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I. Direct titration of sulfate, II. High precision spectrophotometric analysis

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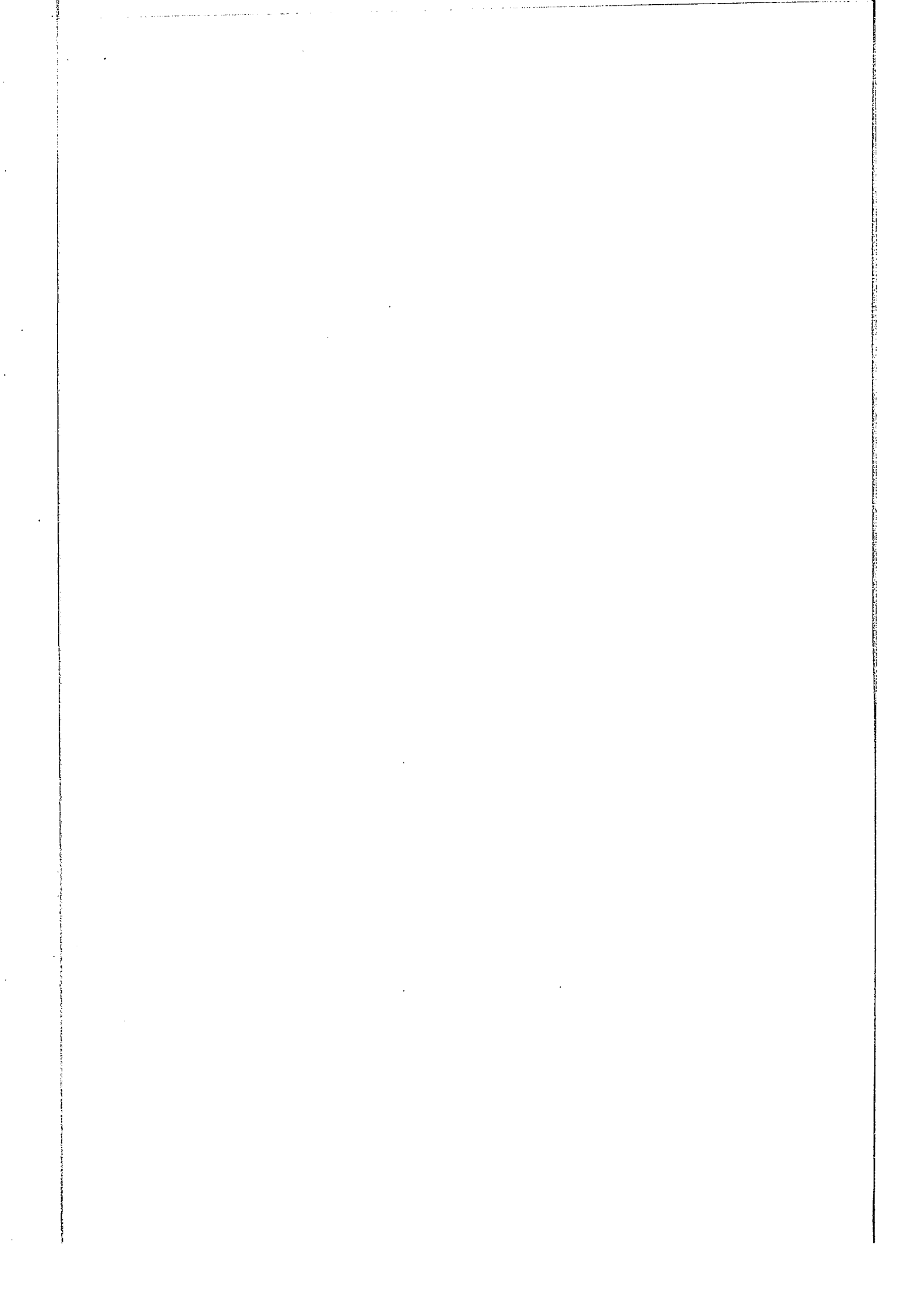
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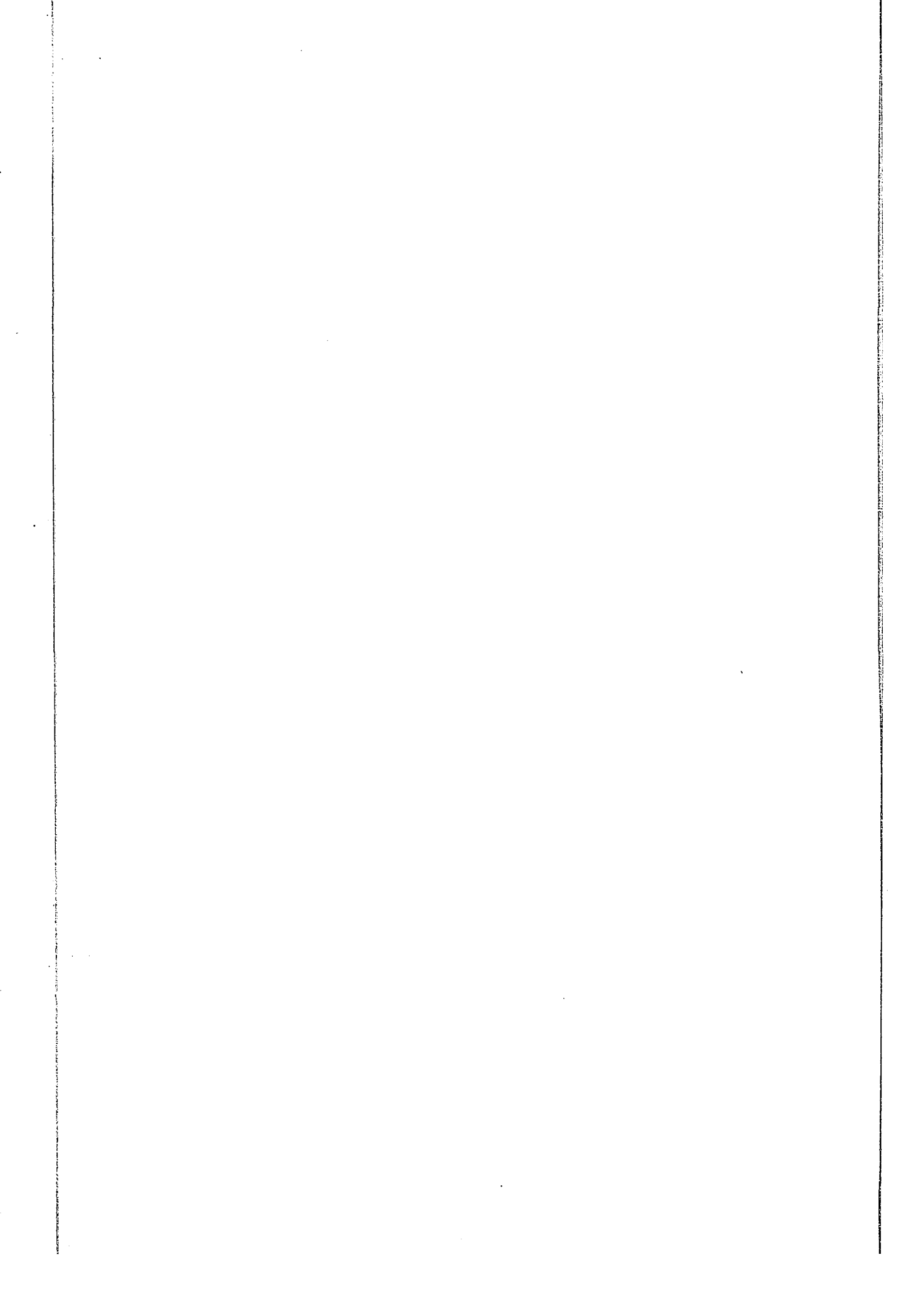
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I. DIRECT TITRATION OF SULFATE
II. HIGH PRECISION SPECTROPHOTOMETRIC ANALYSIS

by

Max Q. Freeland

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILISOPHY

Major Subject: Analytical Chemistry

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1955

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1a

PART I. DIRECT TITRATION OF SULFATE

INTRODUCTION

The quantitative analysis of materials for their sulfate content has been and continues to be an important analysis for many industries. If the category "Sulfate, Determination of" in any recent annual index of Chemical Abstracts is examined it becomes evident that the sulfate analysis is necessary for an enormous number of chemical raw materials and products.

The number of operations and the time required for gravimetric analysis has encouraged many chemists to develop shorter methods. In this quest many titrimetric methods have been developed. Schroeder's review (1) together with the review given in chapter II of this thesis may be consulted to obtain an idea of the many possibilities which have been investigated.

Of all the titrimetric procedures considered, direct titration is the simplest and fastest. Of the direct titrimetric methods, the external indicator method is inherently more time consuming than the use of an internal indicator. For many small laboratories and research groups, the instrumental methods are less desirable because of cost. The instrumental methods require more preparation time and to this is added the uncertainty of the proper operation of the instrument. From the standpoint of time and convenience

the direct titrimetric determination with internal indicator is the most economical.

The most popular direct methods have been based on the use of salts of rhodizonic acid or of tetrahydroxyquinone as the indicator. Many publications have appeared on the use of these two indicators. The references to these publications may be found in the literature review section of this thesis and in the reviews by Schroeder (1), Strebinger, Zombary and Pollack (2), Grant (3), Pieters (4) and Thomson (5).

Thomson (5) says of the use of rhodizonic acid and tetrahydroxyquinone:

In general, however, the use of these two indicators has not proved a great success. The refinements which have been incorporated to improve the end point are indicative of the critical nature of the titration. The present author is aware of several collaborative investigations done to test the efficacy of these indicators, the conclusions of which were, that they are unsatisfactory. Some of the later procedures might, however, repay investigation, in particular the method of Miller.

Most probably Thomson was referring to the methods of Miller (6), Ogg, Willits and Cooper (7) and Alicino (8). However, even if these methods are all that they claim to be, a direct titration to an end point with a sharp color change would be an improvement. This is the need which this investigation has filled.

The basic reaction for this determination of sulfate is the formation of insoluble barium sulfate which takes place when a solution of sulfate is titrated with a solution of a

barium salt. In this investigation the completion of the precipitation is indicated by Alizarin Red S. A color change from yellow to pink accompanies the adsorption of the indicator on the precipitate at this point.

The primary concern of this investigation was to find the best conditions for definition of the end point and to find those conditions which would cause this end point to coincide with the equivalence point. It was also necessary to consider the problem of converting actual samples to these ideal conditions.

From preliminary experiments it was evident that a close control of pH would be necessary to obtain reproducible results. It was also evident that the coprecipitation error which has been extensively studied in relation to gravimetric sulfate analysis, affected this potential volumetric method. Therefore, it was necessary to find an acid and a base which did not coprecipitate and it was also necessary to find a separation method which could be relied on to eliminate the coprecipitation error. With these tools, the extent of coprecipitation of anions and cations could be approximated, the conditions could be varied to obtain the sharpest end point and, most important, the titration became a reliable analytical method.

LITERATURE SURVEY

Scope

The last complete literature review on the titrimetric determination of sulfate was written by Schroeder (1) in 1933. Since that time Kolthoff and Stenger (9) have published a text which contains selected methods of indicator titrations together with helpful notes and explanations of the basic theory of each titration. The annual Reviews of Analytical Chemistry (10, 11, 12) have included a few selected references but have by no means been complete. The following authors have reviewed the literature rather completely in the fields indicated: Strebinger, Zombary and Pollak (2), use of tetrahydroxyquinone and rhodizonic acid for the titration of sulfate; Grant (3) and Pieters (4), titrimetric sulfate methods excluding instrumental methods; Thomson (5), titrimetric methods of sulfate analysis suitable to follow the Pregl combustion method for organics.

This review is fashioned to follow that of Schroeder in that all titrimetric sulfate methods which are referenced as general methods in Chemical Abstracts for the years 1933 to 1953 inclusive have been included in this classification. This classification is based on the convenience of analysis.

Precipitation Methods

Direct titration

Internal indicator. Schroeder (1) gives his own method as well as references to other work using rhodizonic acid and tetrahydroxyquinone. Thomson (5) discusses the method of Alicino (8) and also the method of Ogg, Willits and Cooper (7). Both of these methods employ dipotassium rhodizonate as indicator. Kolthoff and Stenger (9) discuss the method of Sheen and Kahler (13) using tetrahydroxyquinone and the method of Ricci (14) using Eosin as an adsorption indicator and lead nitrate as the titrant. Chaque (15) obtained good results with Ricci's method. Shub and Kaganova (16) state that the use of sodium rhodizonate in neutral or acetic acid solutions is an improvement over Raschig's (17) benzidine method.

