ORNL-1396

DETERMINATION OF SUBMICROGRAM QUANTITIES OF CHROMIUM AND VANADIUM IN ALKALI HYDROXIDES

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A DIVISION OF UNION CARBIDE AND CARBON CORPORATION
OAK RIDGE, TENNESSEE

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Index No. ORNL-1396
This document contains 26 pages.
This is copy 69 of 160, Series A.

Subject Category: Chemistry-General

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September 8, 1952

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Oak Ridge, Tennessee

Contract No. W-7405-eng-26

[redacted]

[redacted]

ABSTRACT

An ion exchange method has been developed for the separation of trace quantities of chromium and vanadium from large samples of alkali hydroxides. These elements can then be concentrated into a small volume. Chromium is determined colorimetrically in the resulting solution by the diphenylcarbazide method, while vanadium is determined by an indirect colorimetric method based on the ferrous-o-phenanthroline complex.

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DETERMINATION OF SUBMICROGRAM QUANTITIES OF CHROMIUM AND VANADIUM IN ALKALI HYDROXIDES

INTRODUCTION

In order to determine extremely small quantities (less than 0.1 ppm) of chromium and vanadium in alkali hydroxides, it is necessary to separate these constituents from large samples of the matrix and concentrate them into small volumes of solutions to which sensitive methods of determination can be applied. Logical choices of methods for the separation of the elements from the hydroxides include those based on solvent extraction and ion exchange techniques.

It is possible that highly sensitive methods based on activation analysis could be developed for the determination of chromium and vanadium, but colorimetric methods are more rapid and convenient.

EXPERIMENTAL

Colorimetric Determination of Chromium

The diphenylcarbazide method,[1] which is the one most commonly used for the colorimetric determination of chromium, is very sensitive. Alkali metal salts, however, were found to have an appreciable quenching effect on the color of the chromium-diphenylcarbazide complex. For this reason, it is desirable to separate chromium from the matrix. Furthermore, in

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the presence of alkali metal salts, the sensitivity of any colorimetric method is dependent on the solubility of the salt.

Separation of Chromium from Alkali Hydroxides

Extraction of Peroxychromic Acid. The formation of blue peroxychromic acid by the action of hydrogen peroxide on dichromates has been used as a qualitative test for chromium. Brookshier and Freund[2] have utilized the solubility of peroxychromic acid in ethyl acetate to separate milligram quantities of chromium from vanadium. Although the extraction of peroxychromic acid apparently had not been used for the quantitative isolation of microgram quantities of chromium, it was believed that such a separation was possible and that an investigation was warranted.

Approximately complete recovery of one milligram of chromium was obtained by extraction according to this procedure. Numerous unsuccessful attempts, however, were made in an effort to separate microgram quantities (5 to 25 μg) of chromium from alkali metal salt solutions by extraction of peroxychromic acid with ethyl acetate and ether, both at room temperature and from cold solutions. No chromium could be detected in the organic phase in any of these tests. It appears that the extreme instability of peroxychromic acid, as evidenced by the almost instantaneous disappearance of the blue color, is responsible for the failure to recover microgram quantities of chromium by this procedure.

Experiments were also performed in an effort to extract the red chromium-diphenylcarbazide complex with organic solvents. The complex was found to be insoluble in ether, ethyl acetate, 2-ethylhexanol and hexane.

Electrolysis with a Mercury Cathode. Deposition of chromium in a mercury cathode by electrolysis of solutions containing microgram quantities of chromium in 0.5 M H_2SO_4 resulted in incomplete removal of chromium from the electrolyte. A survey of the literature[3] confirmed the fact that the last traces of chromium cannot be removed by electrolysis. It had been proposed to collect the chromium in a mercury cathode pool and leach it by prolonged shaking of the mercury with sulfuric acid.

Distillation as Chromyl Chloride. The distillation of microgram quantities of chromium as chromyl chloride was tested as a means of separating the element from the alkali hydroxide matrix. Attempts to distill 12.5 micrograms of chromium by the addition of HCl to a perchloric acid solution of the element at 200-210°C in an all-glass apparatus[4] resulted in an average recovery of only 36 per cent of the chromium in the distillate. Although this procedure is applicable in the removal of milligram quantities of chromium from other elements, it cannot be used as a means of complete separation and recovery of the small traces of chromium which are of interest in this investigation.

