0.001 N ferrous solution.

Record the volume of titrant, and the corresponding current readings (galvanometer deflections) at 0.10 - 0.20 ml intervals before and after the equivalence point. At least four or five good points are required on each side of the equivalence point. Plot a graph of volume of titrant vs galvanometer deflection, and draw lines through the plotted points. A reversed L-shaped titration graph is obtained for this titration. Standardize the iron solution against a vanadium standard solution each day.

If chromium is present, repeat the oxidation and titration steps. In this case, add potassium permanganate to the titrated solution until the solution remains pink. The vanadium (IV) and ferrous ion will oxidize in the cold, but chromium (III) will remain unaffected. Add enough 2% sodium nitrite to decolorize the permanganate, then add 5 g of urea at once and titrate with ferrous solution. The difference between the two titrations represents the chromium present.

EXPERIMENTAL

As the amperometric titration of vanadium with ferrous ammonium sulphate is relatively free of interferences, it was not expected that the presence of other elements in the fly ash and precipitates would lead to any difficulty. Of the commonly encountered ions, only arsenic, antimony, tungsten, cerium(IV) and chromium would be expected to cause trouble unless provision was made for treating them either by a separation or by a

special techniques, such as that described for chromium. None of these interferences has been detected in the Petrofina samples received here, with the exception of traces of chromium found in the boiler fly ash itself.

In carrying out the procedure, difficulty was encountered at times in obtaining good precision between duplicates on high-grade vanadium precipitates, particularly when analyzing large quantities of samples. The high degree of precision required (better than 0.5%) could be obtained, however, by carrying out a double oxidation and titration technique, as used in the procedure when chromium is present. In such a case, chromium, unlike vanadium, is not reoxidized with permanganate in the cold and, therefore, does not affect the second titration. Chromium, in greater than trace amounts was not present in the high-grade precipitates, however. Furthermore, the precision obtained on the standards regularly carried along with each set of samples was not always as good as expected. It was apparent, then, that another explanation was needed for the lack of precision found. An investigation was carried out, therefore, to determine the reason for this by carrying a number of standard vanadium solutions through the procedure while varying certain conditions. This investigation was focused mainly on conditions used in the oxidation and titration steps.

For the oxidation of vanadium before its amperometric titration, it had been customary to fume the sample with perchloric acid and complete the oxidation with potassium permanganate. Destruction of excess permanganate was then carried out by addition of either a measured amount of sodium azide (2) or a small excess of sodium nitrite followed by urea to destroy excess nitrite (3, 4, 5). The solution acidity used during these steps appears from the literature to vary widely, but it is generally considerably greater than 5%. Results obtained by carrying a number of standard vanadium solutions through the procedure while varying the acidity, the order of addition of the reagents used to destroy the excess of permanganate which remains after the oxidation of the vanadium, the waiting time between these additions, and the waiting time prior to titration, are shown in Tables 2 and 3. Application of two procedures to some typical precipitates was then carried out (Table 4) and the precision of the recommended procedure evaluated (Table 5).

RESULTS AND DISCUSSION

It was found that unless urea was immediately added following nitrite addition, partial reduction of vanadium apparently took place. This reduction was accentuated as the acidity of the sample solution increased (Table 2). When analysing large numbers of samples under routine conditions, it was found that variances in the oxidation and titration steps were more likely to occur, hence the adverse effect on the precision was more pronounced.

The effect of varying the order of addition of reagents to permit the addition of urea before permanganate, instead of the normal order of permanganate-nitrite-urea, is shown in Table 3. Where urea was added first, good precision was indicated and this step appeared to obviate the necessity of strictly controlling the waiting time following nitrite addition, and the acidity of the sample during the oxidation and titration steps. It was felt, therefore, that although good precision could be obtained by strict control of the sample acidity and waiting time following nitrite addition, the most satisfactory procedure for general use was to add urea before the oxidation with permanganate. In this way vanadium reduction is prevented, as the nitrite apparently reacts with the permanganate and urea before the vanadium. Also, as a further precaution, the recommended acidity of the sample solution was lowered to 5% in sulphuric acid.

A comparison was made of results obtained on a number of precipitates, adding the urea before permanganate in one case, and carrying out a double oxidation and titration in the other (Table 4). These analyses were carried out with several days spacing between each procedure, and results were calculated from different standards.

A short study was made of the precision to be expected by using Procedure 2 (Table 4). Four typical precipitates were analysed in triplicate and the precision evaluated according to the method of Dean and Dixon (6). Results, shown in Table 5, represent the precision found using a titration range of 10 to 20 ml of ferrous ammonium sulphate, with all determinations being carried out on the same day.

TABLE 2

Effect on the Vanadium Titration of the Acidity and the Waiting Time Before Urea Addition

Test	Order of Addition of Reagents		Acidity		Vanadium* present, mg V ₂ O ₅	Vanadium recovered, mg V ₂ O ₅		Remarks
			5% H ₂ SO ₄ + 5% HClO ₄	5% H ₂ SO ₄		1st titration	2nd titration	
	1st titration	2nd titration						
1	None	-	Yes	-	5.00	4.83	-	-
2	Urea	-	Yes	-	5.00	4.91	-	-
3	KMnO ₄ - NaNO ₂ - urea added immediately.	-	Yes	-	5.00	4.97	-	-
4	KMnO ₄ - NaNO ₂ - 5-minute wait before adding urea.	-	Yes	-	5.00	4.16	-	-
5	"	-	Yes	-	10.0	9.63	-	-
6	KMnO ₄ - NaNO ₂ - 15-minute wait before adding urea.	-	Yes	-	10.0	8.79	-	-
7	KMnO ₄ - NaNO ₂ - 5-minute wait before adding urea - then re- peat all steps before 1st titration.	Repeat all steps before 2nd titration.	-	Yes	10.0	10.0	10.0	Oxidation procedure carried out a total of three times.
8	KMnO ₄ - NaNO ₂ - urea added immediately.	-	-	Yes	5.00	5.03	-	-
9	"	-	-	Yes	10.0	10.0	-	-
10	KMnO ₄ - NaNO ₂ - 2-minute wait before adding urea.	-	-	Yes	10.0	10.0	-	-
11	KMnO ₄ - NaNO ₂ - 5-minute wait before adding urea.	-	-	Yes	10.0	9.95	-	-
12	KMnO ₄ - NaNO ₂ - 15-minute wait before adding urea.	-	-	Yes	10.0	9.84	-	-

* All standard solutions prepared from ammonium vanadate (AR).

TABLE 3

Effect on the Vanadium Titration of the Order of Addition of Reagents

Test	Order of Addition of Oxidation Reagents		Acidity		Vanadium present, mg V_2O_5	Vanadium recovered, mg V_2O_5		Remarks
			5% H_2SO_4 + 5% $HClO_4$	5% H_2SO_4		1st titration	2nd titration	
	1st titration	2nd titration						
1	KMnO ₄ - NaNO ₂ - 5-minute wait before urea.	-	-	Yes	10.0	9.95	-	-
2		-	Yes	-	10.0	9.63	-	-
3	Urea-KMnO ₄ -NaNO ₂ - 5-minute wait before adding urea.	-	Yes	-	5.00	5.02	-	Urea added prior to oxidation with KMnO ₄ .
4	KMnO ₄ - Urea - NaNO ₂ - 5-minute wait before titration.	KMnO ₄ - Urea - NaNO ₂ - 5-minute wait before urea.	-	Yes	5.00	4.98	4.98	-
5	Urea - KMnO ₄ - NaNO ₂ - 5-minute wait before urea.	KMnO ₄ - NaNO ₂ - 5-minute wait before adding urea.	Yes	-	10.0	10.0	10.0	Urea added prior to KMnO ₄ .
6	Urea - KMnO ₄ - NaNO ₂ - urea immediately.	KMnO ₄ - NaNO ₂ - urea immediately.	-	Yes	10.0	10.0	10.0	Urea added prior to KMnO ₄ .
7	KMnO ₄ - NaNO ₂ - 5-minute wait before urea; then repeat all steps before 1st titration.	-	-	Yes	10.0	10.0	-	-

TABLE 4

Comparison of Vanadium Results by Two Titration Procedures

Sample Number	Procedure 1 - double oxidation and titration, % V_2O_5	Procedure 2 - urea added before oxidation and titration, % V_2O_5
5438	88.48	88.75
5439	89.46	89.89
5440	94.41	94.35
5441	92.58	92.53
5442	96.10	95.99
5443	90.01	90.07

TABLE 5

Precision of the Vanadium Determination on Vanadium Precipitates

Sample No.	Vanadium as % V_2O_5			
	1	2	3	Average
885	75.91	75.86	75.86	75.88
4558	58.85	58.85	58.85	58.85
4675	97.10	97.19	97.15	97.15
4734	84.96	84.96	85.01	84.98
<p>Standard deviation = ± 0.028</p> <p>Relative standard deviation = $\pm 0.029\%$ precipitate containing 97% V_2O_5</p> <p>95% confidence limits, for the average of three determinations = ± 0.072</p>				

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Procedure 2

DETERMINATION OF IRON

INTRODUCTION

Ferrous iron forms an orange-red complex with o-phenanthroline which may be used as the basis for a colorimetric procedure. This reaction and its colorimetric application have received extensive attention in the literature (1, 2, 3, 4, 5). The coloured complex formed is stable, sensitive, and relatively free from interference, and forms quantitatively over a pH range of 2 - 9. The pH range over which it may be used, however, is determined by the type of sample material being analysed.