External indicator. The primary reason for the use of rhodizonic acid or tetrahydroquinone as an external indicator stems from dissatisfaction with these reagents as internal indicators (18, 19, 20). A second reason noted by Peabody and Fisher (18) is that large amounts of colored organic material can be tolerated in the titration vessel. Zavarov (19) and Kochor (20) used rhodizonic acid whereas Peabody and Fisher (18) and Lee, Wallace, Hand, and Hannay (21) used tetrahydroxyquinone.

Photoelectric end point. In these methods the end point

is the earliest point of minimum transmittance as determined by a photometric instrument. Ringbom (22) published the original method, Wickbold (23) extended it to smaller samples (0.3 to 1.5 mg. of sulfate). Frey (24), Wickbold and Ringbom used barium chloride as the precipitating titrant whereas Takagi and Yamada (25) used lead nitrate with ethanol and agar-agar to produce a more reproducible turbidity.

Conductometric titration. Three low frequency methods (26, 27, 28) and one high frequency method (29) have been published recently. The method of Duval and Duval (26), that of Anderson and Revelle (27) and also that of Vainshtein (28) make use of a compensating cell in the balancing arm of the Wheatstone bridge. This makes it unnecessary to balance the bridge during the titration. Musha (29) applies his high frequency method to the determination of sulfur in steel.

Amperometric titration. In this method a small voltage, impressed across a dropping mercury electrode causes a current to flow when an excess of lead ion is present beyond that necessary to precipitate the sulfate. The amount of current is proportional to the lead ion concentration. Thus it may be plotted versus the added volume of lead nitrate. The extrapolation of this plot to the residual current line gives the amount of lead ion equivalent to the sulfate present in the sample. Kolthoff and Pan (30) used a voltage of 1.2 volts. Davies (31) applied the method of Kolthoff to sulfate

in alumina. Butenko and Pindas (32) used 0.6 volts. Kalvoda and Zýka (33) used (0.8 to 1.0) volts to titrate sulfate then titrated chloride plus bromide amperometrically in a duplicate sample with silver nitrate. Toropova and Yakovleva (34) used lead acetate to titrate the sum of the phosphate and sulfate in a sample. In a duplicate sample they removed the phosphate as magnesium ammonium phosphate and titrated the sulfate amperometrically in the filtrate.

Potentiometric titration. If the concentration of one of the members of an oxidation-reduction couple changes during the titration reaction the titration can be followed potentiometrically if a suitable electrode pair is available. A lead amalgam-calomel electrode pair was used by Dutta and Ghosh (35) to follow the titration of sulfate with lead nitrate. Barium chloride could be used as the titrant with lead ion present, however the potential break at the end point was not as sharp and the results were about one per cent low. Alcohol-water mixtures gave a larger break than aqueous solutions. Visyagin (36) and Christensen, Wymore and Cheldelin (37) used a platinum-calomel electrode pair and titrated with barium chloride. Visyagin added powdered quinhydrone as the redox couple. Christensen, Wymore and Cheldelin introduced a small amount of ammonium persulfate and used water-methanol as a solvent. Takagi, Shimizu and Nishino (38) also used ammonium persulfate and methanol, however they successfully

used tungsten-calomel, tungsten-molybdenum and platinum-tungsten electrode pairs for their titration.

Reverse titration

Indicator titration. By using a citrate buffer and titrating with the sulfate solution to be analyzed, Abrahamczik and Blümel (39) utilized the stable red barium rhodizonate as indicator at a pH value of three. The color change under these conditions is from the red barium rhodizonate to the colorless decomposition products of rhodizonic acid. They also adsorbed interfering cations on permutite.

Back titration

Alkalimetric indicator methods. In these methods an alkali salt of a basic anion, whose barium salt is only slightly soluble in neutral solution, is used to back titrate an excess of standard barium solution. The first excess of back titrant is indicated by the color change of a suitable acid-base indicator. Denk (40) used sodium carbonate as back titrant. The boiling solution contained thymol blue as indicator. Randall and Stevenson (41) used monohydrogen sodium orthophosphate as titrant, methyl red as indicator and titrated their solutions at room temperature.

Metal ion indicator methods. Miller (6) and Mutschin and Pollak (42) back titrated excess barium chloride with standard ammonium sulfate. Miller used 50% alcohol to slow the decomposition of the indicator in acid solution. A

totally new approach is that of Munger, Nippler and Ingols (43). They titrate the excess barium ion with standard disodium ethylenediaminetetraacetate (EDTA) using Eriochromewarz T as indicator. A drop of 0.1 normal magnesium chloride is added to sharpen the end point. This method was used for the determination of sulfate in water in conjunction with the method for total hardness of Swartzenbach (44) as modified by Diehl, Goetz and Hach (45). They indicate that it is necessary to have a value for the total hardness in order to use this sulfate method.

Filtration and titration of the filtrate

Lead ion as precipitant. An excess of standard lead salt solution is used to precipitate the sulfate as lead sulfate. After filtration or centrifugation, the excess lead is titrated in the filtrate. Pedinelli and Giavarini (46) used lead nitrate as precipitant and titrated the excess with standard ammonium molybdate solution using tannin as the indicator. Le Clerc (47) used lead acetate, titrated it with ammonium molybdate using alizarin red S as an adsorption indicator. Shakhkeldian (48) titrated the excess lead in the filtrate potentiometrically with trisodium orthophosphate. Potassium ferricyanide-lead ferrocyanide was the indicating redox couple.

Barium salts as precipitants. A barium salt which is slightly soluble in neutral or basic solution is added in

excess to the neutral or acid sample. After a period of heating or of waiting in which the sulfate present replaces the anion of this salt, the solution is cooled and filtered or centrifuged. The replaced anion is titrated in the filtrate or centrifugate. Barium oxalate: The oxalate may be titrated with potassium permanganate (49, 50) or with ceric sulfate using ferrous orthophenanthroline as indicator (50). Barium iodate: After the addition of acid and potassium iodide (51, 52) the liberated iodine may be titrated with standard sodium thiosulfate. Barium carbonate: Krüger (53) increased the solubility of barium carbonate sufficiently to react completely by keeping the precipitating solution saturated with carbon dioxide. He titrated the filtrate with standard hydrochloric acid to a methyl orange end point. Barium thiosulfate: Luchinskii and Suzdaleva (54) used ethanol to repress the solubility of barium thiosulfate prior to filtration. The liberated thiosulfate was titrated with standard iodine. They (55) investigated the solubility of barium thiosulfate in ethanol-water mixtures and the adsorption of thiosulfate ion by solid barium thiosulfate. Barium chromate: Elsermann and Wunderlich (56) added an excess of barium chromate dissolved in 5% perchloric acid as the primary precipitant. After heating to complete the barium sulfate precipitation the solution was neutralized with ammonia to precipitate the excess barium chromate. After filtration the soluble chromate is determined iodometrically in the filtrate.

Filtration, dissolution and titration of the precipitate.

Primary precipitate dissolved. An excess of the precipitating cation is added, the resulting precipitate is filtered off, dissolved and titrated: Benzidine methods: The precipitate benzidine sulfate is dissolved in hot water and titrated with standard sodium hydroxide to a phenol red end point (58, 60). McKittrick and Schmidt (59) used acetone in the supernatant and in the wash liquid to reduce the solubility. Barium sulfate: The procedure of Ekedahl and Sillén (61) may be used to determine soluble sulfate or the sulfate content of a barium sulfate mineral or precipitate. Barium sulfate is dissolved in sodium carbonate to form insoluble barium carbonate. The barium carbonate is filtered off, dissolved in an excess of standard hydrochloric acid. The excess acid is titrated with standard sodium hydroxide. Lead sulfate: Pedinelli (46) dissolved the initial lead sulfate precipitate in ammonium acetate-acetic acid solution and precipitated the lead with sodium dichromate. The lead chromate precipitate was dissolved in hydrochloric acid and determined iodometrically. This is the method of Alexander and Low (62).

Secondary precipitate dissolved. An excess of standard barium chloride is added, the excess barium precipitated with an excess of potassium dichromate (63, 64, 65) or an excess of ammonium oxalate (66). After the filtration the barium

chromate or barium oxalate is dissolved in acid and titrated. Gibson and Caulfield's (63) chromate method was modified by Manov and Kirk (64a) who studied the possible errors rather extensively. Werner (64b) used sodium acetate as the base for neutralization of the acid barium sulfate supernatant, otherwise his method follows that of Gibson and Caulfield closely. The excess chromate may be titrated with standard ferrous sulfate or determined iodometrically (64a). Jardim (65a) dissolved the barium oxalate in acid and titrated it with potassium permanganate.

Reduction Methods

Stannous chloride

Rancke-Madsen (65b) and Rancke-Madsen and Theilgaard-Madsen (66a) have reduced soluble sulfate quantitatively to hydrogen sulfide containing one to three per cent of sulfur dioxide. The hydrogen sulfide (and also the sulfur dioxide) is absorbed in a standard iodine solution containing cadmium sulfate and sodium hydroxide. The excess iodine is titrated with standard sodium thiosulfate. Barium, copper and lead in the sample do not affect the results. The sulfur dioxide gives the same titer as an equivalent molar quantity of hydrogen sulfide and therefore does not affect the results.

Hydriodic acid

Cuschnir (66b) applied the method of Auger and Gabillon (67) using hydriodic acid, to the determination of sulfur in

benzidine sulfate. A solid sulfate is heated with hydriodic acid. The hydrogen sulfide evolved is absorbed in zinc acetate solution which is titrated with standard iodine. Barium, lead and strontium sulfates cannot be analyzed by this method.

Ion Exchange Methods

Cation exchange resins

The precipitation of barium sulfate is complicated by coprecipitation. This has been noted and investigated by many authors (68). Not only are foreign ions coprecipitated but this may cause an excess of sulfate or of barium ions in the precipitate. By the use of the sulfonic acid type of cation exchanger, the cationic atmosphere during the precipitation may be controlled. The sample is passed through the ion exchanger which is in the acid form and all cations are replaced by hydrogen ions. These hydrogen ions may be neutralized by a base containing a cation which is but slightly coprecipitated. Samuelson (69) has a good discussion of specific sulfate determinations in which cationic exchange resins have been applied to advantage. It is evident that any one of the methods given heretofore may follow the ion exchange separation. However, the ion exchange step would be of no value in the reduction methods given. If sulfate is the only anion present or if only anions of volatile acids (which may be removed by boiling) accompany it,

the sulfuric acid eluted may be titrated with standard sodium hydroxide. Funasaka, Kawane and Hashino (70) and MacNevin, Riley and Sweet (71) used this method.

Anion exchange resins

The paper by d'Ans, Blasius, Guzatis and Wachtel (72) gives a method for determining small amounts of sulfate by using an anion exchange resin. The sample is passed through a column of resin which is in the iodide form. The iodide which the sulfate displaced is oxidized to iodate with bromine water. Iodine is liberated by addition of acid and potassium iodide. The iodine is titrated with standard sodium thiosulfate.

Chromatographic Methods

The work of Nydahl and Gustafsson (73) has shown that the bisulfate ion is strongly adsorbed on activated alumina from solutions one normal in perchloric acid. This separates sulfate quantitatively from all common ions excepting chromate, phosphate, chromium (III), bismuth (III) and antimony (III). Although it has been applied only to gravimetric analysis to eliminate interfering ions, it could be used equally well with schemes for volumetric analysis. Nydahl (74) applies an empirical correction for the coprecipitation of alkali metal ions which occurs. If he were to use a cation exchange resin at this point, this correction would be unnecessary. As for the cation exchange resin methods, any one

of the precipitation methods, or an alkalimetric titration for simple cases, could follow the chromatographic procedure.

EXPERIMENTAL NECESSITIES

Reagents

Ion exchange resins: Dowex IR-50 cation exchange resin was used throughout the investigation, although three different mesh sizes were used. The initial resin was a coarse unscreened resin. The second lot was 30 to 40 mesh and the last lot was 50 to 100 mesh with a cross linkage of 16. The last lot was the most satisfactory for analytical use.