Application of Ion Exchange Techniques. Since chromium can be converted to the anionic state, Cr(VI), it appeared possible to separate the element from the cation of the base by means of ion exchange techniques. Approximately complete recovery of 250 micrograms of chromium was obtained by retention of the chromate in an acid-washed alumina column followed by elution with aqueous ammonia. Repeated attempts, however, to separate two micrograms of chromium as chromate from three grams of NaCl in aqueous solution by anion exchange in the alumina column proved unsuccessful.

The cation of the base can be retained on the hydrogen form of a cation exchange resin (Dowex-50), whereas it was expected that chromium as chromate would pass into the effluent. Repeated attempts to effect the separation by this procedure resulted in only partial recovery of 50 micrograms of chromium. These tests included a final rinsing of the resin bed with dilute acid in order to wash chromium into the effluent. Since there was a possibility of the reduction in acid solution of chromate by the resin to the cationic state, Cr(III), the tests were repeated using ammoniacal solutions to wash chromate into the effluent. Although the recovery of chromium under these conditions was somewhat improved, it was too low to be of value. Even if the method were found to be satisfactory, a large volume of resin would be necessary to retain the cation of the base.

A test was made of a small volume of the same cation exchange resin as a means of retaining chromium(III) while the alkali-metal ion was being preferentially eluted. One hundred micrograms of chromium was retained on a 20-ml column, but none could be eluted with 200 ml of 1 M sulfuric acid, and this approach was abandoned.

The use of an anion exchange column in which the chromium is retained as the chromate would theoretically require only a small volume of resin. Experiments were performed in which 25 micrograms of chromium as chromate were introduced into a small column containing the chloride form of a strong base anion exchange resin (Dowex-1). The column was eluted with both 7 M NH_4OH and 1 M $HClO_4$, but no chromium was detected in the eluates. The chloride form of a weak base anion exchange resin (Amberlite-IR-4b) was employed unsuccessfully for the same experiment.

A satisfactory procedure for the separation and concentration of traces of chromium from alkali hydroxides makes use of the hydroxide form of Dowex-1. Chromium as chromate in an alkaline solution (1 M alkali hydroxide) is introduced into a small column of the resin in hydroxide form. In the alkaline solution, the possibility of reduction of chromate by the resin is essentially eliminated. The column is washed with water prior to the elution of chromate with 2 M ammonium carbonate solution. Ammonium carbonate is decomposed on heating, making it possible to evaporate the eluate to any desired volume.

In order to assure that all the chromium is in the chromate form prior to passing the solution through the column, about two drops of hydrogen peroxide is added to a 3 to 5 M solution of the alkali hydroxide sample. The excess peroxide can be decomposed by allowing the sample to stand, protected from CO_2, for about 30 minutes at room temperature. A much larger excess of peroxide was added in the original tests and was removed by prolonged boiling of the solution, but this procedure is preferably avoided because a pick-up of carbon dioxide from the air and silica from the glass vessel produces anions which have a great affinity for the resin.

The success of the ion exchange procedure in the separation of chromium from alkali hydroxides led to the application of the same method to the separation of vanadium. In the tests involving the latter element, it was found that elution of the anion by ammonium carbonate was more readily achieved if a "reversible" column (Fig. 1) was used. It was proved experimentally by employing an alkaline solution of phenolphthalein, a colored anion in basic medium, that anions are concentrated and held in a