The quantity of iron present in the samples submitted during this project was important primarily with regard to the purity of the chemical precipitates. Of the elements found in the various sample products from fly ash treatment (Table 1), the only ones which might be expected to cause difficulty in the colorimetric o-phenanthroline procedure as currently used in this laboratory, were nickel and, because of its high concentration, vanadium.

Nickel has been reported by Fortune and Mellon (2) to cause a change in the hue of the solution and raise transmittance readings below a wave length of 540 mm. Hibbitts et al.(3) reported a 100% negative error when 10 mg of nickel was present per 0.1 mg of iron, but no interference was reported when determining 0.1 mg of iron in the presence of 1 mg of nickel. It is generally known, however, that certain cations, such as nickel, tend to consume o-phenanthroline reagent and the result may be low iron results (4, 5).

Iron has been determined in high-vanadium material by Margerum and Banks (5). They found that vanadium in the penta- and trivalent states formed precipitates with o-phenanthroline, but was soluble when converted to the quadrivalent state with hydrolyxamine hydrochloride and gave a completely colourless solution at pH 5. Their procedure included extraction, after addition of sodium perchlorate and o-phenanthroline, of the ferrous complex with nitrobenzene. The success of the method depended upon the slow reaction of vanadium (IV) with o-phenanthroline, and the non-extractability of the perchlorate of this complex (5). Recently, Hibbitts et al.(3) found that a o-phenanthroline procedure may be used to determine 0.1 mg of iron in the presence of 10 mg of vanadium.

An o-phenanthroline procedure for iron already receives considerable use in this laboratory on a variety of sample material. Its application therefore to high-vanadium material offered the advantage of convenience, particularly as the iron content of most of the samples (0.5 - 5%) was expected to fall within the effective range of this procedure.

APPARATUS AND REAGENTS

Apparatus

Spectrophotometer, Beckman Model "B".

Reagents

Hydroxylamine hydrochloride, 10% (w/v)

Sodium acetate, 50% (w/v)

O-phenanthroline, 0.25% (w/v)

Dissolve 1.25 g of 1,10-phenanthroline in water and dilute to 500 ml.

PROCEDURE

Dissolve the sample as described under "Determination of Vanadium" and make the sample solution up to volume in a volumetric flask. Take an aliquot such that 0.02 - 0.2 mg Fe is present and place it in a 50-ml volumetric flask or in a 50-ml beaker, depending on how the pH is to be adjusted. Then adjust the pH to 1.8 - 2.0, checking it by means of a pH meter or pH paper. Add 3 ml 10% hydroxylamine hydrochloride to the sample which is contained in approximately 25 ml volume in a 50-ml volumetric flask. If the solution is coloured brown at this point, allow it to stand until the colour completely fades. In the case of high-vanadium material, this may take 30 - 45 minutes. Then add 10 ml of 0.25% o-phenanthroline reagent and allow it to stand for 20 - 30 minutes. Add 3 ml of 50% sodium acetate solution and make the solution up to volume with water (the pH should now be 5.0 - 5.5). After allowing the solution to stand for 10 minutes, read the optical density on a Beckman "B" spectrophotometer at 510 mμ, using water as a reference. Carry out a reagent blank, or, if the vanadium and/or nickel to iron ratio is very high, a blank containing the approximate quantities of these contaminants found in the sample.

EXPERIMENTAL

Analysis of some early samples indicated that usually the ratios of vanadium to iron would not exceed 200 to 1, while nickel-to-iron ratios would be less than 1 to 1. A number of tests were carried out on synthetic samples to establish the effect on the o-phenanthroline procedure of vanadium and nickel by themselves, together, and in the presence of iron at various

levels of concentration (Tables 6 and 7). The effect of varying the quantity of o-phenanthroline is shown in Table 8. Finally, results obtained on three typical types of samples using an o-phenanthroline procedure directly, and following a sodium hydroxide separation of iron from vanadium, are shown in Table 9.

RESULTS AND DISCUSSION

Results indicated that iron values obtained by the o-phenanthroline procedure would be affected by the presence of large quantities of vanadium and moderate quantities of nickel (Table 6 and 7). Vanadium-nickel-iron ratios of 200-10-1 were acceptable, however, provided an excess of o-phenanthroline was present (Table 8). It is thought that the practical limit of nickel tolerance would be governed partly, at least, by the amount of o-phenanthroline which could conveniently be used. It is shown that 1 mg of nickel and 18 mg of V_2O_5 can be tolerated, but the upper limit was not determined. When carrying out iron determinations by this procedure it is customary, in this laboratory, to work with two different aliquot sizes; this is an aid in detecting when insufficient reagent is present.

For highest accuracy, a blank containing the approximate amount of vanadium and nickel found in the sample is a necessity when these contaminants are high, but care must be taken to use iron-free vanadium and nickel reagents. For control work, on most samples this step is probably unnecessary. A sample blank containing all additions except o-phenanthroline would be of questionable value, as the addition of o-phenanthroline causes a change in hue when it is added to vanadium and nickel blanks. It was found that reagent blanks were not changed by additions of between 3 ml and 15 ml of o-phenanthroline. The amount of hydroxylamine hydrochloride added, however, must be controlled, as its addition increases the optical density reading slightly.

It was found also that if vanadium is present in the sample as the vanadate it forms a brown colour upon addition of hydroxylamine. This colour disappears upon standing for about 30 minutes. If the vanadium is present as the vanadous ion following treatment of the sample with hydrochloric acid, a strong greenish colour forms which does not readily disappear upon standing. In such a case, blanks are higher and some colour fading is encountered. It is best, then, to have vanadium in an oxidized state before the colorimetric finish procedure is begun.

Application of the procedure to a sample of fly ash and two typical precipitates is shown in Table 9. Although a blank correction was not made in all cases for the vanadium and nickel present, a reagent blank correction was always made. Results were compared with those obtained by the o-phenanthroline finish following a single or double caustic separation

from vanadium using titanium as a carrier. These results are in satisfactory agreement, although slightly lower values were found following the separation. This is believed to be more likely due to slight losses in the caustic precipitation steps, rather than to the effect of interfering elements on the direct procedure, in view of the comparatively low contaminant concentration in these samples.

TABLE 6

Blank Effect of Vanadium and Nickel on the O-phenanthroline

Procedure for Iron

Test	Vanadium present, mg V ₂ O ₅	Nickel present, mg Ni	O-phenanthroline added, ml	Optical density (less reagent blank)
1	4.5	--	5	0.000
2	9.0	--	5	0.003
3	18	--	5	0.004
4	--	0.1	5	0.003
5	--	1.0	5	0.007
6	9.0	0.1	5	0.003
7	18	0.5	10	0.011
8	18	1.0	10	0.012

TABLE 7

Effect of Vanadium and Nickel on the O-phenanthroline

Procedure for Iron

(0.080 mg iron and 5 ml of o-phenanthroline present in all tests)

Test	Vanadium present, mg V_2O_5	Nickel present, mg Ni	Optical Density	
			Less reagent blank	Less correction for V + Ni blank (where known from Table 6)
1	--	--	0.320	--
2	--	1.0	0.322	0.315
3	--	2.0	0.297	--
4	9.0	--	0.322	0.319
5	4.5	0.1	0.320	--
6	9.0	0.1	0.321	0.318
7	18	0.1	0.311	--
8	18	0.5	0.316	0.305
9	18	1.0	0.288	0.276

TABLE 8

Effect of Varying Quantities of O-phenanthroline on the O-phenanthroline

Procedure for Iron in the Presence of Vanadium and Nickel

(0.080 mg Fe present in all tests)

Test	Vanadium present, mg V_2O_5	Nickel present, mg Ni	O-phenanthroline added, ml	Optical Density	
				Less reagent blank	Less correction V + Ni blank (where known)
1	--	--	3-10	0.320	--
2	--	1.0	3	0.301	--
3	--	1.0	5	0.322	0.315
4	--	2.0	5	0.297	--
5	9.0	--	5	0.322	0.319
6	9.0	0.1	5	0.321	0.318
7	18	0.1	5	0.311	--
8	18	0.1	10	0.328	--
9	18	0.5	5	0.316	--
10	18	0.5	10	0.328	0.317
11	18	1.0	5	0.288	--
12	18	1.0	10	0.328	0.316

TABLE 9

Determination of Iron on Typical Samples

Sample No.	Sample type	Nickel present, %Ni	Vanadium present, %V ₂ O ₅	Iron found, % Fe		
				No separation	Following single caustic separation	Following double caustic separation
4428	Fly ash	0.60	9.63	1.81	1.77	---
4558	ppt	0.32	49.0	2.25	2.23	---
4581	ppt	Not known	93.3	3.11	- -	3.08

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Procedure 3

DETERMINATION OF SODIUM

INTRODUCTION

Sodium was determined flame-photometrically in fly ash and in products from chemical treatment of the ash, over the range 0.05-0.5%. The method was used without preliminary separation of vanadium or other possible interfering elements, but consideration was given to the possible effect of the sample matrix on the analytical results. The sodium values were required for the calculation of a reagent balance in connection with the leaching process and subsequent purification steps.

The general method used in this laboratory (1) is based upon published procedures (2, 3, 4), with suitable modifications being made for the sample matrix encountered. In the described procedure, a solution of the sample is sprayed under controlled conditions into an oxy-acetylene flame. By using a monochromator, such as in the attachment for the Beckman spectrophotometer, Model "B", interference by emission of other elements is unlikely. Because of the quantity of vanadium present, relative to other possible contaminants and to sodium in this sample material, it was considered that vanadium would be the only contaminant likely to affect sodium results. In such a case, the extent of quenching or enhancement of the emission, is determined by drawing up a calibration curve, prepared by "spiking" samples with increasing amounts of sodium. Also, a synthetic matrix similar to the sample material may be "spiked" with increasing amounts of sodium. The acidity of the sample solution should be duplicated in the standards, as higher acidities tend to have a depressing effect on the emission.