Phenolphthalein: Baker and Adamson U. S. P.

Potassium acid phthallate: Malinkrodt reagent grade, 99.95% to 100.05% potassium acid phthallate.

Alizarin Red S (Sodium alizarin - 3 - sulfonate): Allied Chemical and Dye Co. certified biological stain. During the latter portion of the work, a purified grade was used. It was purified by Ford (75).

Sulfuric acid: Baker's reagent grade.

Sodium hydroxide: Baker's reagent grade.

Barium chloride: Baker's reagent grade.

Magnesium acetate tetrahydrate: Baker's c. p. grade.

Barium bromide: Coleman and Bell c. p. grade.

Perchloric acid: Baker and Adamson reagent grade.

Methanol: Baker and Adamson reagent grade.

Thorin (ortho - (2-Hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid disodium salt): Supplied by analytical

group I of the Ames Laboratory. The preparation and properties are given by Margerum, Byrd, Reed and Banks (76).

Quinizarin-2-sulfonic acid sodium salt: Eastman Kodak practical grade.

Magnesium chloride hexahydrate: Baker and Adamson reagent grade.

Nitric acid: Baker and Adamson reagent grade.

Magnesium perchlorate hexahydrate: G. F. Smith Chemical Co.

Magnesium bromide: Fisher Scientific c. p. grade.

Phosphoric acid: Baker and Adamson reagent grade.

Chemicals for study of interferences due to cations:
Reagent or c. p. grade.

Water: All water used in making solutions was distilled and deionized.

Solutions

Preparation

Sulfuric acid (0.1 normal): Eleven ml. of reagent grade sulfuric acid was measured and diluted to about four liters with deionized water. Sulfuric acid solutions of other normalities were made in a similar manner.

Sodium hydroxide (50%): Twenty grams of reagent grade sodium hydroxide was dissolved in an equal weight of water.

Sodium hydroxide (0.1 normal): Ten ml. of filtered 50%

sodium hydroxide was diluted to about four liters with deionized water.

Barium chloride (0.2 normal): One hundred grams of reagent grade barium chloride dihydrate was dissolved in deionized water. After adding 0.4 ml. of 0.1 normal hydrochloric acid, it was diluted to four liters in a volumetric flask. Barium chloride solutions of other concentrations were made in a similar manner.

Barium bromide (0.5 molar): In 200 ml. of water, 66.6 grams of barium bromide dihydrate was dissolved. To this solution 1600 ml. of methanol was added. This solution was diluted to about 3500 ml., cooled to room temperature, 0.425 grams of one normal perchloric acid added and then diluted to four liters.

Magnesium acetate (0.5 normal): Two hundred fifteen grams of magnesium acetate tetrahydrate was dissolved in four liters of deionized water.

Alizarin Red S (0.2%): About 200 mg. of the commercial dye was weighed out and dissolved in deionized water.

Alizarin Red S, purified (0.18%): About 200 mg. of the purified reagent was dissolved in 50 ml. of deionized water. This was washed through the large cation exchange column (H form) until the eluate became a light yellow. Total volume of eluate was 110 ml.

Thorin (0.025%): Twenty-five milligrams of ortho-(2-hydroxy-3, 6-disulfo-1-naphthylazo)-benzenearsonic acid

disodium salt (Thorin) was dissolved in 100 ml. of water.

Standardization

Sodium hydroxide. This was standardized against potassium acid phthallate using phenolphthalein indicator. Since the sodium hydroxide solution was adequately protected by ascarite tubes it changed very little over a period of weeks.

Sulfuric acid. This was standardized against the standard sodium hydroxide.

Barium chloride solution. This was standardized by passing measured volumes of the solution through the ion exchange column (hydrogen form) and titrating the effluent with standard sodium hydroxide. Preliminary experiments with potassium sulphate were used to determine the amount of wash liquid necessary. These preliminary experiments indicated that (1) the total effluent volume for each sample should be the same, (2) the samples should be of about the same size and (3) a preliminary sample should be used for each series, in order to obtain accurate analyses. These precautions were observed in this standardization.

Barium bromide. Twenty ml. of standard sulfuric acid was accurately measured into a 150 ml. beaker. To this was added 20 ml. of water and 40 ml. of methanol. About 21 ml. of barium bromide solution was added from the burette. Three drops of Thorin were added and the titration completed. The normality of the barium bromide was calculated from that of

the standard sulfuric acid.

Apparatus

Burettes. Fifty ml. Kimble Exax burettes which had been calibrated for each 5 ml. by weighing distilled water, were used for the standard barium, sulfuric acid and sodium hydroxide solutions. The magnesium acetate was added from an uncalibrated 50 ml. Exax burette.

Stirrer. A magnetic stirrer was used with teflon stirring bars.

Ion exchange columns. Three columns were used during the investigation. The first was $1\frac{1}{2}$ in. in diameter and 24 in. long. This was used with the coarse resin for standardizing barium chloride solutions. It was equipped with a sintered glass disk to support the resin and a stopcock to regulate the flow. The second column was smaller and was equipped with a goose neck outlet. It was used with the 30 to 40 mesh resin. The most satisfactory column was the third which was used with the 50 to 100 mesh resin. It consisted of a one cm. tube 20 cm. in length, topped by a two cm. cup $2\frac{1}{2}$ cm. in length. Immediately below the sintered glass disk which supported the resin the column was terminated by a short capillary tube. To this tube a short capillary dropping tip was attached by 20 cm. of three mm. gum rubber tubing. In order to hold the resin in place during reverse flow regeneration a sintered glass disk was fastened to the end of an upper

outlet capillary. This outlet capillary threaded a stopper which fitted the upper extremity of the column tightly. After regeneration and washing the entire regeneration assembly was removed and the column was ready for use.

EXPERIMENTAL

The Titration

Variation of the results with pH

Alizarin Red S procedure. About 15.5 ml. of the standard sulfuric acid solution was accurately measured from a burette into a 250 ml. beaker. The volume of magnesium acetate which was then added to each sample was different and is given in table 1. Forty-five ml. of methanol and sufficient water to make a volume of about 97 ml. was added to each sample. Then four drops of Alizarin Red S indicator was added and the sample titrated with standard barium chloride solution.

Thorin procedure. About 30 ml. of the standard sulfuric acid solution was measured accurately into a 150 ml. beaker. To this beaker, 23 ml. of methanol, the amount of magnesium acetate solution given in table 2, and enough water to make 60 ml., was added. Thirty-three ml. of the standard barium bromide solution was added slowly with stirring. Three drops of Thorin indicator was added and the titration completed. The pH was taken at the end point. The results are given in table 2.

Variation of the results with sample size

Procedure. An amount of the standard sulfuric acid was measured accurately into a 150 ml. beaker and 40 ml. of methanol was added. Sufficient magnesium acetate was added

from a burette to give a pH of about 3.20. Calculating the approximate volume of barium chloride solution to be added, enough water was added to give a final volume of 110 ml. The pH was adjusted again to about 3.20 with magnesium acetate or dilute perchloric acid. Ninety-five per cent of the barium chloride solution was added with stirring before adding 5 drops of purified Alizarin Red S indicator. The solution was then titrated to the end point. The pH of the solution at the end point and other relevant data are given in table 3. To minimize contamination by KCl while measuring pH, the Beckman calomel electrode was used for the shortest time possible with the side arm closed.

Interference Studies

Anions

Procedure for studying the coprecipitation of chloride.

About 30 ml. of standard sulfuric acid solution was accurately measured from a burette into a 150 ml. beaker. Varying amounts (see table 4) of magnesium chloride hexahydrate were added from a weighing bottle and their exact weight obtained. Forty-six ml. of water and 40 ml. of methanol were added. From a burette, 7.41 ml. of magnesium acetate was added. With stirring, 16 ml. of standard barium chloride was added. Then, four drops of Alizarin Red S indicator was added and the titration completed. The pH was taken at the end point. The

results are given in table 4.

Procedures for studying the coprecipitation of other anions. These procedures were exactly the same as that for chloride excepting the perchlorate was added as magnesium perchlorate hexahydrate, the bromide as magnesium bromide hexahydrate and the nitrate as one normal nitric acid. The nitric acid was neutralized to a pH of 3.20 with magnesium acetate solution. The quantity of water added was altered to keep the volume constant during the nitrate study. The results of these studies as well as the results for chloride are graphed in figure 1.

Cations

Procedure with Alizarin Red S. About 30 ml. of standard sulfuric acid was accurately measured into a 150 ml. beaker, three millimoles of the cation was added as a 0.1 molar solution, 40 ml. of methanol was added and sufficient 0.5 molar magnesium acetate was added to give a pH of about 3.2. Three drops of 0.2% Alizarin Red S indicator was added. If the solution assumed the normal yellow color, it was titrated to the regular end point. If an Alizarin Red S complex formed the pH was dropped with hydrochloric acid until the normal indicator color returned and then it was titrated. The results are given in table 5.

Procedure with Thorin. About 20 ml. of the standard sulfuric acid was measured accurately into a 150 ml. beaker

and 25 ml. of 0.1 molar solution of the foreign ion was added to this solution. Forty ml. of methanol was added and then 21 ml. of the standard barium chloride was added slowly with stirring. Three drops of Thorin was added as indicator and the titration was completed. Results are in table 5.

Procedure for studying effect of digestion. About 20 ml. of standard sulfuric acid was accurately measured into a 150 ml. beaker. The amount of standard barium chloride given in table 6 was added with stirring to this solution. The volume of the mixture was reduced to 25 ml. by digesting at a temperature just below boiling on the hot plate. This mixture was allowed to cool, and then 30 ml. of methanol, 20 ml. of standard sodium hydroxide and 5 drops of Alizarin Red S was added and then the titration was completed. The results are in table 6.

Ion Exchange

Inherent automatic shutoff

Apparatus. A 25. ml burette with boro-silicate wool plug and a capillary tip attached to the regular tip by 20 cm. of 3 mm. gum rubber tubing was used. A meter stick clamped behind the apparatus facilitated the measurement of the liquid head and the length of the resin column.

Reagents. Dowex I R-50 (50 to 100 mesh, 16 cross linkage) cation exchange resin and distilled water.

Procedure. Enough resin was placed in the column to

measure 3.8 cm. from the plug top to the resin top. Ten ml. of distilled water was added to the column. The outlet tip was adjusted until it was 20 cm. below the top of the resin. The water was allowed to flow out normally and it stopped flowing when the water level reached the top of the resin. The tip was dropped two cm., ten ml. of water added and the experiment repeated. The procedure was repeated until the critical head (the head at which the water level did not stop at the top of the resin) was reached. The resin was back-washed to remove bubbles, more resin was added and the entire procedure was repeated for this resin bed. A total of eleven different resin depths were used, ranging from the 3.5 cm. bed to a 24.6 cm. bed. The results are given in table 7.

Replacing interfering cations

Resin. Dowex IR-50 (30-40 mesh) cation exchange resin regenerated with hydrochloric acid by direct flow.

Procedure. About 20 ml. of standard sulfuric acid was accurately measured into a 100 ml. beaker from a burette. Twenty-five ml. of a 0.1 molar solution of the foreign ion was also pipetted into the beaker. This solution was washed onto the column and through it with 30 ml. of deionized water. The eluant was evaporated to 20 ml., 20 ml. of methanol and then 21 ml. of the standard barium bromide solution was added with stirring. Three drops of Thorin was added and the titration completed. Results are in table 8.

DATA AND RESULTS

The Titration

Variation of the results with pH

Table 1. Variation of the results with pH using Alizarin Red S indicator

ml. $\text{Mg}(\text{OAc})_2$	ml. H_2SO_4	ml. BaCl_2	pH	Theor. ml. BaCl_2	Error %
36.51	15.49	35.14	3.73	35.23	-0.26
30.00	15.47	35.19	2.69	35.18	0.03
20.00	15.45	35.18	2.27	35.14	0.11
10.02	15.49	35.20	2.01	35.23	0.09
	15.48	35.22	1.88	35.20	0.06

Additional observations

The end point character shows a variation with pH. At a pH of 3.73 the end point color change is from a pinkish-yellow to a deep pink whereas at 1.88 and 2.01 the change is indistinct and from yellow to a pinkish-yellow.

Note

The negative error in the first sample is probably due to the pH being above the useful range of the indicator.