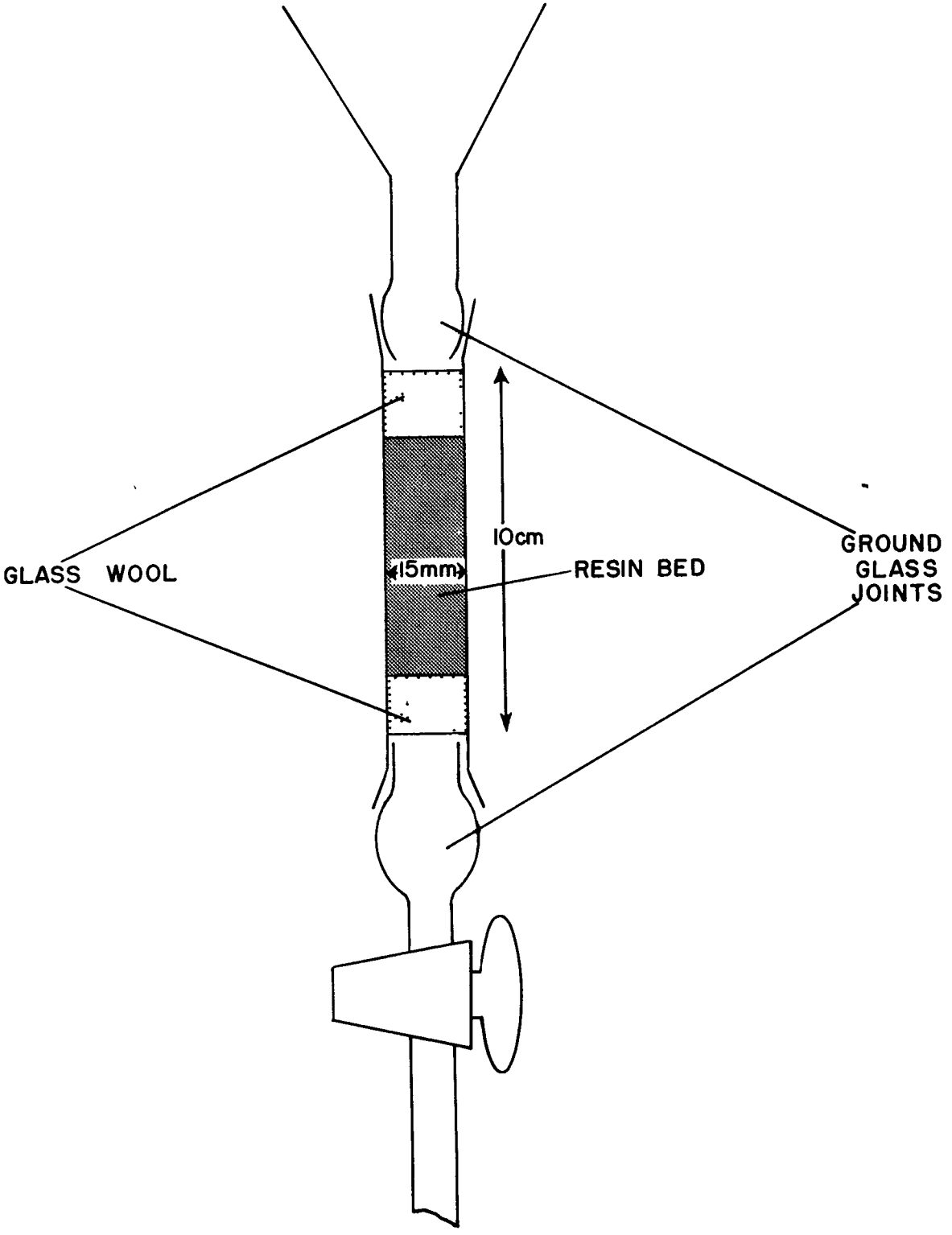

FIGURE I. DIAGRAM OF "REVERSIBLE" COLUMN

narrow band at the top of the anion exchange resin bed. The red phenolphthalein band was washed very slowly down the column by a 2 M solution of K_2CO_3. The "reversible" column is so constructed that it can be inverted prior to the elution step, thus making it possible to elute the narrow anion band from the bottom of the resin column in the direction opposite that in which the solution was introduced. The necessity of washing the band completely through the column during the elution process is thereby avoided. The "reversible" column was eventually applied to the separation of chromium, as well as vanadium, from the alkali hydroxides.