APPARATUS AND REAGENTS

Apparatus

Beckman Spectrophotometer Model "B", with Beckman 9125 flame attachment.

Acetylene tank regulator, two stage, with gauges.

Oxygen tank regulator, two stage, with gauges.

Exhaust system.

Timer, 120-minute type, with alarm.

NOTE: Further information on the above apparatus and its operation in flame photometric work may be found in References 1, 3 and 4.

Reagents

Acetylene, 250 cu ft. cylinder.

Oxygen, 200 cu ft. cylinder.

PROCEDURE

Fly Ash

Weigh out an appropriate sample into a platinum dish and carry out a preliminary ignition over a burner at low temperature to remove most of the carbon. Then leach the residue with concentrated hydrochloric acid and dilute with water until the final concentration is 5% HCl. Carry along standards and a blank with the sample, adding the same amount of acid to each. The blank, and preferably the standards as well, should contain approximately the same amount of vanadium as the sample. Transfer to a volumetric flask of suitable size, depending on the sodium content. Handling of the standards, blank and samples should be in the same type of container (i.e. platinum, glass, Teflon). Carry out the flame photometric procedure for sodium as described in Reference 1.

Precipitates

Weigh out an appropriate sample into a beaker, add concentrated hydrochloric acid, and leach until the sample is completely in solution. Dilute with water and transfer to an appropriate volumetric flask, keeping the acidity at about 15% HCl. Carry along standards and a blank as described for Fly Ash (above).

Solutions

Take an appropriate aliquot and dilute in a suitable volumetric flask, adjusting the acidity to 5% in hydrochloric acid. Carry along standards and a blank as described for Fly Ash (above).

EXPERIMENTAL

In order to determine the effect of vanadium on sodium values, a number of synthetic samples were run consisting of vanadium alone and vanadium plus sodium. Ratios as high as 1000 to 1 of vanadium to sodium were tried and sodium recovery determined after making a blank connection taking into account the amount of vanadium present. Results of these tests are shown in Table 10.

In other tests, two levels of sodium were added to three typical precipitates and the recovery of sodium was determined. Sodium results were calculated on the samples after making a correction for added sodium and were compared with those obtained by making an additional correction taking into account the amount of vanadium present. The results are shown in Table 11.

TABLE 10

Effect of Vanadium on Sodium Determinations in Synthetic Samples

Sample type	Vanadium added, g/l V_2O_5	Sodium added, g/l Na	Sodium recovered, g/l Na	Remarks
Water blank	-	-	0.0004	-
Vanadium blank	2.0	-	0.0013	-
Vanadium blank	10.0	-	0.004	-
Vanadium blank	20.0	-	0.010	-
Synthetic V_2O_5 -Na, 50-1	2.0	0.040	0.041	After blank correction
Synthetic V_2O_5 -Na, 100-1	2.0	0.020	0.020	After blank correction
Synthetic V_2O_5 -Na, 200-1	2.0	0.010	0.010	After blank correction
Synthetic V_2O_5 -Na, 500-1	10.0	0.020	0.020	After blank correction
Synthetic V_2O_5 -Na, 2000-1	20.0	0.010	0.010	After blank correction
Synthetic V_2O_5 -Na, 4000-1	20.0	0.005	0.006	After blank correction

TABLE 11

Effect of Vanadium on Sodium Determinations in Precipitates

Sample	Apparent ratio present, V_2O_5 -Na	Vanadium present in sample, g/l V_2O_5	Sodium added to sample, g/l Na	Added sodium recovered, g/l Na	Sodium found in sample		
					After correction for added sodium, % Na	After correction for added sodium and a vanadium blank, % Na	Calculated from vanadium matrix with standards spanning samples, % Na
4292 ppt (72% V_2O_5)	200-1	1.8	-	-	0.32	0.29	-
	150-1	1.8	0.005	0.005	0.33	0.29	-
	100-1	1.8	0.010	0.010	0.33	0.30	-
	200-1	3.6	-	-	0.34	0.32	-
	100-1	3.6	0.020	0.022	0.38	0.35	-
4293 ppt (95% V_2O_5)	2500-1	10	-	-	0.09	0.05	-
	1000-1	10	0.005	0.0055	0.09	0.05	-
	700-1	10	0.010	0.011	0.10	0.06	-
	3000-1	20	-	-	0.10	0.07	0.04
	400-1	20	0.010	0.012	-	-	-
	600-1	20	0.020	0.026	0.11	0.06	-
4456 ppt (95% V_2O_5)	20-1	0.2	-	-	4.90	4.86	-
	13-1	0.2	0.005	0.005	4.95	4.88	-
	10-1	0.2	0.010	0.010	5.00	4.93	-
	20-1	0.4	-	-	4.96	4.93	4.88
	13-1	0.4	0.010	0.020	-	-	-
	10-1	0.4	0.020	0.020	4.93	-	4.90

RESULTS AND DISCUSSION

The tests carried out on synthetic samples containing vanadium alone, and vanadium and sodium together, indicated that a definite blank effect resulted from the presence of vanadium. Results also indicated that up to the level of 2000-1, vanadium to sodium, 0.020 g/l sodium could be determined if a blank correction was made. At a level of 4000-1, vanadium to sodium, however, recovery of sodium showed a positive error.

In the case of the three samples tested, recovery of added sodium was satisfactory at lower sodium levels but there was an indication that results would tend to be higher as the quantities of sodium and vanadium increased over a certain level. The necessity of compensating for the presence of vanadium is shown by comparing results obtained with and without vanadium blank correction, and, in two cases, with values calculated on a vanadium matrix with sodium standards spanning the sample. Results indicated that it would be desirable to work at as high a dilution level as possible in order to minimize the effect of vanadium, and, also, to work at two aliquot levels.

It was felt that for highest accuracy a separation of vanadium and sodium would be required, with reagent blanks and standards carried through the procedure. For control analysis, satisfactory results could be obtained by correcting for a vanadium blank, or better, adding vanadium to standards and closely spanning the samples. In any of these procedures for control analysis the approximate vanadium content would need to be known. In the vanadium blank correction technique, special care should be taken to use a sodium-free vanadium reagent. It should also be noted that the sodium blank varies with the type of vessel used in the analysis. For example, some types of glass will give a blank four times that of platinum.

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Procedure 4

DETERMINATION OF PHOSPHORUS

INTRODUCTION

Phosphorus is determined colorimetrically by a procedure based upon the formation of an orange-yellow phosphovanado-molybdic acid which can be extracted into isoamyl alcohol. The coloured compound has been found to obey Beer's Law, either when read directly or following extraction with isoamyl alcohol.

Misson (1) reported the use of this reaction for a colorimetric method in 1908. It has been used recently for the determination of phosphorus in fertilizers (2) and in iron ore and plain carbon steels (3, 4). A more recent advance has been reported by Elwell and Wilson (5), who extracted the complex with isoamyl alcohol and improved the sensitivity and selectivity of the procedure. The method has been used in this laboratory on a number of different types of sample material (6) and it appeared to be well suited to the present application, particularly for the determination of the phosphorus content of high-grade vanadium precipitates, on which an upper limit of 0.05% has been set.

APPARATUS AND REAGENTS

Apparatus

Beckman spectrophotometer, Model "B".

Centrifuge, 10-ml test tube size.

Reagents

Ammonium vanadate - ammonium molybdate solution

Dissolve 1 g of ammonium vanadate (NH_4VO_3) in about 300 ml of water, using a magnetic stirrer. After dissolution, add 140 ml of concentrated nitric acid. Cool. To this add 40 g of ammonium molybdate $[(\text{NH}_4)_2\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ which has been dissolved in 400 ml of water, using a magnetic stirrer. Dilute to one litre. Prepare fresh every few days, as the blank gradually increases.

Standard phosphate solution

Dry potassium dihydrogen phosphate at 105°C until constant weight is reached. Dissolve 4.393 g in water and dilute to 1 litre. Dilute 10 ml to one litre.

$$1 \text{ ml} = 0.01 \text{ mg P}$$

PROCEDURE

Precipitates

Weigh out 0.5 g of the precipitate into a 250-ml beaker and add dilute hydrochloric acid. Warm on the hot plate until the sample goes into solution. Add 2-3 ml of concentrated nitric acid and 5 ml of concentrated perchloric acid and take to fumes. Add 50-100 ml of water and enough hydrochloric acid to effect solution with the aid of boiling.

Place a suitable aliquot (20 - 100 γ P) in a 100-ml beaker. Add 5 ml of 20% v/v nitric acid and enough concentrated perchloric acid to make a total of 5 ml. Dilute with water to about 50 ml and heat to 80°C on the hot plate. Add 25 ml of the ammonium vanadate-molybdate reagent to the warm solution and cool to room temperature.

Transfer the sample to a 125-ml separatory funnel and adjust the aqueous volume to approximately 80 ml. Cool. Add by pipette 10 ml of N-amyl alcohol (peroxide free) and shake the funnel contents for exactly one minute. Let the layers separate for 5 minutes. Drain off and discard the aqueous layer. Wash the organic layer with 5 ml of 5% perchloric acid solution and discard the aqueous layer. Repeat the washing step if the vanadium content is high.

Place the organic layer in a 10-ml centrifuge tube and centrifuge for 30 seconds. Transfer to a 1-cm cell and read the optical density at 425 $m\mu$ with N-amyl alcohol in the comparison cell. Compare optical density readings against a standard curve covering the range from 20 to 100 micrograms of phosphorus per 10 ml final volume. Carry a reagent blank through the procedure with each set of samples and make a correction.