Solutions

Sulfuric acid, 0.02784 normal; barium chloride, 0.05019 normal; magnesium acetate, 0.05 normal; Alizarin Red S, 0.2%.

Results

The titration results have no significant dependence on the pH at which the titration is carried out when the pH is between 1.9 and 3.7.

Table 2. Variation of the results with pH using Thorin indicator

Ml. Mg(OAc) ₂	Ml. H ₂ SO ₄	Ml. BaBr ₂	pH	Theor. Ml. BaBr ₂	Error %
	28.93	37.42	1.48	37.45	-0.08
2.01	28.86	37.25	1.48	37.33	-0.21
4.00	28.86	37.28	1.98	37.33	-0.13
6.00	28.87	37.30	2.27	37.34	-0.11
7.00	28.85	37.35	2.33	37.33	0.05
7.51	28.89	37.33	2.60	37.38	-0.13
8.02	28.89	37.37	3.14	37.38	-0.03

Additional observations

The end point seems to be sharper than the Alizarin Red S end point and the character of its color change does not vary nearly as much.

Solutions

Sulfuric acid, 0.1289 normal; barium bromide, 0.09960 normal; magnesium acetate, 0.5 normal; Thorin, 0.025%.

Results

There is no significant variation in the titration results with changing pH between a pH of 1.5 and 3.1.

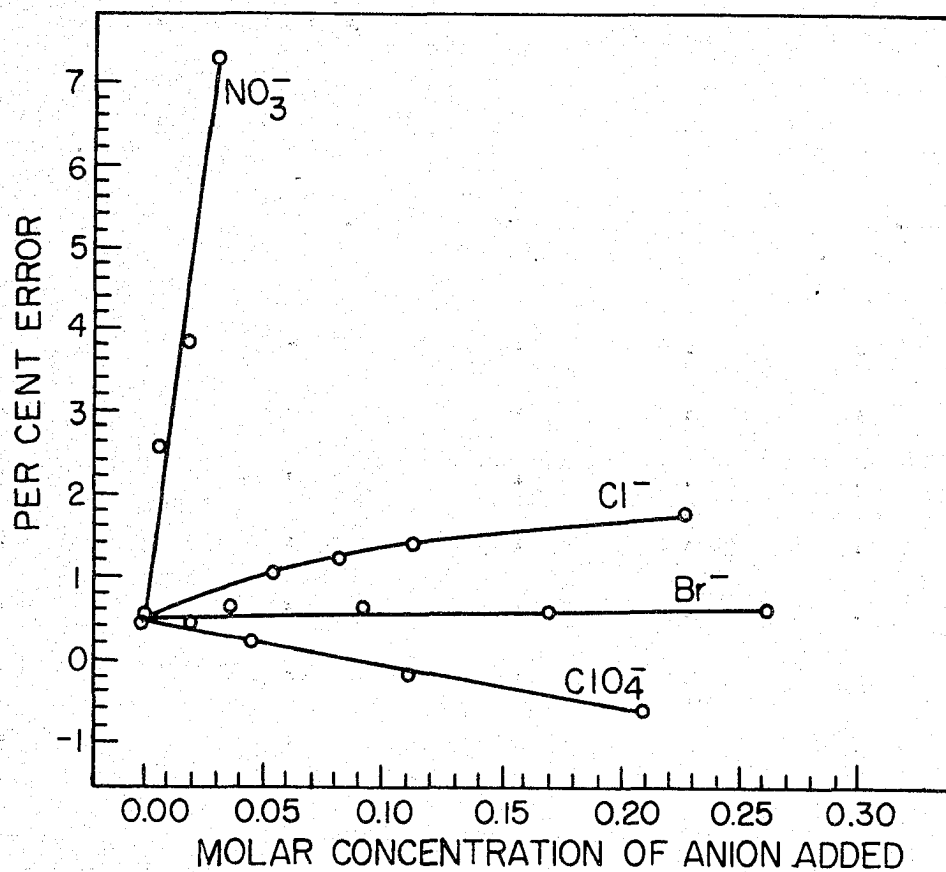


FIG. I EFFECT OF ANIONS ON ACCURACY. ANIONS ADDED AS THE MAGNESIUM SALT

Variation of results with sample size

Table 3. Variation of the results with sample size

Ml. $\text{Mg}(\text{OAc})_2$	Ml. H_2SO_4	Ml. BaCl_2	Theor. Ml. BaCl_2	Error %
11.47	49.95	28.44	28.31	0.46
9.51	39.97	22.72	22.65	0.31
7.29	29.88	17.01	16.93	0.47
4.70	19.85	11.31	11.25	0.53
4.71	19.86	11.32	11.25	0.62
2.19	9.83	5.59	5.57	0.36
2.21	9.84	5.62	5.58	<u>0.72</u>
			Average	0.50
				0.11

Solutions

Sulfuric acid, 0.1162 normal; barium chloride, 0.2051 normal; magnesium acetate, 0.5 normal; Alizarin Red S (purified), 0.18%.

Results

There is no significant variation of results with the size of the sample excepting that the reproducibility becomes poorer as would be expected.

Interference Studies

Anions

Table 4. The coprecipitation of chloride

Milligrams of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	Ml. H_2SO_4	Ml. BaCl_2	pH	Theor. Ml. BaCl_2	Error %
2524.3	29.87	16.92	3.35	16.62	1.80
1256.2	29.86	16.87	3.24	16.62	1.50
904.9	29.86	16.82	3.31	16.62	1.20
608.6	29.87	16.80	3.34	16.62	1.08
	29.88	16.71	3.40	16.63	0.48

Solutions.

Sulfuric acid, 0.02784 normal; barium chloride, 0.2051 normal; magnesium acetate, 0.5 normal; Alizarin Red S, 0.2%.

Results

There is a significant variation of the results with the concentration of chloride in the solution.

Coprecipitation of other anions

The same procedures and reagents were used for perchlorate, bromide and nitrate. The results are graphed in figure 1.

Cations

Table 5. Effect of cations

Salt added	Difference from theory, %	
	BaCl ₂ titrant, Aliz. Red ind.	BaBr ₂ titrant, Thorin ind.
Al(ClO ₄) ₃	Interferes	- 1.2
BeCl ₂	1.1	---
Ca(ClO ₄) ₂	Interferes	-10.0
CdCl ₂	- 1.8	---
Co(ClO ₄) ₂	- 0.7	---
Cu(ClO ₄) ₂	- 0.4	---
LaCl ₃	- 1.7	Interferes
LiClO ₄	- 0.9	---
Mn(ClO ₄) ₂	- 1.2	---
NaClO ₄	- 2.8	- 3.5
NH ₄ ClO ₄	- 2.2	- 2.1
Ni(ClO ₄) ₂	- 0.3	---
KCl	- 6.3	- 6.4
Zn(ClO ₄) ₂	- 1.2	- 1.3
ZrOCl ₂	Interferes	- 5.8

Solutions for Alizarin Red S procedure

Sulfuric acid, 0.1162 normal; barium chloride, 0.2051 normal; magnesium acetate, 0.5 normal; Alizarin Red S, 0.2%.

Solutions for Thorin procedure

Sulfuric acid, 0.1289 normal; barium bromide, 0.09960 normal; magnesium acetate, 0.5 normal; Thorin, 0.025%.

Other observations

The cations which formed colored complexes with Alizarin Red S at a pH of 3.2 are: beryllium, stannous, aluminum, copper, ferrous, uranyl, ferric, lanthanum and cerium. The

chromium (III) color obscured the end point. Ferric and ferrous iron interfere totally in both procedures. Lanthanum and zirconium formed complexes with Thorin. The dashed spaces in the above table indicate that the ion was not tried with that procedure.

Results

All cations tested, interfered to some extent in the sulfate titration.

Table 6. Variation of amount of sulfate precipitated prior to digestion

Ml. H_2SO_4	Ml. $BaCl_2$ added before digestion	Ml. NaOH	Ml. $BaCl_2$	Ml. $BaCl_2$ Theor.	Error %
20.01	24.45	20.19	26.41	26.71	1.12
20.00	16.47	20.20	26.04	26.70	2.47
20.00	11.47	20.20	25.80	26.70	3.37

Solutions

Sulfuric acid, 0.02810 normal; barium chloride, 0.02105 normal; sodium hydroxide, 0.01866 normal; Alizarin Red S, 0.2%.

Other observations

The end point of the first sample in the above table was vague. The end points became progressively better as the volume of barium chloride added before the digestion became

less. After the precipitate settled the finer particles (on top) were the deepest color. The heavier particles were barely colored.

Results

The sodium error is decreased by withholding the base until after precipitation and digestion of most of the barium sulfate, but the end point becomes progressively worse.

Ion Exchange

Variation of critical head with resin bed depth

Table 7. Variation of critical head with resin bed depth.

Trial	4.0	2.0	5.0	1.0	6.0	3.0
Resin Depth	3.5	4.0	7.7	9.0	10.6	12.2
Critical Head	43.1	31.9	45.2	42.8	44.9	45.5
Trial	9.0	7.0	10.0	8.0	11.0	
Resin Depth	13.4	13.6	17.4	19.0	24.6	
Critical Head	48.8	44.7	42.2	41.7	43.6	

Additional observations

The critical head was not reproducible. It seemed that the critical head depended somewhat on whether the topmost resin had been exposed to the air and the amount of water which had washed over it since its exposure. Some of the resin particles clung tenaciously to air bubbles. Also,

once the liquid surface broke away from the top of the column it did not stop until the bottom of the tube was reached.

Results

Insofar as this experiment was able to determine it, there was no dependence between the length of the resin column and the critical head. However, for this size of resin and with water as solvent a safe liquid head would be 30 cm.

Replacement of interfering cations

Table 8. Titration of sulfate using ion exchange procedure

Salt Added	Difference from Theory, %
$\text{Al}(\text{ClO}_4)_3$	- 0.3
$\text{Ca}(\text{ClO}_4)_2$	+ 0.1
$\text{Fe}(\text{ClO}_4)_2$	\pm 0.0
$\text{Fe}(\text{ClO}_4)_3$	- 0.1
LaCl_3	+ 0.9
NaClO_4	+ 0.3
NH_4ClO_4	+ 0.2
KCl	+ 0.4
ThCl_4	- 0.9
$\text{Zn}(\text{ClO}_4)_2$	\pm 0.0
$\text{K}_2\text{TlO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	- 1.24
$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$	-41.6

Solutions

Sulfuric acid, 0.1289 normal; barium bromide, 0.09960 normal; magnesium acetate, 0.5 normal; Thorin, 0.025%.

Other observations

In one experiment the titanium solution was placed on the column immediately after the zirconium. The result for sulfate in the titanium solution was about 80% high. The eluate from the titanium solution given in the above table which was passed through a freshly regenerated column was a light yellow color indicating that some of the titanium (IV) had not been replaced by hydrogen ion. Neither chromium (III) nor chromate, which had been reduced with hydrogen peroxide, were removed completely by the cation exchange column.

Results

Aluminum, calcium, iron (II), iron (III), ammonium, potassium, sodium and zinc can be removed by cation exchange and the sulfate accurately determined in the eluate.

RECOMMENDED PROCEDURES

The following procedures are recommended on the basis of the experimental work which has been described. It is apparent from the data on coprecipitation interference that the titration procedures by themselves are of worth only when approximate results are desired or for the titration of sulfuric acid or magnesium sulfate samples. The regeneration of the column probably can be carried out in the normal manner without serious error. The reverse flow regeneration is recommended here for the reasons given in the discussion. Samuelson (69) also discusses this point. If purified Alizarin Red S is used, more latitude can be used in the point of its addition in the procedure. If a calomel reference electrode is used in the solution, it should be withdrawn immediately after use if accurate results are desired.

Alizarin Red S Procedure

Dissolve a sample containing 2 to 4 millimoles of sulfate in 35 ml. of water, add 40 ml. of methanol and adjust the pH to 3.0 to 3.5 with dilute magnesium acetate or perchloric acid. Rapidly add about 90% of the required 0.1 molar barium chloride or barium bromide, then add 5 drops of Alizarin Red S and titrate to the first permanent pink color. Allow a timelapse of 3 to 5 seconds between addition of the last few increments of titrant.

Thorin Procedure

Dissolve a sample containing one to two millimoles of sulfate in 20 ml. of water, add 40 ml. of methanol and adjust the pH to 1.8 to 2.8 with 0.5 molar magnesium acetate or 0.5 molar perchloric acid. Add 80 to 90% of the 0.05 molar standard barium chloride or barium bromide, then add three drops of Thorin and titrate to the first permanent color change.