A series of tests has indicated that by taking a large sample (20 to 25 g) for analysis, as little as 0.01 ppm of chromium can be determined in alkali hydroxides. In order to increase the sensitivity obtainable by use of 1-cm absorption cells, optical density measurement of the chromium-diphenylcarbazide color complex is made in 2.5-cm cells with a final volume of only 10 ml. The sensitivity cannot be enhanced further by employing a cell of longer path length, since commercially available absorption cells of a path length longer than 2.5 cm require greater volumes of solution. The sensitivity can be increased only by increasing the ratio of path length to final volume.

Column "blanks" were found to be negligible. The "blanks" were measured by passing 250 ml of 2 M ammonium carbonate through the resin in the basic form, evaporating the resulting elute, and adding the color-forming reagent in the usual manner.

In Table I are shown some experimental results which illustrate the precision of the method in separating chromium from 400 ml of 1 M NaOH and determining the element by the diphenylcarbazide method.

TABLE I

Determination of Chromium in Sodium Hydroxide by The Diphenylcarbazide Method After Ion Exchange Separation

Chromium		Length of Absorption Cells, Cm	Optical Density, 540 mμ	Factor, μg/ml/O.D. (Unit Cell Length)
Total μg(1)	ppm(2)			
5.0	0.31	2.500	0.485	2.58
5.0	0.31	2.500	0.470	2.65
5.0	0.31	2.500	0.512	2.45
5.0	0.31	2.500	0.315	3.98
1.00	0.06	2.500	0.110	2.28
0.50	0.03	2.500	0.040	3.12
5.0	0.31	1.000	0.190	2.63
5.0	0.31	1.000	0.180	2.78
5.0	0.31	1.000	0.163	3.06
5.0	0.31	1.000	0.165	3.03
5.0	0.31	1.000	0.165	3.03
1.00	0.06	1.000	0.050	2.00
Average factor, μg/ml/O.D.				2.80
Standard deviation, absolute				0.50
Standard deviation, per cent				18

(1) The chromium was added to 400 ml of 1 M NaOH
(2) On the basis of the solid alkali hydroxide

Determination of Vanadium

Three well-known colorimetric methods, those based on the use of 8-hydroxyquinoline,(5) benzidine,(6) and phosphotungstic acid,(7) were tested as means of determining vanadium. Although the phosphotungstic acid procedure proved to be quite reliable, none of these methods was sufficiently sensitive to determine extremely small quantities of vanadium, less than 0.1 ppm, in alkali hydroxides unless complete separation of the element could be effected from a very large sample and the vanadium then concentrated into a small volume. In order to render the requirements for the separation procedure less exacting, or possibly to eliminate the need for a separation altogether, a search was made for a more sensitive method of determination.

Polarographic Method. A study of polarographic methods revealed that 0.1 to 0.05 micrograms of vanadium per ml can be detected by means of the ORNL high-sensitivity polarograph.(8) A supporting electrolyte of 4 M NH_4OH and 0.02 M NH_4Cl was found to be satisfactory. Polarograms of standard solutions of vanadium indicated that the diffusion current was proportional to the vanadium concentration.

Experiments were conducted in an effort to obtain polarograms of vanadium in samples from which the alkali hydroxides had been separated by means of an anion exchange column. Attempts to obtain well-defined polarograms were unsuccessful. The increase in migration current with increase in applied potential was so great at maximum sensitivity that the recording pen would move off scale before the reduction potential of vanadium was reached. Vanadium in the low concentrations encountered could not be detected at lower instrument sensitivities. It is believed

that the increased electrolytic content and resultant high migration current was a consequence of the introduction of impurities from the anion exchange resin and eluting agent.

Determination Based on Catalytic Action. The catalytic effect of small amounts of vanadium upon the reaction between $KBrO_3$ and p-phenetidine[9] was investigated as a means of estimating the element. Experiments in which the reagents were added to solutions containing only known amounts of vanadium indicated that the lower limit of detection was about 0.001 micrograms per ml. Attempts to apply the test in the presence of alkali salts, however, were unsuccessful. Experiments designed to separate the element from the matrix by means of anion exchange techniques prior to the application of the catalytic test were also unsuccessful, chiefly because of the abnormally high "blanks" obtained. Several of these experiments indicated that the results were not reproducible.