If chromium is present, boil the sample aliquot containing 3 ml concentrated perchloric acid with 10 ml of saturated SO_2 water for 10 minutes (covered for 5 minutes), then add 5 ml of 20% v/v nitric acid and boil for 2-3 minutes. Add 25 ml molybdovanado reagent to the warm solution and continue as described above.

EXPERIMENTAL

Preliminary tests on high-vanadium material showed that a direct method using this reaction without extraction of the coloured complex would not be satisfactory due to the highly coloured nature of the sample solution, which caused the sample blank effect to be very high. Accordingly, a series of synthetic samples containing phosphorus and vanadium were made up and phosphorus recovery determined. Due to the extraction of some coloured material from the sample, it was found advisable to carry out a wash of the organic layer. This washing technique was integrated into the procedure for application to high-vanadium precipitates. Examples of the use of the procedure on synthetic samples and on four typical precipitates are shown in Table 12. Due to the lack of suitable standards, it was necessary to check the efficiency of the procedure on the precipitates by adding phosphorus to them and determining its recovery.

RESULTS AND DISCUSSION

During these tests it was found that a washing step is essential on high-vanadium material. Where an extraction without washing was carried out on synthetic samples containing large amounts of vanadium, high blanks were obtained and results were inconsistent. In addition, the colour gradually faded. Following a double wash of the organic layer with 5 ml of 5% perchloric acid, no fading was observed and the blanks decreased to a satisfactory level. As can be seen from Table 12, recovery of phosphorus on both synthetic and actual samples appeared to be satisfactory.

TABLE 12

Determination of Phosphorus in the Presence of Vanadium

Sample	Vanadium present, mg V		Number of washes	Phosphorus added, $\mu\text{g P}$	Phosphorus recovered, $\mu\text{g P}$
Synthetic	44		2	20	20
"	30		2	50	52
"	44		1	50	50
"	44		2	50	52
"	22		2	100	100
"	44		2	100	100
	Vanadium and Phosphorus present				
	% V_2O_5	% P			
4500 (ppt)	59.5	0.02	2	50	48
4506 (ppt)	77.6	0.03	2	50	49
4517 (ppt)	80.4	0.03	2	50	51
4558 (ppt)	49.0	0.02	2	50.5	51

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Procedure 5

DETERMINATION OF TITANIUM

INTRODUCTION

Titanium is often determined spectrophotometrically in this laboratory and elsewhere (1) from the colour formed when hydrogen peroxide is added to an acidic titanium (IV) solution. The procedure is relatively insensitive, but is capable of giving high precision over a wide range of acidity conditions. Because vanadium is a serious interferent in the procedure, it was expected that it would first be necessary to separate the titanium from the vanadium by means of a sodium hydroxide precipitation(2). In view of the low titanium-vanadium ratio, it was considered advisable to carry out a double or triple precipitation of titanium to ensure complete removal of vanadium. Iron, or another suitable carrier, should be added if no other element is present which precipitates in appreciable quantity in sodium hydroxide medium. The effect of iron is compensated for in the colorimetric finish by adding phosphoric acid to complex the ferric ion.

Fluoride interferes seriously with colour development and must be removed completely, although traces of fluoride may be permissible if they are complexed by adding boric acid before developing the colour.

APPARATUS AND REAGENTS

Apparatus

Beckman spectrophotometer, Model B.

Reagents

Standard titanium solution

Dry reagent-grade titanium dioxide(TiO_2) in the oven for 2 hours. Weigh 0.8349 g TiO_2 into a 50-ml platinum dish, fuse with 5 g of potassium pyrosulphate, and dissolve the melt in 10% sulphuric acid solution. Alternatively dissolve by heating with 10 g of ammonium sulphate and 25 ml of sulphuric acid. Dilute to 500 ml with 5% sulphuric acid in a volumetric flask.

Boric acid solution, 10%

Dissolve 10 g of solid boric acid in hot water ($>80^\circ\text{C}$). Dilute to 100 ml.

Hydrogen peroxide solution, 30%

Sodium hydroxide solution, 50%

Phosphoric acid, 85%

PROCEDURE

Weigh 0.5 g of the precipitate into a platinum dish and contact it with 4-5 ml of 45% hydrofluoric acid. Warm the sample for 15-20 minutes and repeat this step if dissolution of the sample is incomplete. Cool, add about 2 ml of concentrated nitric acid, and heat the sample to low volume but not to dryness. Repeat this step. Add 15 ml of 1:1 sulphuric acid and take to heavy fumes of sulphuric acid for 20 minutes.

Cool, wash out the dish with 5% sulphuric acid, and carry out three sodium hydroxide precipitations to separate the soluble sodium vanadate from the titanium(2). If the iron content of the sample is known to be less than 10 mg, add enough iron to provide a suitable carrier for the titanium.

After removal of vanadium is complete, dissolve the precipitate in hot 5-10% sulphuric acid and dilute to an intermediate volume ready for aliquotting. If no dilution is made, reduce the solution to a volume of approximately 25 ml. Add 3 ml of 10% boric acid solution (if fluoride has been used), then enough acid to make the final solution 10% in sulphuric acid. Add 5 ml of concentrated phosphoric acid, then 2 ml of 30% hydrogen peroxide and dilute to 50 ml in a volumetric flask. Read at 425 mμ on the spectrophotometer against a reagent blank.

It may be desirable to check the efficiency of the procedure by analysing at the same time a synthetic standard containing titanium, iron and vanadium in the approximate quantities expected in the sample. In this case, calculate the sample results from the results obtained on the synthetic standard. As a further check on titanium recovery, add standard titanium solution to a duplicate aliquot of the sample and calculate recovery of the added titanium.

EXPERIMENTAL

The limited program of experimental work carried out to establish the efficiency of the procedure was confined to the following tests:

- (a) A synthetic sample was made up consisting of quantities of vanadium, iron and titanium in the approximate amounts found in the sample. Results for the sample were calculated on the basis of the recovery of titanium found on the synthetic sample.
- (b) Standard titanium was added to two weighings of the Petrofina sample, and a third weighing carried along as a control. Three aliquots were analysed in each case and recovery of titanium calculated.
- (c) An absorption spectrum for the sample was run on the coloured solution from the colorimetric finish and was then compared with the absorption spectrum of pure titanium standard solution under the same conditions. As absorption maxima for peroxidized titanium and vanadium are 410 mμ and 460 mμ respectively (1), it was expected that a comparison of the absorption curves would be an aid in establishing the purity of the peroxidized titanium compound in the colorimetric finish.

RESULTS AND DISCUSSION

The Petrofina sample was found to contain 0.81% titanium by each of the procedures for calculation described under PROCEDURE.

- (a) It was found that recovery of titanium on the synthetic sample was complete. The synthetic sample, which was made up to be 80% V_2O_5 , 2% Fe and 0.50% Ti, yielded 0.50% Ti.
- (b) Recovery of titanium on the sample to which standard titanium had been added showed a recovery of about 99.5% of the added titanium (average of 6 results).
- (c) The absorption curves for the peroxidized titanium solution on the sample and on standard titanium solution were virtually identical, indicating that the sample was free of vanadium following a triple sodium hydroxide precipitation.

Precision

The precision of the procedure, as calculated from the results obtained on this sample according to the procedure of Dean and Dixon (3), showed a standard deviation of 0.0047. This gives a relative standard deviation of 0.57%, and 95% confidence limits of ± 0.012 . These calculations were based on five weighings, with two or three aliquots from the solution of each weighing, and with results calculated from two different sets of titanium standards.

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Procedure 6

DETERMINATION OF ALUMINUM

INTRODUCTION

Aluminum is determined in high-vanadium sample material by a procedure based on the extraction with chloroform of the complex formed by aluminum and 8-hydroxyquinoline at a controlled pH (1, 2, 3, 4). Measurement of the aluminum may then be made either fluorimetrically or spectrophotometrically, depending on the sensitivity desired. A fluorimetric finish is used to detect quantities of aluminum from 2-15 μg in the final aliquot, while the spectrophotometric finish is used for the range 10-100 μg of aluminum.

A considerable amount of conflicting information may be found in the literature concerning the best pH conditions for the extraction (5, 6, 7). It has been found, in this laboratory (4), that with the procedures as described, extraction is complete over the pH range 5.5 to 7. As more interference from other ions can be expected at higher pH values, it is desirable to keep the pH as low as possible. In the recommended procedures, therefore, a pH of 5.6-5.7 is used.

The procedures are prone to interference from a number of common ions and a preliminary separation of some type is usually necessary. In the sample material concerned in this work, iron, vanadium and nickel may be present in quantities which would interfere. The tolerance of the fluorimetric procedure is very low for iron and vanadium in particular, although some iron can be tolerated if it is complexed by the addition of o-phenanthroline (4, 7). In general, the spectrophotometric finish is more tolerant of interferences than the fluorimetric finish. Manganese, which is often added as an oxidant before the cupferron separation, can be tolerated in manganese-to-aluminum ratios of 10-1 when using the spectrophotometric finish (8). A quenching of the fluorescence by manganese under some conditions has been reported (2). As the ratio of contaminant to aluminum in the vanadium sample material encountered tends to be very high, it has been found advisable to carry out a cupferron separation of iron and vanadium on all samples (9). In addition, if the nickel content of the sample is appreciable it is necessary to separate it by means of a mercury cathode separation (9, 10). Fluoride is a serious interferent and must be removed by fuming with sulphuric acid in platinum or Teflon containers. Care should be taken to avoid the use of glass if fluoride is present, or if caustic sample solutions are being handled, for considerable amounts of aluminum are present in many types of glass and may be leached out during sample handling (4).