Ion Exchange Procedure

Agitate the resin (H form) in a beaker and decant the finer particles. Repeat this several times. With the column open pour in 14 ml. of resin, measured wet. Backwash with a slow stream of distilled water for a few minutes, then place the sintered-glass disk, with capillary tube attached, on top of the resin column and run 50 ml. of 3.5 normal hydrochloric acid through from the bottom at a flow rate of about four ml. per minute, washing it through with distilled water. Continue the washing until only a faint chloride test is obtained. This will require about 150 ml. and 30 minutes. Remove the regeneration assembly and the column is ready for use. Introduce the five ml. sample containing one millimole of sulfate by pipet directly onto the resin column and wash it through with 20 ml. of distilled water in small portions, allowing the liquid level to come to rest at the top of the

resin column each time before a new rinse is added. Titrate the sulfate in the eluate by the standard procedure.

Standardization of the Barium Solution

Measure out two millimoles of standard sulfuric acid accurately into a 150 ml. beaker. Titrate this by the procedure to be used in the analysis with the 0.05 molar barium solution to the end point preferred. Calculate the molarity of the barium solution from the molarity of the standard sulfuric acid.

DISCUSSION

Indicators

Several indicators were tried qualitatively. Of these, only three gave the required adsorption color change. These were (1) Alizarin Red S (sodium alizarin-3-sulfonate), (2) Thorin [ortho-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzene-*ar*sonic acid, disodium salt], and (3) quinizarin-2-sulfonic acid, sodium salt. On further experimentation it was found that quinizarin-2-sulfonic acid, sodium salt required a pH above eight in order to give an effective color change. This is a disadvantage because coprecipitation is more serious and carbonate interferes at high pH values. Thorin and Alizarin Red S are both stable compounds in both acidic and basic solutions. This is a distinct advantage over the tetrahydroxyquinone or rhodizonic acid methods. Thorin and Alizarin Red S both give a reversible adsorption end point in acid solution. Thorin seems to be slightly better because it is effective over a wider range of pH and at a lower pH than is Alizarin Red S. The pH range for use of Alizarin Red S was found to be about 2.4 to 3.4, that for Thorin was 1.5 to 3.2. The Thorin end point also seems to be sharper. Although the change in color intensity or hue is not as great in the Thorin end point, the color change takes place in a relatively short titrant interval. Alizarin

Red S was used throughout most of this problem because the application of Thorin was discovered after most of the work had been completed.

Factors Influencing the Color Change

Several conditions of the titration were found to influence the color change at the end point. These are: (1) the amount of miscible organic solvent added, (2) the amount of salt present, (3) the acidity, (4) the place in the procedure where the indicator is added, (5) the digestion of the precipitate of barium sulfate and (6) the volume of the solution and the concentration of the titrant.

Alizarin Red S

Organic solvent. The first two factors may both operate just by changing the dielectric constant of the supernatant. Methanol was used throughout the investigation because it is inexpensive and easy to obtain in a relative pure state. An experiment was performed which is not described above, in which the water-methanol proportion in the titration was varied from zero per cent methanol to 80% methanol. The end point was poorly defined below 30% methanol and was slow above 60% methanol. An experiment with pure methanol solutions of barium chloride as titrant and of sulfuric acid as sample gave an end point change in the vicinity of a ratio of one barium ion to two sulfate ions. Perhaps the replacement of

the second hydrogen of sulfuric acid becomes slower with a decrease in the polarity of the solvent.

Salt concentration. The end point changes its character with increasing salt concentration. At low salt concentrations the end point change is a rapid and distinct change from yellow to pink. At high salt concentrations the reddish shade appears gradually with addition of titrant and the end point color change is from a peach color to a deep pink. With a large excess of salt there is only a gradual change in color throughout the entire titration.

Acidity. The end point changes its character with changing pH in the same manner as with increasing salt concentration. This change is noted on page 27.

Indicator addition. If the indicator was added later in the titration, less indicator gave the same change in the intensity of the color. If the indicator anion coprecipitated this effect would be anticipated.

Heating the barium sulfate. In the procedure on page 25 and in table 6, the details are given for the experiment which was used to determine the variation of the analytical result and of the end point character with digestion. Apparently heating destroys the ability of the precipitate to adsorb the indicator, resulting in a poor end point. The poor end point could be due to an insufficient precipitate surface for the complete adsorption of the indicator and also due to the

dilution of the colored precipitate with the white non-adsorbing precipitate. It would be interesting to omit the heating in this experiment. Judging from the results obtained by varying the quantity of methanol, the end point would probably be better than the case in which the precipitate was digested, but poorer than those cases in which the base and methanol were present from the beginning of the titration.

Volume of solution and concentration of the titrant. The end point seemed to be sharper in the more concentrated solutions and, as usual, a more concentrated titrant gave a sharper end point.

Thorin

The effect of organic solvent, place in the procedure where the indicator was added and precipitate digestion were not studied for this indicator. However, the effect of these factors on Thorin should be similar to their effect on Alizarin Red.S.. Perhaps these effects would be less in magnitude since Thorin proved to be less sensitive to acidity and salt concentration.

Interferences

These are of three types: (1) substances which form insoluble precipitates with barium or sulfate, (2) ions which form a complex with the indicator rendering it inoperative

and (3) ions which coprecipitate with barium sulfate.

Substances forming insoluble sulfates

The substances which form insoluble precipitates with sulfate can not be present in major amount because they must be removed during the preparation of the sample for analysis. These substances are calcium, strontium, barium and lead. In minor amount they may be removed by ion exchange in the same manner as coprecipitable cations.

Substances forming insoluble barium salts.

The common substances which form insoluble barium salts are phosphate, carbonate, sulfite, fluoride and chromate. Some work was done on the interference of phosphate, fluoride and chromate. However, no short method was found to remove these interferences. The fluoride and carbonate interference could perhaps be removed by volatilization from a perchloric acid solution. The sulfite might be determined by titration with iodine which oxidizes it to sulfate (68) and the sulfate results corrected for the original sulfite present. Chromate may be reduced to chromium (III) by boiling with concentrated hydrochloric acid and ethanol. Perhaps the chromium (III) could be reduced to chromium (II) and adsorbed on catex resin. Phosphate has been successfully removed as the insoluble magnesium salt by Fritz and Yamamura (77) when present in small amounts in boiler water. Bespristis (78) removed phosphate by precipitating it with iron (III) and ammonia.

Substances forming complexes with the indicator

The substances which form complexes with the two indicators are noted on page 32. These are cations and with the exception of zirconium, titanium and chromium (III), they may be removed satisfactorily with cation exchange resin just as coprecipitable ions may be removed. In the absence of oxalate, titanium might also be removed satisfactorily.

Coprecipitation

Methods of avoiding coprecipitation. The best methods available for coping with the error of coprecipitation are by ion exchange, which has been adequately discussed by Samuelson (69), and by chromatographic adsorption, discussed by Nydahl and Gustafsson (73) and by Nydahl (74). They are of nearly equal worth. The chromatographic method has the advantage of separating sulfate from quantities of other salts, but still fails to separate it from fluoride, phosphate, sulfite and chromate, the most serious interferences. As they use it, ammonium or sodium ion is also introduced into the sample. The ion exchange method leaves the acids of iodide, bromide, chloride, nitrate, permanganate, perchlorate, acetate and sulfide which would have been eliminated from the sample in the chromatographic method. However, most of these may be boiled off or do not interfere in acid solution.

Requirement of alkali. The use of the ion exchange method required the use of a basic substance to adjust the

acidity for the Alizarin Red S titration. Allen and Johnston's work (79) indicated that magnesium ion was not coprecipitated. Of the basic magnesium compounds, magnesium acetate is the only one which is soluble and, fortunately it proved to be ideal for the purpose.

Reasons for coprecipitation studies. The studies on coprecipitation were pursued to positively identify the errors which were noticed early in the investigation, to find ions which did not seriously interfere and also for possible use in furthering the understanding of the phenomenon. There are better methods available for studying coprecipitation. The errors of titrimetric measurement are too large compared to the magnitude of the variations.

Identification of error. The identification seems reasonably positive. The curves in figure 1 are of the same general shape as those found by other investigators (79). A plot of the error involved versus the concentration of potassium ion was made from preliminary experiments and is also of this shape. The error is of the correct sign. Coprecipitable cations give results which are too low. Coprecipitable anions result in an apparent over titration. The order of coprecipitation of the anions (nitrate > chloride > bromide > perchlorate) are in the reverse order of their molar solubilities as required by the Paneth-Fajans rule. This order has also been found by gravimetric procedures (68).

The cations found which did not seriously coprecipitate were magnesium, copper, nickel and hydrogen ion.

Anion curves. The perchlorate curve (figure 1) indicates that the cation coprecipitation is exceeding that of the anion. This could be true if magnesium did coprecipitate the amount indicated. The bromide curve could be the result of (a) bromide and magnesium coprecipitation being exactly equal and opposite in sign or (b) the bromide ion does not coprecipitate and the magnesium is effectively complexed as $MgBr^+$ which does not coprecipitate.

Miscellaneous effects. The effect of the chloride which is added with the barium ion and the sodium ion which is added with the Alizarin Red S indicator can be identified tentatively in several experiments. In figure 1 the termination of all curves at about $+ 0.5\%$ is probably due to the chloride. The significant difference in results between table 1 and table 3 could have resulted from the sodium and chloride errors balancing in table 1 but only the chloride error being involved in the results of table 3.

Use of Cation Exchange Resin

Regeneration

In the usual method of regeneration by normal flow, the ions to be removed pass the full length of the column being taken up and released by the resin in the bottom of the column which was comparatively free of these ions before regeneration

was started. In order to get the column clean of the unwanted ions more solution and more time are necessary. If reverse regeneration is used, the safety zone at the bottom of the column is cleansed with the fresh acid and in a comparatively short time is freer of the unwanted ions than it was before the column was used. With a comparatively small amount of acid and in a short time the column is ready for washing and reuse. If the column is washed by reverse flow without disturbing the resin bed, the cleanest resin remains at the bottom in the safety zone and the resin which may still be slightly contaminated remains at the top where, during use, it may release some of the unwanted ions without danger of their going through to the eluate.

Automatic shutoff

In the usual method of introduction of samples onto a column the sample is diluted into the resin with small rinses to avoid the use of a large volume to get the sample through the column. If the liquid level is allowed to fall below the level of the resin top, air bubbles are introduced and the efficiency of the column decreased. It was observed that the liquid level did not fall below the top of the resin if the column of resin was short and the resin particle size was small. If this automatic shutoff could be depended on, it would materially decrease the amount of attention necessary during the use of an ion exchange column. This force which holds the liquid up is capillary force and it would be ex-

pected to vary with the capillary size (resin size) and the properties of the liquid.

Effect of resin depth and liquid head. The variables which were of primary interest because they would be important in the design of an effective ion exchange column were resin depth and liquid head. The specific problem was to find the maximum head for a given resin depth in order that the greatest flow rate would be obtained and still retain the convenience of the automatic stoppage of flow. The critical value of the liquid head varied very irregularly with resin depth which implies that this value was more dependent on some unknown variable or variables. However, it was found that a liquid head of 30 cm. or less would dependably give the desired result. Short columns are desirable because they have a higher flow rate and require less wash liquid than longer columns. Due to this desirability the 30 cm. height should not be a serious limitation in the design of an ion exchange column.

Stoichiometry

Barium chloride titration.

The barium chloride solutions and sulfate solutions were both standardized against the same standard sodium hydroxide. Two separate solutions were also made up by ignited weight and found to correspond to better than one part per thousand

with the ion exchange value, so it is fairly certain that the consistently positive values obtained by titration of standard sulfuric acid with barium chloride are real and probably are due to the coprecipitation of the chloride added as barium chloride.

Barium bromide titration

An attempt was made to standardize the barium bromide solutions in the same manner as had been used for the barium chloride solutions. The methanol was removed from the sample and water substituted before the introduction of the barium bromide samples into the ion exchange column. The values obtained were reproducible but did not agree with values calculated from the weight of barium bromide used to prepare the solution. After purification of the barium bromide salt of strontium bromide by a method essentially the same as that of Browning (80), the two values were more nearly in agreement, but not sufficiently close to warrant the use of either as a standardization value to study absolute stoichiometry. The standardization against standard sulfuric acid which was finally used gave very good values for the purpose of titrating sulfate. However, the errors which are recorded in these titrations can not be used to draw conclusions on coprecipitation.