Benzohydroxamic Acid Method. Benzohydroxamic acid, which is reported[10] to be a sensitive colorimetric reagent for vanadium, was tested. The results indicated, however, that this reagent offers no advantage in sensitivity over phosphotungstic acid[7] for the colorimetric determination of vanadium.

Indirect Colorimetric Determinations. Investigations were made of an indirect colorimetric test for vanadium employing the iodine-starch reaction. Iodide is oxidized to iodine by vanadium(V), forming the blue color in the presence of starch. Sensitivity tests indicated that 0.05 micrograms of vanadium per ml could be detected, but the method is not

practical for quantitative work because of the rapid increase in color intensity as a result of air oxidation of the iodide.

Another indirect colorimetric method involves the addition of a standard excess of iron(II) to slightly acid solutions containing vanadium(V). An equivalent quantity of iron is oxidized by the pentavalent vanadium, and the excess iron(II) is determined colorimetrically by the o-phenanthroline method.[11] It is necessary to apply a correction factor for chromium if this element is present.

A slightly different procedure,[12] employing the same color reaction and requiring no correction for chromium, involves the reduction of vanadium(V) to vanadium(IV) by hot hydrochloric acid. A small amount of iron(III) and o-phenanthroline are added and the solution is made ammonical, causing reduction of the iron(III) by the vanadium(IV). The sequence of reactions is as follows:

$$VO^{+++} + 2\ Cl^- \xrightarrow{H^+} VO^{++} + Cl_2$$

$$VO^{++} + Fe^{+++} + 4\ OH^- \longrightarrow VO_3^- + Fe^{++} + 2\ H_2O$$

The absorbancy of the ferrous-phenanthroline complex is measured after acidifying the solution. Tests have indicated that as little as 0.05 micrograms of vanadium per ml can be detected by this method, which has proved to be the most satisfactory of those tested.

Chromium does not interfere with the above method. Although a complete study of interferences has not been made, it was determined from the reagent blank that no interfering elements are present in the eluate from the anion exchange column method, which is the best available means of separating vanadium from the hydroxide matrix.

Separation of Vanadium from Alkali Hydroxides

Extraction of the Cupferrate or Neocupferrate. A well-known method for the extraction of vanadium from aqueous solution is based on the solubility of the vanadium cupferrate or neocupferrate in organic solvents. Ether was used as the extracting agent in this study because it is more easily evaporated after extraction than is chloroform, which is commonly employed.

In the precipitation and extraction of microgram quantities of vanadium as the neocupferrate, it is necessary to add a "carrier" element if the vanadium is to be successfully extracted into the organic phase. Iron(III) was added for this purpose in the first experiments in which the final determination was made by the phosphotungstic acid method.[7] The introduction of a high "blank", however, prohibited the use of iron as a gathering agent in later experiments in which the determination of vanadium was made by the more sensitive indirect colorimetric method. Zirconium was added as a carrier in the latter tests prior to the precipitation with neocupferron. After extraction of the precipitate with ether, water was added to the organic layer, and the ether was evaporated. The organic material was finally destroyed by fuming with nitric and perchloric acids.

Although a few experiments resulted in approximately quantitative recovery of vanadium, a loss of the element was indicated in most of the tests. It is believed that the incomplete recovery of vanadium may have been caused by volatilization as $VOCl_3$ during the treatment with boiling perchloric acid. It is generally accepted that only a slight loss of

vanadium occurs under conditions which volatilize chromyl chloride, but this conclusion is based on studies with macro quantities of vanadium and does not necessarily apply in the present case. It was planned to study more fully the cause of the incomplete recoveries, but the success of the anion exchange method for the separation of vanadium from alkali hydroxides rendered further investigation unnecessary.

Anion Exchange Separation. The use of small columns of anion exchange resin, which had proved successful in the separation of chromium, was tested as a means of separating microgram quantities of vanadium from large samples of alkali hydroxide. The results indicated that application of the method to vanadium was possible, although recoveries were not complete. By employing the small "reversible" columns (Fig. 1), approximately complete recovery of vanadium was realized. The procedure for the separation of vanadium from the hydroxide matrix is identical with that described for the separation of chromium. Vanadium, being a strong reducing agent in basic solution, is likely to be present in the hydroxide solution only in the anionic state. The addition of a few drops of peroxide, however, will insure complete oxidation to the vanadate ion.