Although the effect of the blank is considerably greater on the fluorimetric finish than on the spectrophotometric finish, a blank determination should always be carried out with each set of determinations, using either procedure. The precision of the procedure is adversely affected by variations in the described techniques; therefore, care should be taken to follow the directions exactly with regard to the order of addition of reagents and the volumes employed.

APPARATUS AND REAGENTS

Apparatus

pH meter, EIL Model 23.

Separatory funnels, Squibb's pear-shape with Teflon plugs.

Stoppers, polyethylene; Nalgene, No. 2.

Spectrophotometer, Beckman, Model B.

Mercury cathode, Eberbach Dyna-Cath.

Fluorimeter

A General Electric Model H-100 A₄ lamp (stabilized by a Sola constant-wattage 100-watt transformer), in a water-cooled housing, illuminates the solutions contained in Corex fluorimeter cells in a Cat. No. 2980 Beckman Fluorescence Attachment through a filter which isolates the 3650Å mercury line. The fluorescent light from the sample, passed through a yellow filter to remove reflected ultra-violet light, is picked up by a Farrand Electron Multiplier Photometer. This latter unit consists of a detector unit containing a 1P 21 photomultiplier tube, and its power supply. A Leeds and Northrup 10,000-ohm Ayrton shunt and a spotlight galvanometer are used to measure the output of the photomultiplier tube.

Fluorimeter cells, Corex, 1 cm light path, with transparent bases.

Preparation of Calibration Curves

Measure out aliquots of standard solution, to contain 0, 2, 4, 8, 10, 25, 50, 75 and 100 µg aluminum, into 100-ml beakers and dilute them each to 20 ml with distilled water. Add 2 ml of 8-quinolinol reagent, 5 ml of buffer, stir, and allow the solutions to stand for 5 minutes. Adjust the pH to 5.6 to 5.7 with 10% ammonium hydroxide (v/v), using a suitable pH meter.

Transfer the solutions to 60-ml separatory funnels with a minimum amount of distilled water (2 to 3 ml) and shake each solution with a 25-ml portion of chloroform for one minute. Let the layers separate, draw the chloroform layers into separate 50-ml flasks containing 1 to 2 g of anhydrous sodium sulphate, and cap with plastic stoppers. For the fluorimetric curve, measure the 0 to 10 μg aluminum extracts fluorimetrically as described below under "Fluorimetric Operation". Plot a curve of average fluorescent readings, corrected for the blank, against μg of aluminum. For the spectrophotometric curve, read the 0 to 100 μg aluminum extracts on a spectrophotometer at 387 m μ and plot these values, corrected for the blank, against aluminum concentrations.

Reagents

8-hydroxyquinoline, 1%

Dissolve 1 g of 8-hydroxyquinoline in 2 ml of 6N hydrochloric acid and dilute to 100 ml with distilled water.

Aluminum stock solution

Dissolve 1.000 g of aluminum metal, 99.99% pure, which has been cleaned with acetone, in 40 ml hydrochloric acid (1:1) and dilute to 1 litre with distilled water.

Standard aluminum working solutions

(1) For fluorimetric curve, 5 ml of stock solution diluted to 2 litres with distilled water. 1 ml = 2.5 μg Al.

(2) For spectrophotometric curve, 10 ml of stock solution diluted to 1 litre with distilled water. 1 ml = 10 μg Al.

Buffer solution

Dissolve 193 g of ammonium acetate in distilled water and dilute to 1 litre. Adjust the pH to 5.8 with 1:1 hydrochloric acid.

Quinine sulphate solution

Dissolve 1 mg of quinine sulphate in 1 litre of 0.1 N sulphuric acid.

PROCEDURE

Take an aliquot from the main solution which has been prepared as described under Determination of Vanadium (page 4) and take the aliquot to fumes of sulphuric acid.

Cupferron Separation

Carry a blank and a standard through the procedure from this point. Cool, dilute to about 100 ml with water, and transfer to a 250-ml separatory funnel. Add enough sulphuric acid to make the acidity about 10% (V/v), then just enough 1% $KMnO_4$ dropwise to give the solution a permanent pink tinge. Chill to 5°C and add 25 ml of 6% cupferron solution (W/v) which is also at 5°C. Shake well for 1 minute or, preferably, until the precipitate floats to the top of the solution. Add 25 ml more cupferron solution and shake again. If the precipitation is complete or virtually so, the precipitate will float at the top of the solution and the aqueous portion will be light in colour. If this is not the case, add more cupferron and shake again. When the appearance of the aqueous solution indicates that precipitation is virtually complete, drain off the aqueous layer into a second separatory funnel and wash the precipitate twice with 30 ml of 10% (V/v) sulphuric acid solution containing a little cupferron. Combine the washings with the main aqueous portion. At this point the bulk of the aluminum will be in the aqueous portion, whereas only small amounts should be caught with the cupferrates.

Add 25 ml of wash solution to the solid cupferrates (top separatory funnel), add 25 ml of chloroform (5°C), and shake for one minute. Allow the layers to separate, and discard the chloroform layer. Add 5 ml of 6% cupferron solution to the main aqueous portion (bottom separatory funnel), shake, establish complete precipitation (white), add 25 ml of chloroform and shake the mixture for about 30 seconds. Drain off the organic layer into the top separatory funnel and shake. Discard the organic portion. Repeat this operation several times if necessary, or until the aqueous portion in the lower separatory funnel is water white. Give the upper separatory funnel one more wash with 25 ml of chloroform. Combine the two aqueous fractions and evaporate to about 200 ml. Add about 35 ml of concentrated nitric acid and evaporate to fumes of sulphuric acid. Cool, add concentrated nitric acid, and take to fumes again. Repeat until the organic matter is all destroyed, using a little perchloric acid near the end, if necessary, to aid in the destruction of the organic matter. Dilute with water and make up to volume in a volumetric flask preparatory to a fluorimetric or spectrophotometric finish.

Mercury Cathode Separation

If nickel is high, place the whole sample or an aliquot in a mercury cathode cell after adjusting the acidity to about 1% in sulphuric acid with sodium hydroxide solution (not ammonium hydroxide). Electrolyze at 10 to 15 amps for 30 minutes. Dilute to the mark in a volumetric flask preparatory to a fluorimetric or spectrophotometric finish.

Extraction of Aluminum 8-quinolinolate

(N.B. Carry two blanks through the procedure from this point.) Transfer a suitable aliquot (4 to 100 μ g of aluminum) to a 100-ml beaker and dilute to 20 ml with distilled water. Add, in order, 2 ml of 8-hydroxyquinoline reagent and 5 ml of buffer. Mix, and allow to stand for 5 minutes. Adjust the pH to 5.6 - 5.7 with dilute ammonium hydroxide, using a pH meter, and transfer to a 60-ml separatory funnel with a minimum of distilled water (2-3 ml). Extract with 25 ml of chloroform for one minute. Run off the chloroform into a 50-ml Erlenmeyer flask containing 1-2 g of anhydrous sodium sulphate, and cap with a plastic stopper. Depending on the aluminum content observed in the chloroform extract, complete the determination fluorimetrically or spectrophotometrically.

Fluorimetric Finish

Turn on the water supply to the lamp-housing of the fluorimeter. Turn on the ultra-violet lamp, and leave it on for 15 minutes to ensure stable operation. Set the Ayrton shunt at position 0.01 and turn on the galvanometer and power supply. Zero the galvanometer. Use the quinine sulphate solution as the standard for comparison; put this solution, the two blanks and a sample each in a separate 1 cm Corex fluorimeter cell. Place the holder in the fluorimeter and replace the cover. Move the quinine sulphate solution into the light path and open the photomultiplier shutter. With the Ayrton shunt set at 0.01, adjust the power supply control so that the galvanometer reads 500 (the galvanometer scale is 10 cm in length graduated in millimetres, and the actual reading is the galvanometer reading in cm taken to the nearest 0.05, divided by the shunt setting). Move the blanks and sample successively into the light path and record their respective readings. Leave the number one cell filled with the quinine sulphate solution. Refill the three remaining cells with the next samples and repeat the scale adjustment and reading operation.

Correct the fluorimeter readings by subtracting the average value obtained for the two blanks. Read the μ g of aluminum per final aliquot from the prepared calibration graph.

Spectrophotometric Finish

Measure the samples against a blank in 1-cm cells on the spectrophotometer at 387 m μ . Record the absorbance and read the μ g. of aluminum per final aliquot from the prepared calibration curve.

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Procedure 7

DETERMINATION OF AMMONIA

INTRODUCTION

Ammonia is distilled from a strongly alkaline solution and collected in an almost saturated solution of boric acid (1). The borate formed is determined by titration with a standard hydrochloric acid solution using an indicator which is effective in the pH range 5 to 6 (2). The mixed indicator bromocresol green-methyl red is suitable for this purpose. This procedure, which is designed for samples in which the ammonia is present as a salt, may be used for determining amounts of ammonia greater than 0.1%.

APPARATUS AND REAGENTS

Apparatus

Distillation apparatus, all glass (see Fig. 1, page 42).

Distilling flasks: Erlenmeyer, 300 ml, with 24/40 ground glass joint.

Reagents

Standard ammonia solution

Dissolve 15.5167g of ammonium sulphate in distilled water and dilute to 1 litre. 1 ml = 4.0 mg NH_3 .