Sulfuric acid standardization of barium solutions

The most practical and convenient method for arriving at the useful concentration of the barium solution which was

used as titrant, is the standardization against standard sulfuric acid. This useful concentration may not be the true concentration since it may contain a small error due to the coprecipitation of the anion associated with the barium in the solution or of the magnesium ion which was used to neutralize the acid. However, the results which are calculated for sulfate content of samples need not be corrected for any coprecipitation error if the sample has been converted to sulfuric acid by the recommended ion exchange procedure.

Comparison of Procedures

Of the titrimetric procedures for sulfate the Thorin procedure given in this thesis is preferred by this author. Both procedures given here have the following advantages over the tetrahydroxyquinone or rhodizonic acid methods: (1) the titration can be carried out in distinctly acid solution without taking special precautions, (2) the end point is sharp, (3) the indicator is stable and (4) the end point is reversible. The Thorin procedure is better than the Alizarin Red S procedure on points one and two, however some analysts may prefer the greater contrast of the color change of the Alizarin Red S indicator.

RECOMMENDATIONS FOR FURTHER STUDY

Comparison of Visual End Points

This study of the character of the end point change was done without objective measurement. It would be of benefit to titrimetric analysis to establish a method for measuring the comparative value of an end point. This would include the use of a photometric instrument as well as the judgment of experienced personnel.

Theory of Coprecipitation of Monovalent Ions

The literature which has been studied on the coprecipitation theory for barium sulfate has paid particular attention to the divalent ions, but very little to the coprecipitation of monovalent ions. It would be interesting to develop the theory for the kinetics of the coprecipitation of monovalent ions.

Indicator Development

The indicators used in this investigation are the best that have been proposed for this titration. Although they are not perfect, they should be a good starting point for the synthesis and investigation of other indicators for this titration. In order to do this intelligently, the manner of operation of these indicators should be studied in more detail.

PART II. HIGH PRECISION SPECTROPHOTOMETRIC ANALYSIS

INTRODUCTION

High Precision Spectrophotometric Analysis

The most economical analyses are those which are shortest and simplest in their execution. From this standpoint spectrophotometric analysis is very attractive. It is one of the leading methods for trace analysis but, due to its lack of reproducibility, has been little used for the determination of major components.

Ringbom (81), Hiskey (82, 83, 84, 85) and Bastian (86, 87) have shown that very good reproducibility may be obtained in spectrophotometric analysis if a solution of high absorbance is used for the blank. Hiskey (82) has shown that the error in comparing two solutions of similar absorbance may be as low as 0.04% based on concentration. By this method, colorimetric analysis can compete with other types of analyses in the accurate determination of major components. The precise determination of manganese in pyrolusite ores by conversion to permanganate was carried out by Young and Hiskey (85). Bastian (86) determined copper in bronzes. Both used a blank of high absorbance in their determination. The amount of sample used in each case would classify them as macro methods, but Bastian (86) recognized the possible use of this method for microchemical analysis.

In a very recent article, Reilley and Crawford (88)

have made the high precision spectrophotometric method more general so that it may be used to improve the precision of analysis for minor and trace constituents. The key to their extension is that they realized that both the zero per cent and 100 per cent transmittance limits on the scale could be set with standard solutions. They discuss most of the errors associated with high precision spectrophotometric methods but do not discuss the errors introduced by not having equally transparent cuvettes.

The spectrophotometer is an instrument for measuring relative light intensities. As it is usually used, the scale represents no light (zero per cent transmittance) to practically the total light emitted from the entrance slit. In terms of the concentration of a colored substance this is essentially infinite concentration to zero concentration. High precision spectrophotometry is essentially a method of operation of a spectrophotometer so that the scale of the instrument represents a smaller concentration interval. Each scale division then represents a smaller concentration differential and an error in reading the scale represents a smaller absolute error and, since more concentrated samples may be used, an even smaller relative error. For a detailed description of the principles and accuracy of the method see Hiskey (82) and Reilley and Crawford (88).

These methods require the use of carefully matched cuvettes. If the use of the high absorbance blank is to be

extended to routine analysis, however, it is difficult to obtain four cuvettes which are closely matched. It is also likely that the cuvettes may become unmatched with use. For these reasons it is desirable to include the transparency ratio in the basic equation and also in the analytical procedure.

In this thesis, the Beer-Lambert law is modified to correct for differences in the thickness and transparency of the cuvettes used. The thickness ratio, β' , does not change and is only determined once for each pair of cuvettes. The transparency ratio, R , is determined at the slit width used in the analysis. The value of the absorptivity K' changes only with the thickness of the blank cuvette, so it is determined only once for each No. 1 cuvette. This method gives precise results and permits the use of ordinary borosilicate cuvettes. It is assumed that the colored system obeys Beer's law.

Micro Vanadium Analysis

Four methods have been published for the microchemical determination of vanadium. In the sole microgravimetric method (89) vanadium is precipitated and weighed as silver vanadate. The three volumetric methods differ in the mode of reagent addition and of end point detection, but all depend on the reduction of vanadium (V) to vanadium (IV) with ferrous ion. The coulometric-amperometric method of Furman,

Reilly and Cooke (90) seems to be the most accurate of the three. The method of Gale and Mosher (91) is a dead stop method in which standard ferrous solution is added from a weight microburet. The method of Parks and Agazzi (92) is a standard amperometric titration. All three of these methods were extended into the microgram range.

The method proposed in this thesis is comparable to those mentioned above in simplicity and equals the accuracy of the method of Furman, Reilly and Cooke. Since it is based on a different reaction (hydrogen peroxide with vanadium (V)), it may be considered as a complementary method to those outlined above. It can readily be adapted to large numbers of samples and it represents a type of analysis which should be readily applicable to other stable, well behaved colorimetric systems.

This method is based on the standard peroxy-vanadium method investigated by Wright and Mellon (93) and also by Telep and Boltz (94). It contains features from both papers. No prior publications have been found in which a blank of high absorbance was used in micro analysis.

DERIVATION OF THE BASIC EQUATION

Use of the Beer-Lambert Law in Existing Methods

The work of Bastian (87) and Hiskey (82) was based on the following statement of the Beer-Lambert law:

$$(1) \quad \frac{P_2}{P_1} = 10^{-ab_1 (\beta c_2 - c_1)}$$

Inverting and taking the logarithm of both sides, this becomes,

$$(2) \quad \log \frac{P_1}{P_2} = a b_1 (\beta c_2 - c_1) = K(\beta c_2 - c_1)$$

in which β is the ratio b_2/b_1 of the lengths of the two cuvettes and a is the absorptivity. This equation does not attempt to describe the container and the solution but only the solution. The use of this equation for the calculation of accurate analytical results is valid only if (1) no container is used or (2) if the container has no effect whatsoever on the light beam, or (3) if the effect of the container is compensated for by the effect of a second container on this light beam. All existing high precision spectrophotometric methods attempt to experimentally fulfill condition three. The equation derived below allows the use of an experimentally determined correction.

The Need for Equation Modification

In practical spectrophotometric determinations, the time required for analysis is decreased if more than two cuvettes can be used. For high precision analysis it is shown below that the blank cuvette must be matched to better than one per cent transmittance with each of the cuvettes used for the above equation to give an accuracy of one part per thousand. If a cuvette transparency term is introduced in the above equation, the cuvettes need not be matched so exactly and the extension of this method to more than one cuvette is simplified. It is recommended in the Beckman DU operation manual (95) that the absorbance difference of the two cuvettes filled with distilled water be subtracted from the absorbance reading of the absorbing sample. This correction is valid for the usual spectrophotometric analysis, but is not valid for high precision analysis due to the difference in slit width. The equation justifying this correction may be derived from the Beer-Lambert law and a consideration of the changes taking place in the intensity of a light beam passing through a cuvette. It is shown later that this more general equation is experimentally applicable to the determination of the correction value in high precision analysis.

Equation Derivation

Figure 2A illustrates the changes which take place in the intensity P_0 of an incident light beam while passing through a colorless blank and figure 2B represents these changes for a colored solution in the same cuvette. The symbols x and y represent the transmittances of the cuvette walls indicated. Figure 2B illustrates the decrease of light intensity from P_0 to P_0x before entering the solution and the decrease from P to Py after leaving the solution. Equation (3) is a simple mathematical statement of the Beer-Lambert law applied to the solution only, in cuvette 1B:

$$(3) \quad \log \frac{P_0x}{P} = a b c$$

If P_0x/P is multiplied by y/y and the subscripts applied which indicate that this is cuvette number one,

$$(4) \quad \log \frac{P_0x_1y_1}{Py_1} = a b_1c_1$$

The same treatment may be used for a second cuvette containing a solution of concentration c_2 :

$$(5) \quad \log \frac{P_0x_2y_2}{Py_2} = a b_2c_2$$

Subtracting (4) from (5) and rearranging:

$$(6) \quad \log \frac{P_0x_2y_2}{P_0x_1y_1} \cdot \frac{Py_1}{Py_2} = a(b_2c_2 - b_1c_1) = a b_1 (\beta'c_2 - c_1)$$

P_0

P_0X

P_0XY

P_0

P_0X

P

$P Y$

A

B

FIG. 2 ILLUSTRATION OF THE CHANGE IN LIGHT INTENSITY P_0 IN ITS PASSAGE THROUGH A CUVETTE

Simplifying the symbols:

$$(7) \quad \log R + \log \frac{P_1}{P_2} = K' (\beta' c_2 - c_1)$$

This equation represents the comparison of solutions of concentrations c_1 and c_2 in two different cuvettes which have wall transmittances x_1, y_1 and x_2, y_2 . In this equation, R is the ratio of transparencies of the two cuvettes. Since β and K no longer contain any effect of cell transparency they are marked with primes. In the derivation of the equation above, the following basic assumption was made: A glass wall will decrease the intensity P_0 of a normally incident light beam by a constant fraction x , which is a constant for this glass wall.

The equivalent equation using Hiskey's symbolism is:

$$(8) \quad P_1 = \frac{P_2}{R} 10^{A_1 (\beta' \alpha - 1)}$$

in which $\alpha = \frac{c_2}{c_1}$.

NECESSITIES FOR EXPERIMENTAL PROCEDURES

Reagents and Solutions

Standard vanadium solution

Vanadium pentoxide (1.8 grams) of known purity was accurately weighed and dissolved in 800 ml. of 25% perchloric acid. After cooling to room temperature it was diluted to one liter with deionized water. This standard vanadium solution contained 1.0842 mg./ml. at 31°C and had a measured density of 1.1074 grams/ml. at 28.5°C.

Reagents

Aluminum perchlorate (2 mg./ml.). Reagent grade aluminum perchlorate nonahydrate (9.0 grams) was dissolved in about 250 ml. of distilled water.

Perchloric Acid. Reagent grade.

Hydrogen peroxide. Reagent grade 30% hydrogen peroxide was diluted to 5% in a mixing graduate.

Apparatus

The Beckman Model DU spectrophotometer with four one-centimeter borosilicate cuvettes. This spectrophotometer was voltage stabilized.

Microbalance.

Standard Solution Preparation

The necessary amount of standard vanadium solution was weighed into a 25 ml. volumetric flask. Sufficient concentrated perchloric acid was added to bring the total amount of concentrated perchloric acid to five ml. (The standard vanadium contained 0.2 ml. of concentrated perchloric acid per ml. of solution.) The approximate amount of aluminum perchlorate to equal the amount of aluminum in the sample was added to the flask. This solution was diluted to about 20 ml., mixed by swirling and cooled to room temperature. One ml. of 5% hydrogen peroxide was added and the solution diluted to the mark on the flask. The weight of vanadium added, was calculated from the measured density of the standard vanadium solution and the weight of solution added.

General Spectrophotometric Procedure

Handling cuvettes

The cuvettes were marked so that they could always be replaced in the cuvette holder in the same slot and with the same side facing the photocell. The cuvettes were cleaned thoroughly, filled with distilled water and the outside of the optical surfaces dressed with Desicote using a cotton swab. The excess Desicote was wiped from them with benzene on a tissue. The cuvettes were allowed to age three hours and then placed in the cuvette holder. The cuvette in slot number one

was the blank cuvette. The filling, emptying and rinsing operations were always carried out with long barreled reagent droppers. The cuvettes were left in the holder during these operations. The cuvettes, when not in use were filled with distilled water.