By using 2.5-cm absorption cells in conjunction with the indirect colorimetric determination, as little as 0.05 ppm of vanadium can be quantitatively determined in alkali hydroxides if a 20 g sample is taken for analysis. Approximately 0.01 ppm can be qualitatively detected in the same sample.

In Table II are reported some experimental results indicating the precision of the method for determination of vanadium in solutions of NaOH. Column "blanks" were found to be negligible.

Table II

Determination of Vanadium in Sodium Hydroxide by The Indirect Colorimetric Method After Separation by Ion Exchange

Total μg(1)	ppm(2)	Length of Absorption Cells, cm	Optical Density	Factor, μg/ml/O.D. (Unit Cell Length)
5.0	0.31	2.500	0.112	11.2
5.0	0.31	2.500	0.155	8.1
5.0	0.31	2.500	0.110	11.4
5.0	0.31	2.500	0.125	10.0
5.0	0.31	2.500	0.050	25.0
5.0	0.31	2.500	0.155	8.1
5.0	0.31	2.500	0.160	7.8
5.0	0.31	2.500	0.165	7.6
5.0	0.31	2.500	0.125	10.0
5.0	0.31	2.500	0.170	7.4
5.0	0.31	1.000	0.060	8.3
5.0	0.31	1.000	0.070	7.1
5.0	0.31	1.000	0.025	20.0
5.0	0.31	1.000	0.045	11.1
2.0	0.12	1.000	0.009	22.2
2.0	0.12	1.000	0.013	15.4
2.0	0.12	1.000	0.015	13.3
2.0	0.12	1.000	0.021	9.5
1.0	0.06	1.000	0.008	12.5
1.0	0.06	1.000	0.012	8.3
1.0	0.06	1.000	0.010	10.0
1.0	0.06	1.000	0.020	5.0
Average factor, μg/ml/O.D.				11.3
Standard deviation (absolute)				5.1
Standard deviation, per cent (relative)				45

(1) The vanadium was added to 400 ml of 1 M NaOH
(2) ppm is based on the solid alkali hydroxide

SUMMARY

An anion exchange method has been developed for the separation of submicrogram quantities of chromium and vanadium from alkali hydroxides. These elements can then be concentrated in a small volume of solution and determined colorimetrically.

Chromium is determined by the diphenylcarbazide method and vanadium by an indirect method based on the colorimetric (o-phenanthroline) determination of the iron(II) which is formed in an oxidation-reduction reaction of iron(III) with vanadium.

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APPENDIX

Procedure For Separation of Chromium and Vanadium From Alkali Metal Hydroxide by Anion Exchange

Apparatus

Column, "Reversible": (See Figure 1).

Reagents

Dowex-1, strong base anion exchange resin, 50 to 100 mesh.
Sodium hydroxide, 2 M.
Hydrogen peroxide, 3-per cent.
Ammonium carbonate, 2 M.

Procedure

Steps	Comments
1. Prepare a reversible column of Dowex-2, anion exchange resin (50-100 mesh). Insert glass wool plugs at both ends of the resin column.	1. A resin bed 5-1/2 cm long and 1-1/2 cm in diameter has been found satisfactory. Reversible columns can be inverted prior to elution, thus placing the adsorbed anion band on the bottom. This avoids washing the anion band completely through the column during the elution process.
2. Convert the resin to the hydroxide form by flushing the column with 150 ml of 2 M NaOH. Follow with a 200-ml water wash.	2. A flow rate of 5 to 10 ml per minute is convenient for both operations.