Standard hydrochloric acid solution, 0.1N

Dilute 17 ml of concentrated HCl to 2 litres. Standardize this solution against standard ammonia solution as described under PROCEDURE.

Boric Acid Solution

Dissolve 50 g of boric acid in 1 litre of distilled water.

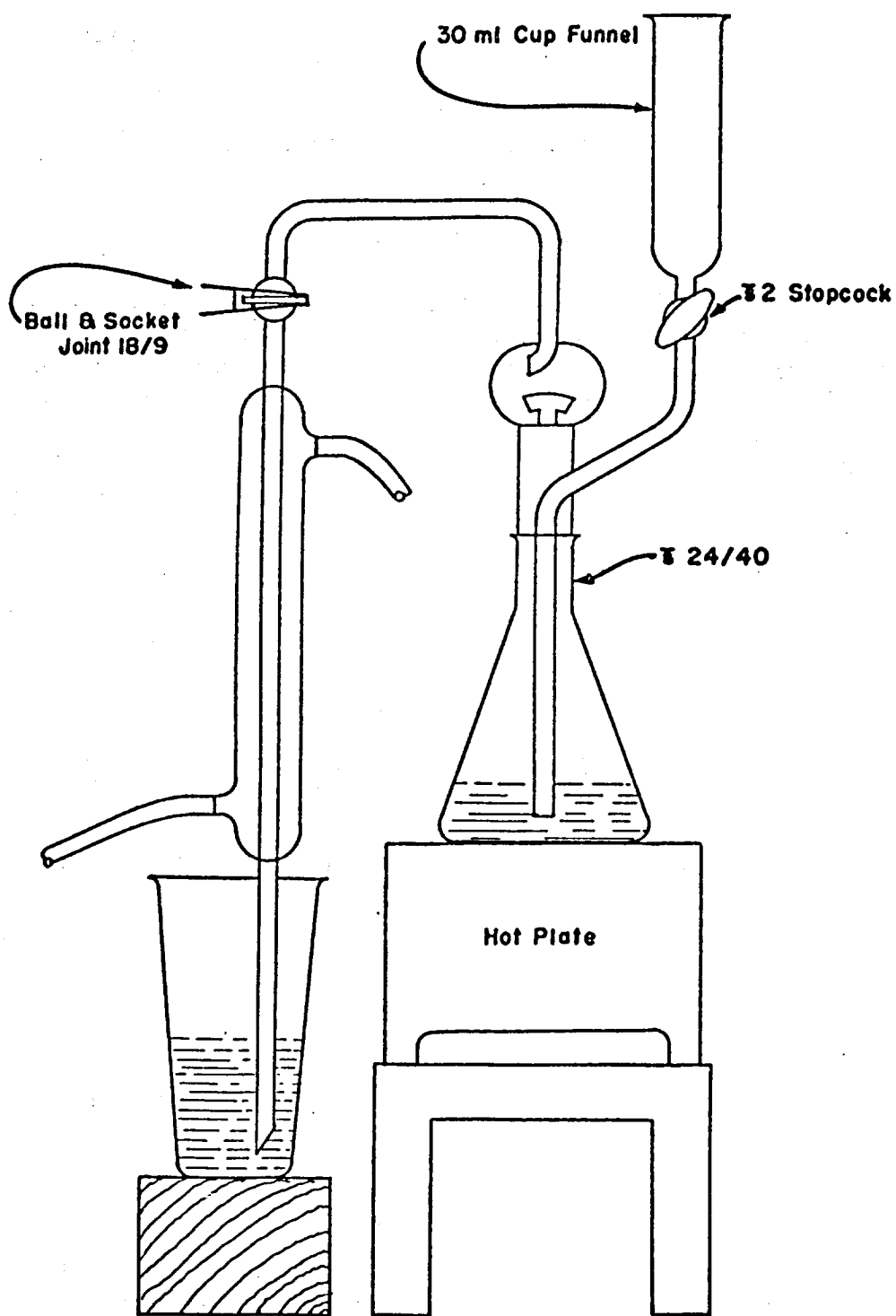


Fig. 1 - Distillation Apparatus For Ammonia

Methyl red solution

Dissolve 0.2 g of methyl red in 100 ml of ethanol.

Bromocresol green solution

Dissolve 0.1 g of bromocresol green in 100 ml of ethanol.

Mixed indicator

Mix one part of methyl red solution and three parts of bromocresol green solution. Renew if its colour is orange in the boric acid.

PROCEDURE

Wash all equipment with hot tap water and then with distilled water.

Solids

Weigh out a sample containing 25-75 mg of ammonia. Transfer the sample to a 300-ml distilling flask, add 5 ml of 6N H_2SO_4 , and warm to dissolve. Dilute to about 175 ml with distilled water.

Solution Samples

Transfer an aliquot containing 25-75 mg of ammonia to a 300-ml distillation flask and dilute to 175 ml with distilled water.

Distillation

Lubricate the 24/40 joint lightly with stopcock grease. Add about six glass beads to the flask containing the sample and connect it to the distilling apparatus. Place the receiving flask containing 50 ml of boric acid solution (50 ml of 4% boric acid solution will recover 95 mg of ammonia (1)) and 4 drops of mixed indicator solution under the condenser. Make sure that the end of the condenser extension tube is below the surface of the boric acid. Slowly add to the solution through the separatory funnel, 15 ml of 50% sodium hydroxide solution. Check that all connections are tight, turn on the cooling water to the condensers, and set the hot plate switch to high. Swirl the distillation flask after the addition of the sodium hydroxide solution. When the ammonia reaches the boric acid solution it will turn the indicator from pink to greenish-blue. Continue heating until about 150 ml of distillate has passed over, at which time all the ammonia will have been evolved. Be sure to keep water running through the condenser fast enough to prevent the boric acid solution from

becoming warm. Disconnect the condenser and wash down the inside of the condenser and the outside of the condenser extension tube.

Titration

Titrate the boric acid - ammonia solution with standard 0.1N hydrochloric acid solution to the pink color of the mixed indicator (the ammonia solution can stand for up to 24 hours and give quantitative results). Put a reagent blank through the procedure with every set of samples.

Standardization of the 0.1N HCl solution

Measure out duplicate samples from the standard ammonium sulphate solution to contain 60 mg of NH_3 (15 ml) and transfer to a 300-ml distilling flask. Dilute to about 175 ml with distilled water and carry on as for samples. Do the same for two blanks.

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2. A.I. Vogel, "A Text-Book of Quantitative Inorganic Analysis", 3rd ed., Longmans, Green and Co. Ltd., London, 1961, p.257.

Procedure 8

DETERMINATION OF CARBON

Carbon is determined by means of a tube-type combustion furnace and conventional purifying train, the carbon being collected on Ascarite and determined by weight.

Procedure 9

DETERMINATION OF CHLORIDE

INTRODUCTION

Chloride is determined by potentiometric titration following its separation from vanadium salts by distillation with 25% nitric acid according to the procedure of Sporek (1). The distillate is caught in a solution of dilute hydrogen peroxide and the chloride titrated with silver nitrate solution. A standard chloride solution alone, and with a vanadium matrix, and the vanadium matrix alone, should also be carried through the procedure to establish chloride recovery.

The potentiometric titration is based on the procedure developed by Laux and Brown (2), and applied to uranium concentrates by Hitchen (3). Iron and vanadium(V) will interfere in the titration but considerable quantities of these elements will not interfere if they are complexed with ascorbic acid. In the determination of small amounts of chloride in high grade vanadium precipitates, however, it is considered to be desirable to separate the chloride from contaminants by the described distillation procedure. Methanol is added to reduce the solubility of the silver chloride formed during the titration. The procedure is suitable for the determination of chloride in the range 0.005 to 0.2%.

APPARATUS AND REAGENTS

Apparatus

pH or meter, EIL, Model 23A.

Precision Dow Recordomatic Titrometer.

Distilling flasks (300 ml) and condensers.

Silver electrode, Beckman No. 1261.

Mercury - mercuric sulphate electrode.

Reagents

Silver nitrate solution 0.01 N.

Supporting electrolyte; 95% methanol and 5% 16 M nitric acid (v/v).

PROCEDURE

Establishing Equivalence Potential of Supporting Electrolyte

Using a graduated cylinder, transfer 75 ml of the supporting electrolyte (methanol-nitric acid) to a 250-ml beaker. Immerse the freshly-cleaned electrodes in the solution and equilibrate by stirring for 15 minutes. Using a graduated cylinder, transfer a second 75-ml portion of the supporting electrolyte into another 250-ml beaker and measure the potential of the solution, using an EIL pH meter. Record the potential in millivolts. This value is the "apparent" equivalence potential for that specific batch of supporting electrolyte and it must be determined for each fresh batch of electrolyte prepared. The value should also be checked several times a day. If the Recordomatic Titrometer is used, the end-point can be established from the inflection of the recorded curve, and the above step can be omitted.

Sample Treatment

Weigh sufficient sample to contain 100 to 1000 micrograms of chloride and transfer it to a 300-ml distilling flask. Set up the apparatus as for the determination of ammonia (Fig. 1, p. 42). Connect the flask to a condenser, the tip of which is immersed in 25 ml of 3% hydrogen peroxide contained in a 250-ml beaker. Add 50 ml of 25% nitric acid (v/v) to the distilling flask. Add glass beads or "Boileezers" and heat until a distillate of 25 ml is collected. Add 25 ml more of 25% nitric acid and collect 25 ml more of distillate. Repeat this step once more. Make the total distillate just alkaline with 10% sodium hydroxide (^w/v), and evaporate to 10 ml. Neutralize the sample with a little nitric acid, then add 2 ml of concentrated nitric acid and 75 ml of supporting electrolyte (methanol-nitric acid).