Adjustment of the slit width

The dark current was adjusted normally. The sensitivity knob was set $2\frac{1}{2}$ turns from its counter-clockwise limit, the wave length was set at 460 m μ and the diaphragm was opened to the blank cuvette. The slit width was adjusted until the galvanometer was approximately in balance with the selection switch on check. The dark current and 100% adjustments were then made in the standard manner for the instrument. These adjustments were made as exactly as possible then the per cent transmittance of the comparison cuvette was measured. The reading was estimated to 0.1% transmittance unit. The dark current and 100% adjustments, and the reading were repeated. These were repeated until two check readings were obtained.

DETERMINATION OF CONSTANTS

Determination of β' Discussion

For that comparison in which cuvettes one and two both contain a solution of concentration c , equation (7) may be written as follows:

$$(9) \quad \log \frac{P_1}{P_2} = K' c (\beta' - 1) - \log R$$

If this comparison is carried out for each of a series of concentrations, a plot of $\log P_1/P_2$ versus concentration should yield a straight line of slope $K' (\beta' - 1)$ and of intercept $\log R$. An example of this type of plot is given in figure 3. The data for this plot were obtained from the peroxy-vanadium complex. An approximate value of K' is sufficient to calculate the value of β' . The usual Beer's law plot gives a sufficiently accurate value for this calculation. The adherence of the experimental points to the straight line is a measure of the constancy of the transparency ratio with varying slit width. If this variation is excessive for any cuvette it should be replaced. If a pattern of excessive variation is evident in the experimental points for all three cuvettes, cuvette one should be replaced and the measurements repeated. In the accompanying plot the experimental error illustrated is $\pm 0.1\%$ transmittance which is

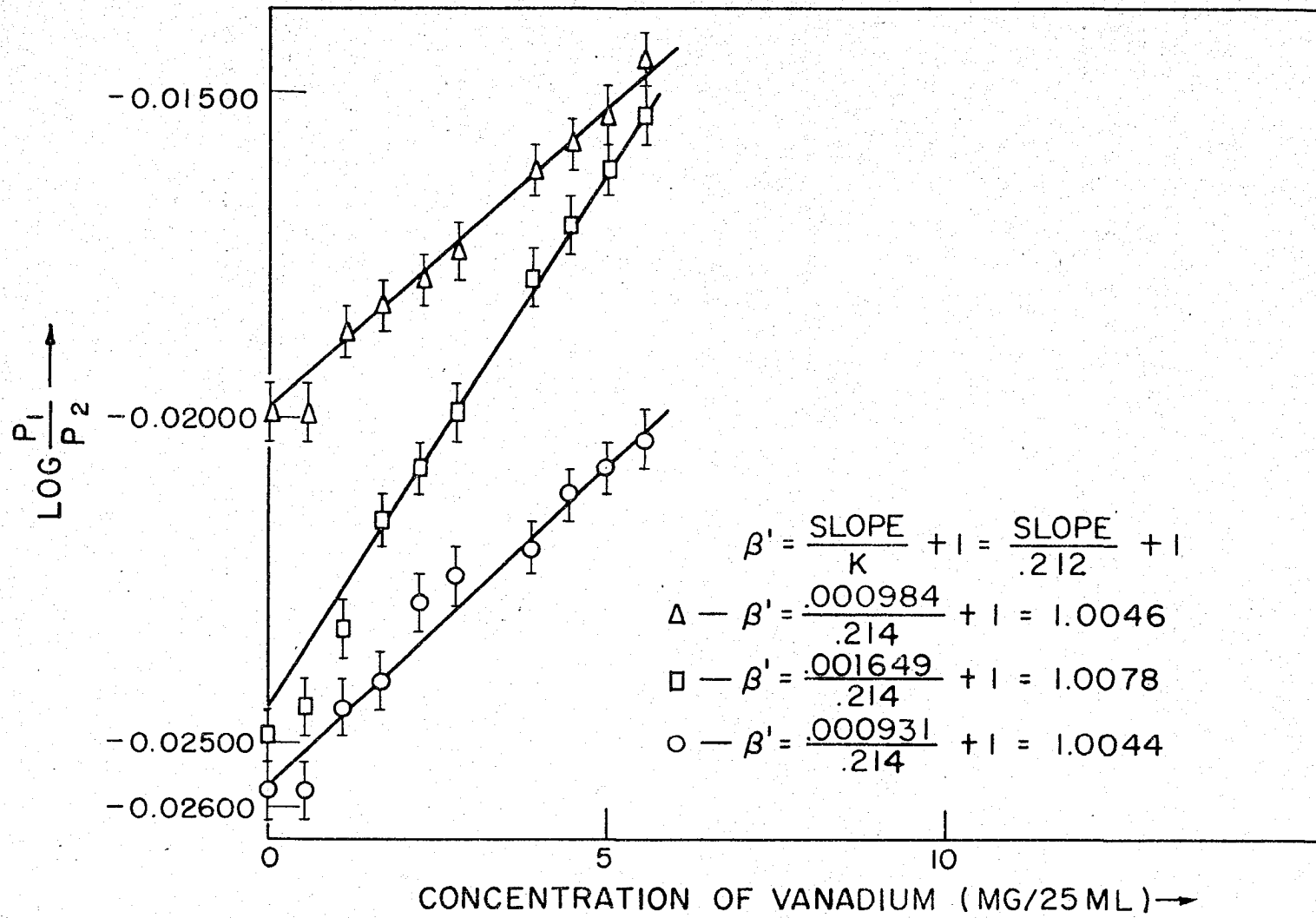


FIG.3 PLOT TO DETERMINE β'

probably good for nine of ten readings. Therefore, these cuvettes are satisfactory, although there is a slight defect in cuvette one which can be seen at a concentration of .55 mg/25 ml. The procedure given below is for the vanadium-peroxy complex; however, it is adaptable to other stable systems which obey the Beer-Lambert law.

Procedure

Ten peroxy-vanadium solutions whose vanadium content ranged from zero to five milligrams per 25 ml. were prepared by the standard procedure given on page 64 with the omission of the aluminum perchlorate (See table 9). All four cuvettes were emptied of the distilled water and then rinsed and filled with the solution containing no vanadium. Each of the cuvettes was compared with cuvette one by the spectrophotometric procedure given above. The cuvettes were emptied and then rinsed and filled with the solution containing 0.5404 milligrams of vanadium in 25 ml. Each of the cuvettes was compared with cuvette one by the spectrophotometric procedure given above. These operations were repeated for each of the solutions prepared.

Data

The significant data is given in table 9.

Table 9. Data for the calculation of ρ' for cuvettes, two, three and four

Solution concentration (mg./25 ml.)	Slit width (millimeters)	Per cent transmittance $(P_2)_2^*$	$(P_2)_3^*$	$(P_2)_4^*$
0.00000	0.034	106.1	105.9	104.7
0.54044	0.039	106.1	105.8	104.7
1.08050	0.045	105.8	105.5	104.4
1.62137	0.051	105.7	105.1	104.3
2.16078	0.058	105.4	104.9	104.2
2.70145	0.066	105.3	104.7	104.1
3.78280	0.085	105.2	104.2	103.8
4.32085	0.097	105.0	104.0	103.7
4.85971	0.111	104.9	103.8	103.6
5.40185	0.129	104.8	103.6	103.4

*Parenthetical subscripts refer to the cuvette identification number.

Calculations

The absorbance values were calculated for each of the per cent transmittance values given in table 9. For example, the per cent absorbance for cuvette four with no vanadium $(P_2)_4$, was calculated as follows:

$$\log \frac{P_1}{(P_2)_4} = \log \frac{100.0}{104.7} = -0.01995$$

These values of absorbance are plotted versus their respective concentrations in figure 3. The slope was measured

for each cuvette and its value of β' was calculated from the equation:

$$\beta' = \frac{\text{slope}}{K'} + 1$$

These calculations are given in figure 3 for cuvettes two, three and four.

Results

In addition to the cuvettes used in this experiment, the β' values for one other set were measured at a later date. The β' values for all cuvettes used are given in table 10.

Table 10. Values of β'

Cuvette number	2	3	4	6	7	8
β' value	1.0046	1.0078	1.0044	0.9973	1.0047	1.0086

As given in the procedure above, cuvettes two, three and four were compared with cuvette one. In the same manner, cuvettes six, seven and eight were compared with cuvette five.

Determination of K'

Discussion

The value of K' is given by rearranging equation (7):

$$(10) \quad K' = \frac{\log R + \log \frac{P_1}{P_2}}{\beta' c_2 - c_1}$$

In this equation $\log (P_1/P_2)$ can be measured for two solutions of known concentrations c_1 and c_2 . Log R for cuvettes two, three and four can be determined by using only one solution of concentration c_1 in all four cuvettes. Log R is then given by:

$$(11) \quad \log R = K' c_1 (\beta' - 1) - \log (P_1/P_2).$$

In principle, with the values of β' previously determined, K' can be calculated. However, since K' is sensitive to the value of $\log R$ and vice versa, the two equations should be solved simultaneously to give:

$$(12) \quad K' = \frac{\log \frac{P_1}{P_2} \cdot \frac{P_2'}{P_1'}}{\beta' (c_2 - c_1)} = \frac{\log \frac{P_2'}{P_2}}{\beta' (c_2 - c_1)}$$

It is convenient to determine the value of K' at the same time as the first analysis. The standard solution used as blank in the analysis may also be used as the blank in the determination of K' . The other three standard solutions are made to have concentrations 0.9, 1.0, 1.1 milligrams (per 25 ml.) greater than the standard solution used as a blank.

Procedure

Eight standard peroxy-vanadium standards were prepared according to the procedures given above. The concentrations were about 1.4, 2.3, 2.4, 2.5, 2.8, 3.7, 3.8 and 3.9 milligrams per 25 ml. For exact concentrations see table 11.

Cuvette five was the blank cuvette and it was rinsed and filled with the 1.4 ml./25 ml. standard for the first group of solutions given in table 11. Cuvettes seven and eight were rinsed and filled with the 2.3 and 2.4 mg./25 ml. standards, then these cuvettes were compared with cuvette five by the spectrophotometric procedure given above. The remaining solutions were placed in the cuvettes indicated and compared in the same way. The 2.8 mg./25 ml. standard was used as the comparison standard for all solutions listed below it in table 11.

Data

The data is given in table 11.

Table 11. Data obtained for determining K' and $\log R$.

Cuvette number	β'	Solution* concentration mg./25 ml.	Per cent transmission		K'	Log R
			P'_2	P_2		
5		1.4085				
6	0.9973	1	99.6	59.7		-0.00091
7	1.0047	2.2775	99.6	64.6	0.2154	-0.00030
8	1.0086	2.3892	98.3	60.3	0.2146	-0.00476
7	1.0047	2.4969	99.6	57.8	0.2161	-0.00030
5		2.8227				
6	0.9973	2	99.8	63.8		
6	0.9973	3.6926	99.8	64.6	0.2177	-0.00253
8	1.0086	3.7989	98.0	59.9	0.2172	-0.00348
7	1.0047	3.9090	99.4	57.4	0.2185	0.00029

*

Numbers 1 and 2 refer to actual vanadium-aluminum alloy samples.

The column P_2 contains the transmittance readings obtained from the above procedure, the column P_2' contains the readings taken to calculate the value of $\log R$.

Calculations

These are based on equation (12). Using the 2.2775 mg./25 ml. standard as an example:

$$K' = \frac{\log \frac{P_2'}{P_2}}{\beta'(c_2 - c_1)} = \frac{\log \frac{99.6}{64.6}}{1.0047 (2.2775 - 1.4085)} = 0.2154$$

Results

The individual K' values calculated are given in column six of table 11. The average value of K' for the first series is 0.2154 and the average value of K' for the second series is 0.2178.

Determination of $\log R$

Discussion

The value of K' and of β' are constants for the cuvette pairs used. However, $\log R$ will vary with the preparation of the cuvette and perhaps with the slit width used. The value of $\log R$ is calculated from equation (11) using for the value of P_2' , the per cent transmittance measured when both cuvettes are filled with solution of concentration c_1 . This measurement is made with the slit width unchanged from the analysis.