3. Dissolve the hydroxide sample in sufficient water to form a 3 to 5 M solution; add two drops of 3-per cent H_2O_2, stir thoroughly and allow the solution to stand for 30 minutes. Standards are prepared by adding known amounts of vanadium(V) and chromium(VI) to a solution of NaOH.	3. A large sample size, 10 to 25 g, is necessary if the concentrations of chromium and vanadium are in the submicrogram range. The peroxide treatment assures complete oxidation of chromium and vanadium to the anionic state. Removal of excess peroxide by boiling is not necessary.
4. Dilute the sample with water to form a 1 M solution and pass through the column at a flow rate not to exceed 2 ml per minute.	4. Cationic components pass through the column. Chromium and vanadium are retained as chromate and vanadate, respectively.
5. Wash with 150 ml of water at a flow rate of 5 to 10 ml per minute.	
6. Invert the column and elute the chromium and vanadium by allowing 250 ml of 2 M $(NH_4)_2CO_3$ solution to pass through the column at a flow rate of 5 to 10 ml per minute. Then wash the column with 150 ml of water and combine the washings with the eluate.	6. Ammonium carbonate was chosen as the eluting agent, since this substance can be decomposed by heating the solution.
7. Evaporate the eluate and adjust the volume to 10 ml. Take a 5-ml aliquot for the estimation of chromium. Use the other 5 ml of solution for the estimation of vanadium.	7. After the eluate has been evaporated to a small volume, it should be filtered if any suspended material appears to be present. This material is the result of the presence of impurities in the eluting agent.
8. Determine chromium by the diphenylcarbazide method, and vanadium by the indirect ferrous-o-phenanthroline method.	

Procedure for the Determination of Chromium

By the Diphenylcarbazide Method

Reagents

Sulfuric acid, 1 N

Diphenylcarbazide Reagent: Dissolve 0.25 g of diphenylcarbazide and 4 g of phthalic anhydride in 100 ml of 95-per cent ethanol.

Procedure

Steps	Comments
1. To a 10-ml volumetric flask transfer a 5-ml aliquot of the evaporated eluate from the anion exchange column and add 1 ml of 1 N H_2SO_4 and 1 ml of diphenylcarbazide reagent. Dilute to 10 ml.	1. If a determination of vanadium is not desired, the entire eluate from the column may be used after evaporation to approximately 5 ml.
2. Allow to stand for 15 to 20 minutes. Measure the optical density against a reference solution containing the same concentration of reagents.	2. Vanadium forms a coloration with the diphenylcarbazide reagent, but the color fades within 15 minutes.
3. Calculate the quantity of chromium from a colorimetric factor which is pre-determined by carrying a series of at least 10 standard samples through the separation and color-formation procedures.	

Procedure For The Determination of Vanadium By The Indirect Ferrous-o-Phenanthroline Colorimetric Method

Reagents

Hydrochloric acid, concentrated
Ammonium hydroxide, concentrated
Sulfuric acid, 10 N
o-phenanthroline, 0.2 per cent: Dissolve 0.2 g of o-phenanthroline monohydrate in 100 ml of water.
Iron(III) solution: Dissolve 0.1 g of iron wire in 1 to 10 H_2SO_4 solution. Add 3 ml of concentrated HNO_3 and dilute to 1 liter. Each ml contains 100 micrograms of iron.

Procedure

Steps	Comments
1. To the sample aliquot, standards and blank, add 5 ml of concentrated HCl and 0.5 to 1.0 ml of iron(III) solution.	1. If a determination of chromium is not desired, the entire eluate from the column may be used after evaporation to approximately 5 ml.
2. Evaporate the solutions to about 4 ml. Add 5 ml of concentrated HCl, evaporate to about 1 ml. Cool, add 3 to 6 ml of water and transfer to 10-ml volumetric flasks.	2. Avoid evaporation to dryness. If the solutions appear turbid, filter prior to transferring to the volumetric flasks.
3. Add 1 ml of 0.2-per cent o-phenanthroline reagent.	
4. Add NH_4OH drop by drop until just basic to test paper. Add 1 to 3 drops of 10 N H_2SO_4. Dilute to the mark.	

5. Measure the optical densities of the solutions against the reference solution at 540 mμ within 10 minutes after color formation.

6. Calculate the quantity of vanadium by means of a colorimetric factor obtained by reference to the optical density of standards which have been carried through the separation and color formation procedure.

5. If the vanadium concentrations are low, the color fades appreciably after 15 minutes. Greater sensitivity can be obtained if 2.5-cm absorption cells are used for optical density measurements.