Potentiometric Titration

Clean the electrodes by immersing them in 10% nitric acid solution for a few minutes, then rinse thoroughly with distilled water. Repeat this procedure after every 6-7 samples, or if the electrodes have not been used for several hours. This treatment is essential if reliable results are to be obtained.

Titrate the chloride potentiometrically with 0.01N silver nitrate, using a silver electrode and a mercury/mercuric sulphate electrode with a sodium sulphate bridge, to the "apparent" equivalence potential which has been determined previously. Alternatively (and preferably), carry out the titration on the Precision Dow Recordomatic Titrometer, and establish the volume of reagent consumed up to the inflection point of the recorded titration curve.

Carry out the above procedure, using standard chloride solution alone and with a vanadium matrix chosen so as to simulate the amount of vanadium in the sample. Run a blank for the vanadium matrix.

REFERENCES

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Procedure 10

DETERMINATION OF FREE ACID

INTRODUCTION

The free acid content of the liquors resulting from leaching of Boiler Fly Ash with sulphuric acid cannot be determined by direct titration, due to the presence of hydrolyzable ions such as iron. By adding a neutral complex-forming reagent, such as potassium oxalate, stable complexes of some ions are formed which only hydrolyze at hydrogen ion concentrations below that at which all the free acid is consumed. As a result, an inflection corresponding to the consumption of the free hydrogen ion concentration is obtained when the complexed solution is titrated with standard potassium hydroxide solution. This inflection point is usually distorted and displaced by a variable amount, due to the high and varying content of salts in solutions. Also, due to the weak ionization of oxalic acid, the pH change at the end-point is seldom more than 1 or 2 pH units. For this reason it is difficult to choose a suitable indicator for the system. By first plotting a curve and determining the end-point from the inflection, a number of similar solutions may be titrated, using a pH meter or a recording titrator. In the procedure described here, a Precision Dow Recordomatic Titrometer is used (1, 2, 3).

APPARATUS AND REAGENTS

Apparatus

Precision Dow Recordomatic Titrometer.

Reagents

Potassium oxalate solution

Dissolve 280 g of potassium oxalate ($K_2C_2O_4 \cdot H_2O$) in 1 litre of distilled water. Adjust the pH to 8.0 - 8.5 with potassium hydroxide or oxalic acid as required.

Potassium hydroxide solution

Dissolve approximately 5.6 g of potassium hydroxide per litre of water. Standardize against potassium biphthalate, using the same method and apparatus that will be used for analysing samples. Do not

expose to the carbon dioxide of the atmosphere any more than necessary.

One gram of potassium biphthalate will neutralize about 49 ml of 0.1 N KOH.

$$\text{Normality of KOH} = \frac{\text{wt of biphthalate (g)} \times 1000}{204.2 \times \text{titration (ml)}}$$

Standard acid solution

Prepare a solution approximately 0.1N of hydrochloric, nitric or sulphuric acid. Determine the normality, preferably by some method other than the one used for determining free acid. Commercially available standard acids are also suitable for this procedure.

Standard buffer solution, pH 7.0

PROCEDURE

Standardize the recording titrator according to the manufacturer's instructions.

After this has been done, titrate a sample of standard acid and, if the recovery is good, proceed with the titration of samples. If recovery is not good, the cause of the trouble must be identified and corrected.

Pipette the sample into a 250-ml beaker and add distilled water to a total volume of 75 ml (the approximate size of sample which will yield a titration with base of about 10 ml may be determined by dividing the equivalent weight of the acid in the sample by its estimated concentration in gm/l). Add 25 ml of 25% potassium oxalate and titrate until the chart of the recording titrator shows that the first inflection point has been over-shot by several ml of potassium hydroxide.

Determine the volume of base used from the chart and then calculate the concentration of acid in the unknown using the following formula:

$$\text{Free acid (g/l)} = \frac{T \times N_B \times E \times 1000}{1000 \times S}$$

where

T = volume in ml of KOH used,
N_B = normality of KOH used,
E = equivalent weight of acid sought,
S = volume in ml of sample used.

REFERENCES

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2. "Instruction Manual for the Recordomatic Titrator", Index TS-68890-1, issued December 28, 1950, by the Precision Scientific Company, 3737 West Cortland Street, Chicago 47, Ill. Sheets 3-6 cover operation.
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Procedure 11

DETERMINATION OF NICKEL

A.

GRAVIMETRIC PROCEDURE

INTRODUCTION

Nickel is determined by weight following its precipitation with dimethylglyoxime from a weakly alkaline solution. The procedure used is a classical one and has been described in standard reference texts such as Hillebrand et al.(1). In the procedure given here, a double nickel-dimethylglyoxime precipitation is carried out in order to avoid mechanical contamination of the precipitate by the large quantities of vanadium present.

APPARATUS AND REAGENTS

Apparatus

Crucibles; fritted glass, high form, medium porosity, 50-ml size.

Flask, filtering, with tubulature.

Crucible adapter for filtering flask.

Reagents

Dimethylglyoxime solution, 1%

Dissolve 1 gm of dimethylglyoxime in 100 ml of ethyl alcohol.

PROCEDURE

Take an aliquot containing from 1 to 50 mg nickel from the main solution, which has been prepared as described under Vanadium. Dilute to 200 ml, add 2-3 ml of bromine water, and boil from 5-10 minutes, finally removing the cover and boiling to expel all the bromine. Filter if not perfectly clear. Add 1 - 2 g of ammonium chloride and 3 - 4 g of tartaric acid. Make the solution just alkaline with ammonium hydroxide, adding a few drops in excess.

Heat to 60-80°C, and add 5 ml of 1% (w/v) dimethylglyoxime in ethyl alcohol for each 0.01 g of nickel present (not more than 10 ml if the nickel is low). Stir and add ammonium hydroxide dropwise until the solution is alkaline to litmus. Add 2 ml of ammonium hydroxide in excess. Stir well and set aside in a warm place for 30 minutes, or for 12 hours if the precipitate is not heavy.

Filter through a tared, sintered glass filtering crucible (medium porosity). Wash the precipitate with cold water. Dry for 1 hour at 110 - 120°C, cool in a dessicator, and weigh. Record the weight, subtract the tare of the crucible, and record the precipitate weight.

If the vanadium content is high, a second dimethylglyoxime precipitation is advisable. In this case, filter the precipitate from the first precipitation on Whatman 541 paper and redissolve the precipitate from the paper with a mixture of 3N hydrochloric acid and 1N nitric acid. Add 10 ml of 1:1 sulphuric acid and evaporate to SO₃ fumes, cool, and add concentrated nitric acid until the organic material is destroyed. Take to SO₃ fumes again and cool. Wash down the sides of the beaker with water and fume again. Cool. Dilute to 200 ml and reprecipitate the nickel with dimethylglyoxime, first filtering off any insoluble material, such as silica, which may be present.

B.

COLORIMETRIC PROCEDURE

INTRODUCTION

Nickel is determined colorimetrically by means of the characteristic red, water-soluble complex of nickel (IV) with dimethylglyoxime. Oxidation of the nickel is carried out by addition of an oxidizing agent, such as bromine, iodine or persulphate, to a slightly alkaline solution before the addition of the dimethylglyoxime (2, 3).

A number of contaminants, such as copper, cobalt, manganese, cerium, chromium, the platinum metals, and vanadium, interfere in the direct procedure. The effect of vanadium results from its consumption of oxidant so that the resulting redox potential is insufficient for the oxidation of all the nickel, leading to low results. With moderate amounts of vanadium, this can be substantially overcome by adding a large excess of oxidant before colour development (2). The quantities of vanadium encountered in this particular sample material are high, however, so that a separation of nickel and vanadium is desirable. This is achieved by extracting nickel (II) from an ammoniacal dimethylglyoxime solution, using chloroform (4, 5, 6). Nickel (IV) dimethylglyoxime is not extracted with chloroform, so that strong oxidants, such as chlorate, permanganate,

cerate, etc., must be absent. The addition of hydrogen peroxide, followed by boiling to remove the excess peroxide, serves to reduce permanganate and cerate, as well as ensure the presence of oxidized iron, in which form it does not use up dimethylglyoxime. Elements such as iron and the remainder of the R_2O_3 group are kept in solution at the high pH by complexing them with citrate or tartrate.

APPARATUS AND REAGENTS

Apparatus

Beckman Spectrophotometer, Model "B".

Reagents

Dimethylglyoxime solution, 1%

Dissolve 1 g of dimethylglyoxime in 100 ml of ethyl alcohol.

Standard nickel solution

Digest 1.000 g of pure nickel wire, or an equivalent amount of a pure nickel salt, in nitric and hydrochloric acid until it is completely dissolved, and evaporate the solution to dryness. Dissolve the residue in 20 ml of concentrated hydrochloric acid and make up to 1 litre. 1 ml of the above solution = 1 mg Ni. Dilute 5 ml of the above solution to 1 litre for a working solution. If a salt was used to prepare the solution, standardize the solution gravimetrically.

Ammonium citrate solution, 20%

Dissolve 200 g of citric acid in 1 litre of 1:1 ammonium hydroxide.

Preparation of the standard photometric curve

Transfer aliquots of the weak nickel solution covering the range 10 γ to 500 γ of nickel, and a blank, to 100-ml volumetric flasks. Add 4 ml of 1:1 hydrochloric acid, and 5 ml of 20% ammonium citrate solution. Mix and add 5 ml of 1:1 ammonium hydroxide solution. Dilute to 30-40 ml with water, and add 18-20 drops of bromine water. Swirl, add 3 ml of 1% alcoholic dimethylglyoxime solution, and swirl again. Dilute to the mark, mix well, and let stand for 5 minutes. Read on the spectrophotometer at 530 m μ against a reagent blank.

PROCEDURE

Dissolve the sample as described under Vanadium. Place an appropriate aliquot in a beaker, add 10 ml concentrated hydrochloric acid, and boil for 10 minutes. Add 3 drops of 30% hydrogen peroxide and boil until the excess of peroxide is destroyed. Add 5 ml of 20% ammonium citrate solution and adjust the pH to 7 with 1:1 ammonium hydroxide solution (litmus paper), then add 10 drops in excess. Transfer the solution to a separatory funnel, add 20 ml of dimethylglyoxime solution, mix thoroughly, then let stand for 10 minutes. Add 15 ml chloroform and shake the funnel for 2 minutes. Allow the phases to settle and transfer the organic phase to a clean, lower funnel. Repeat the extraction twice more, using 15 ml of chloroform each time. Discard the aqueous layer. If the chloroform extract (which should be pale yellow or colourless) is coloured blue, pink, or brown, then copper, manganese or cobalt has probably been extracted. In this case, add 15 ml of 2% ammonium hydroxide solution to the combined chloroform extracts. Shake the funnel for 2 minutes and let the phases separate. Run the chloroform extract into a clean separatory funnel. Repeat the washing procedure using 2% ammonia until the chloroform extract is colourless or pale yellow. As a rule, two washings are sufficient (unless copper is present). Reserve both the aqueous and chloroform layers. Scrub the combined ammonia wash solutions with 10 ml of chloroform and add this to the washed chloroform extract, discarding the scrubbed ammonia washings.

To the funnel containing the combined chloroform extract, add 20 ml of 4% hydrochloric acid. Shake for 2 minutes, let the phases separate, and run the chloroform into a clean separatory funnel. Repeat the stripping twice more, using 10 ml of 4% acid each time (the stripped chloroform can be reused).

Transfer the solution to a 100-ml volumetric flask. Pipette duplicate aliquots (10 to 500 γ Ni), one to each of two 100-ml volumetric flasks, and dilute to 50 ml. In the case of samples with very low nickel contents, carry duplicates through the whole procedure. Transfer each to a separate 100-ml volumetric flask. To both flasks, add 5 ml of ammonium citrate solution and 5 ml of dilute ammonium hydroxide solution. Swirl to mix, add 20 drops of bromine water, and mix again. Finally, add 3 ml of dimethylglyoxime solution to one flask only. Dilute both flasks to the mark and mix well. Let stand for 5 minutes. Read the optical density of the sample solution containing dimethylglyoxime, against the other sample as a blank, at 530 m μ using a spectrophotometer. Compare results with those of standards prepared from nickel wire or a pure nickel salt.

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Procedure 12

DETERMINATION OF SILICA

INTRODUCTION

Silica is determined by a standard procedure (1, 2, 3) whereby the silica in the sample solution is dehydrated with hydrochloric acid at a low temperature, filtered, ignited, and weighed as an impure silica precipitate. The silica in the precipitate is then volatilized with hydrofluoric acid; the impurities which remain behind are weighed and the silica content determined by weight difference. As the silica in the vanadium precipitates is generally quite low, a large sample must be taken to ensure that the silica weight difference will be at least 2 mg.

PROCEDURE

Weigh 5 g of sample into a 250-ml beaker, add 25 ml of concentrated hydrochloric acid and a little hydrogen peroxide, and cover with a watch glass. Take the sample solution to dryness at low temperature (steam plate), dehydrating until no drop remains on the cover glass. Take up the soluble salts with 50 ml of 2N hydrochloric acid, digest below boiling for 20 minutes, and filter on a No. 42 Whatman filter paper. Wash the residue and paper a few times, first with hot 2N hydrochloric acid, then with hot water. Transfer the paper to a platinum crucible, dry on the hot plate, and burn off the paper at a low heat using a burner. Ignite the residue in a muffle furnace at 950°C, cool in a dessicator, and weigh. Cover the residue in the platinum crucible with 8-10 drops of 1:1 sulphuric acid and 4-5 ml of hydrofluoric acid. Evaporate the mixture to complete dryness. If the amount of residue is large, repeat this operation. Heat gently over a burner until all sulphuric acid is expelled, and then ignite in a muffle at 950°C, cool in a dessicator, and weigh.

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Procedure 13

DETERMINATION OF TOTAL SULPHUR AND SULPHATE

INTRODUCTION

Sulphur is determined on boiler fly ash following leaching of the sample using an oxidizing acid attack with, for example, HNO_3 and KClO_3 . Sulfate sulphur on the precipitates is determined following leaching with a) water, b) carbonate, or c) hydrochloric acid. In the use of procedure b), difficulty may be encountered when converting the solution to the acidic form preparatory to a barium sulphate precipitation. In such a case, vanadium and other elements tend to form compounds that precipitate and that may occlude sulphate which would thus be lost. When using procedure c) it is often necessary to use a considerable quantity of hydrochloric acid, thereby making it difficult to keep the acidity below 2% for the subsequent barium sulphate precipitation.

With any of the leach procedures described, final determination for total sulphur or sulphate sulphur is carried out by means of the classical barium sulphate precipitation, which is extensively discussed in the literature (1, 2).

PROCEDURE

Total Sulphur on Fly Ash

Weigh 0.5 - 1.0 g of sample into a 250-ml beaker and add 10 ml concentrated nitric acid and 1 g potassium chlorate. Heat until the sample is in solution (except for carbon) and take just to dryness. Add 10 ml concentrated hydrochloric acid and take just to dryness. Leach the insoluble residue with a minimum of dilute hydrochloric acid, filter on Whatman number 42 paper and wash the paper with hot water, then dilute to about 200 ml, keeping the acidity less than 2% in hydrochloric acid. With constant stirring, add 10% barium chloride (w/v) in slight excess (1 ml for each 0.01 g sulphur). Stir well and digest just below boiling (at about 90°C) for an hour, or preferably overnight. Decant the supernatant solution through a Whatman number 42 filter paper into a clean beaker. Reserve the filter paper for the main filtration step. Add 50 ml of water, 1 ml of hydrochloric acid and 1 ml of 10% barium chloride solution to the precipitate, and digest for 30 minutes on the hot plate.

Filter through the reserved filter paper from above, into the beaker containing the decanted supernatant solution, and test the first portion of the filtrate with a few drops of barium chloride solution. Wash with warm water in small portions until the filtrate no longer gives a test for chloride with silver nitrate-nitric acid solution. Transfer the paper to a tared ignited crucible. Dry and cautiously burn off the paper over a low gas flame. Place the crucible in a muffle at 900°C for 30 minutes. Cool in a dessicator and weigh. Record the weight of barium sulphate and calculate as sulphur.

Sulfate Sulphur on Precipitates

Effective digestion of the high-grade vanadium precipitate may be obtained by leaching with water, sodium carbonate, or hydrochloric acid. Difficulties may be encountered when using carbonate or hydrochloric leaching as described in Introduction on page 59. When using a water leach there is a danger, on some types of sample material, that sulphate will be incompletely leached.

Water Leach

Digest 1 to 2 g of sample with 150 ml of hot water for one hour. Filter off the insoluble residue on Whatman number 42 paper and wash the residue with hot water. Acidify the filtrate with hydrochloric acid and proceed with the barium sulphate precipitation as described for Fly Ash.

Carbonate Leach

Digest 1 to 2 g of sample with 5 g of sodium carbonate, plus two pellets of sodium hydroxide, in 200 ml of water for 30 minutes. Filter the insoluble material, using Whatman number 42 paper, and wash the residue with hot water containing a little sodium carbonate. Acidify the filtrates with hydrochloric acid and add 1-2 ml in excess. Boil to expel carbon dioxide. If a precipitate appears, filter on Whatman number 42 filter paper and wash the precipitate with very dilute hydrochloric acid and water. Carry out the barium sulphate precipitation as described for Fly Ash.

Hydrochloric Acid Leach

Digest 1-2 g of sample with enough concentrated hydrochloric acid to effect complete solution (about 30 ml acid and 500 ml of water required). Dilute the solution so that the acidity is less than 2% in hydrochloric acid, and carry out a barium sulphate precipitation as described for Fly Ash.

Note: To evaluate the recovery of sulphate by the procedure chosen, add a standard sulphate solution to a separate sample and carry it through the complete procedure at the same time as the sample alone.

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Water Leach

Digest 1 to 2 g of sample with 150 ml of hot water for one hour. Filter off the insoluble residue on Whatman number 42 paper and wash the residue with hot water. Acidify the filtrate with hydrochloric acid and proceed with the barium sulphate precipitation as described for Fly Ash.

Carbonate Leach

Digest 1 to 2 g of sample with 3 g of sodium carbonate, plus two pellets of sodium hydroxide, in 250 ml of water for 30 minutes. Filter the insoluble material, using Whatman number 42 paper and wash the residue with hot water containing a small amount of sodium carbonate. Acidify the filtrate with hydrochloric acid and add 1-2 ml in excess. Boil to expel carbon dioxide. If a precipitate appears, filter on Whatman number 42 filter paper and wash the precipitate with very dilute hydrochloric acid and water. Carry out the barium sulphate precipitation as described for Fly Ash.

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Acid Leach

Digest 1-2 g of sample with enough concentrated hydrochloric acid to effect complete solution (about 30 ml acid and 500 ml of water required). Dilute the solution so that the acidity is less than 2% in hydrochloric acid and carry out a barium sulphate precipitation as described for Fly Ash.