Procedure

In the procedure above for the determination of K' , the data were also obtained for the calculation of $\log R$. Immediately at the conclusion of the first series (top of table 11) and before changing the slit width, cuvettes six, seven and eight were emptied and refilled with the 1.4 mg./25 ml. standard. Then these cuvettes were compared with cuvette five by the spectrophotometric procedure given earlier. The same procedure was followed at the conclusion of the second series with the 2.8 mg./25 ml. standard.

Data

The data is presented in column four of table 11.

Calculation

The calculations are based on equation (11). If the 2.2775 mg./25 ml. standard is used as an example:

$$\begin{aligned} \log R &= K'c_1 (\beta' - 1) - \log \frac{P_1}{P_2} \\ &= (0.2154) (2.2775) (0.0047) - \log \frac{100}{99.6} \\ &= 0.00091 \end{aligned}$$

Results

The calculated values of $\log R$ are given in column 7 of table 11.

ANALYSIS OF VANADIUM-ALUMINUM ALLOYS

Outline of Procedure

The analysis of procedure follows this outline:

Preparation

Reagent solutions are prepared.

β' values are obtained for the cuvettes.

K' value is measured.

Analysis

Sample is dissolved, perchloric acid and hydrogen peroxide are added and it is diluted to 25 ml.

Sample is compared against distilled water blank to obtain approximate concentration.

Standard solution is prepared for blank.

Samples are compared to blank at 460 m μ .

Log R is measured and calculated.

Sample concentrations are calculated.

Since the preparation steps have been adequately discussed in the last two chapters, only the analysis steps are presented in this chapter.

Sample Preparation

Three samples were weighed out in micro combustion boats on the microbalance. Sample one weighed 17.331 mg., sample two weighed 26.618 mg. and sample three weighed 16.834 mg. These were placed in 16 mm. test tubes which were supported

in 125 ml. Erlenmeyer flasks. One ml. of water and two ml. of concentrated perchloric acid were added to each of the samples. These were mixed and placed on the hot plate. They were heated until the fumes of perchloric acid appeared. The samples were not quite dissolved, so one ml. of water was added to each and the heating repeated. By the time the perchloric acid fumes appeared again, the samples had dissolved. They were allowed to cool and then rinsed into 25 ml. volumetric flasks. Three ml. of concentrated perchloric acid was added to each and they were diluted to about 20 ml. with distilled water. They were mixed and allowed to cool to room temperature. One ml. of 5% hydrogen peroxide was added, then they were diluted to the mark. Each flask was inverted with swirling ten times to thoroughly mix the solution.

The Analysis

Approximate

Sample three was compared against a distilled water blank at 460 m μ using one centimeter borosilicate cells. A value of 32.5% transmittance was obtained. The approximate vanadium percentage was calculated as follows:

$$\text{Per cent vanadium} = \frac{(\log \frac{P_1}{P_2}) (100)}{K S} = \frac{(\log \frac{100}{32.5}) (100)}{(0.214) (16.834)}$$

$$= 13.5\%$$

High precision analysis

The approximate vanadium concentration in milligrams per 25 ml. was calculated for samples one and two using the approximate per cent vanadium. The concentration of the standard samples were calculated so that the standards used to determine K' bracketed the approximate concentration of each sample and the standard solution to be used as a blank was about one milligram per 25 ml. less in concentration. These standard solutions were prepared according to the procedure given before. The concentrations of these solutions are given in table 11.

The procedure is the same as that given for the determination of K' . The samples noted in table 11 were analyzed at the same time as these standard solution were measured to determine K' . Rather than place standard solution in the cuvettes indicated, the unknown sample indicated was placed in the cuvette and measured against the standard blank for that concentration group.

Data

The data is given in table 11.

Calculation

The per cent vanadium was calculated from the following equation:

$$\text{Per cent vanadium} = \frac{100}{S} \frac{(\log R + \log \frac{P_1}{P_2} + K'c_1)}{K' \beta'}$$

For illustration the following calculation of sample one is given:

$$\text{Per cent vanadium} = \frac{100}{17.331} \frac{-0.00091 + \log \frac{100}{59.7} + (0.2154)}{(0.2154)(1.4085)} = \frac{(1.4085)}{(1.4085)} = 14.14\%$$

Results

Sample one	=	14.14 %
Sample two	=	13.97 %
Average	=	14.06 %

The Effect of Aluminum

Procedure

Five standard solutions were prepared. Each contained very nearly 4.87 mg./25 ml. of vanadium (accurately measured) and a different quantity of aluminum perchlorate. These were compared to a standard blank containing 3.499 mg. of vanadium in 25 ml. The value of K' was calculated from equation (12). These values of K' are given in table 12 along with the calculated sample size and per cent vanadium which these synthetic solutions would represent.

Table 12. Effect of aluminum

ml. of 0.1 M $\text{Al}(\text{ClO}_4)_3$	Per cent vanadium	Sample size	K'
0	100	4.9	.2155
1	64	7.6	.2148
2	47	10.3	.2138
5	27	18.4	.2124
10	15	31.9	.2128
		Average	.2139 .0010

Analytical Results

The analytical results are summarized in tables 13 and 14. The analysis of aliquots one, two and three in table 13 and alloy one in table 14 were based on the addition of the standard vanadium solution from a calibrated five ml. burette. The remainder of the analyses were based on the weighing procedure given.

Table 13. Results on synthetic samples

Aliquot	Actual concentration mg./25 ml.	Measured concentration mg./25 ml.	Error %
1	2.098	2.105	0.3
2	1.998	2.003	0.3
3	2.198	2.198	0.0
4	3.0434	3.0453	0.06
5	3.1532	3.1531	0.00
6	3.2588	3.2585	0.01
7	3.3629	3.3621	0.02
8	3.4699	3.4756	0.16
		Average	0.11%

Table 14. Alloys Analyzed

Alloy	Measured concentration mg./25 ml.	Per cent vanadium	Ave. reproducibility
1	2.094	20.91	0.3%
	2.079	20.96	
2	2.984	24.70	0.1%
	3.133	24.72	
3	2.450	14.14	0.08%
	3.719	13.97	

DISCUSSION

Comparison of Methods

The method of Hiskey (82, 85), based on equation (2), will give exact results in two cases; (a) with matched cuvettes ($R = 1$), or (b) if the value of K is calculated from measurements on a standard solution of the same concentration as the unknown sample. Since (b) is impractical, both Hiskey and Bastian used condition (a).

The comparison of the two equations is important for two reasons. First, the importance of using the $\log R$ term in the equation for very accurate work should be emphasized. Second, this comparison points out the best conditions for the use of Hiskey's method insofar as the cuvette transparencies affect the analytical results. In order to evaluate the expected error using Hiskey's method with unmatched cuvettes, the equation was written for each measurement of the two methods. The equations for the measurement of β and β' are:

$$(13) \quad \log \frac{P_1}{P_2} = A (\beta - 1) = ab_1c(\beta - 1)$$

$$(14) \quad \text{and} \quad \log \frac{P_1}{P_2} = A' (\beta' - 1) - \log R.$$

Since the measured value of $\log \frac{P_1}{P_2}$ is the same for the

two methods at the concentration c and $A \cong A'$ is a reasonable assumption in this case:

$$(15) \quad \beta' - \beta = \frac{\log R}{A}$$

By defining the value of R and of A , the deviation of β from the true value β' can be calculated.

Although the methods are identical for the measurement of A and A' , the value of β is different from that of β' . Also the measured value of $\log R$ affects the actual value obtained for A_1' . In figure 4 the variation of the A_1 value obtained by Hiskey's method with the value of R is graphed for some values of α_3 .

The methods are also identical for the analysis. However the calculation of the unknown concentration involves a measured value of $\log R$ and the values A_1' and β' in the modified case and the values A_1 and β in the unmodified case. The appropriate equations were written, the dependence of c_2 on c_2' solved for and the value of c_2 calculated for various values of R and α_2' . The values of $c_2' - c_2$ were converted to per cent of c_2' and are graphed in figure 5.

The values assigned for the above calculation were:

$$A_1' = 0.212 \text{ (True absorptivity)}$$

$$C_1 = 1.000 \text{ mg./25 ml. (Standard blank)}$$

$$\beta' = 1.000 \text{ (True length ratio)}$$

$$C_2' = \text{Concentration of unknown solution}$$

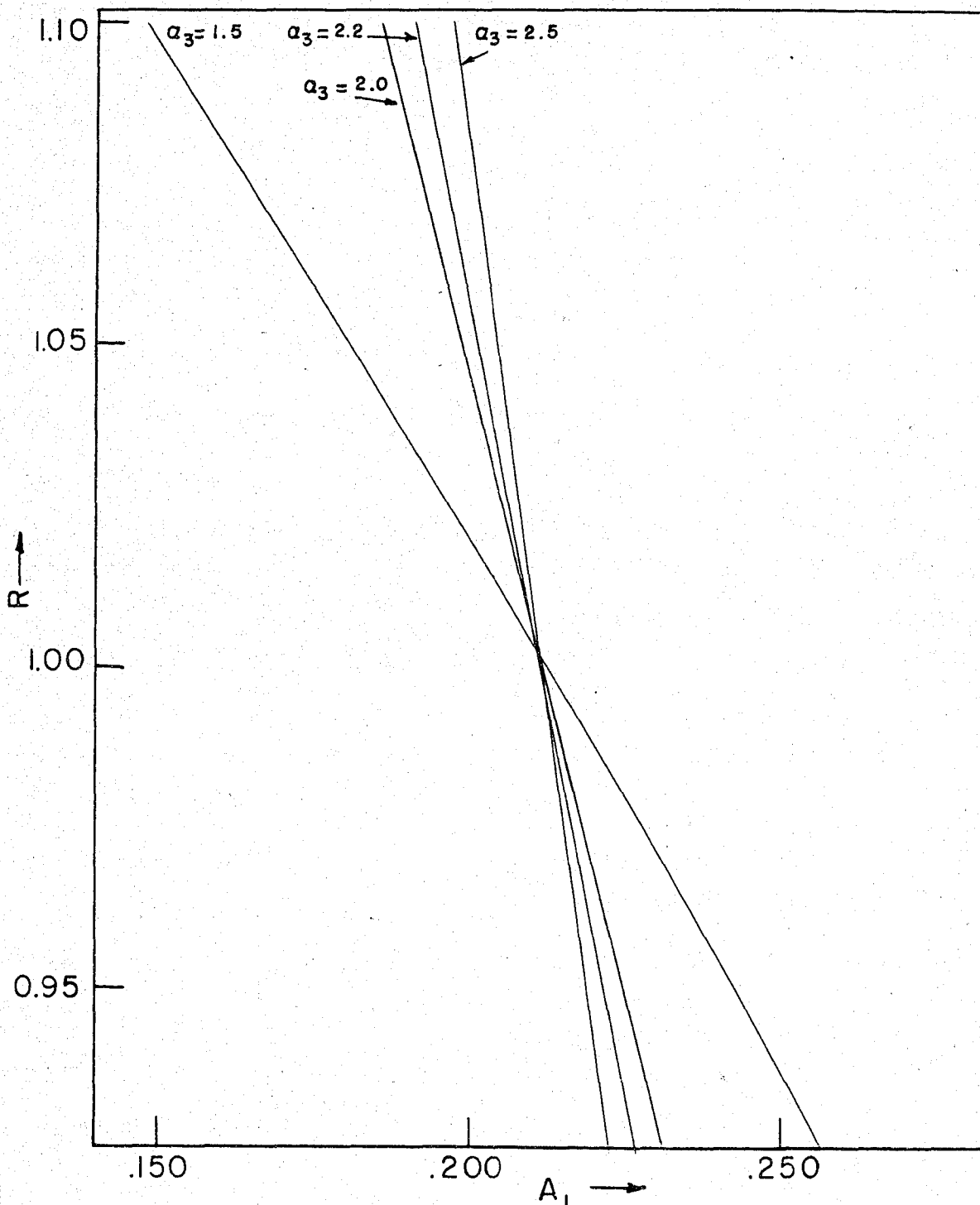


FIG. 4 CALCULATED VARIATION OF ABSORBANCE CONSTANT A_1 WITH THE CUVETTE TRANSPARENCY RATIO FOR SELECTED VALUES OF α_3 EQUATION (13)

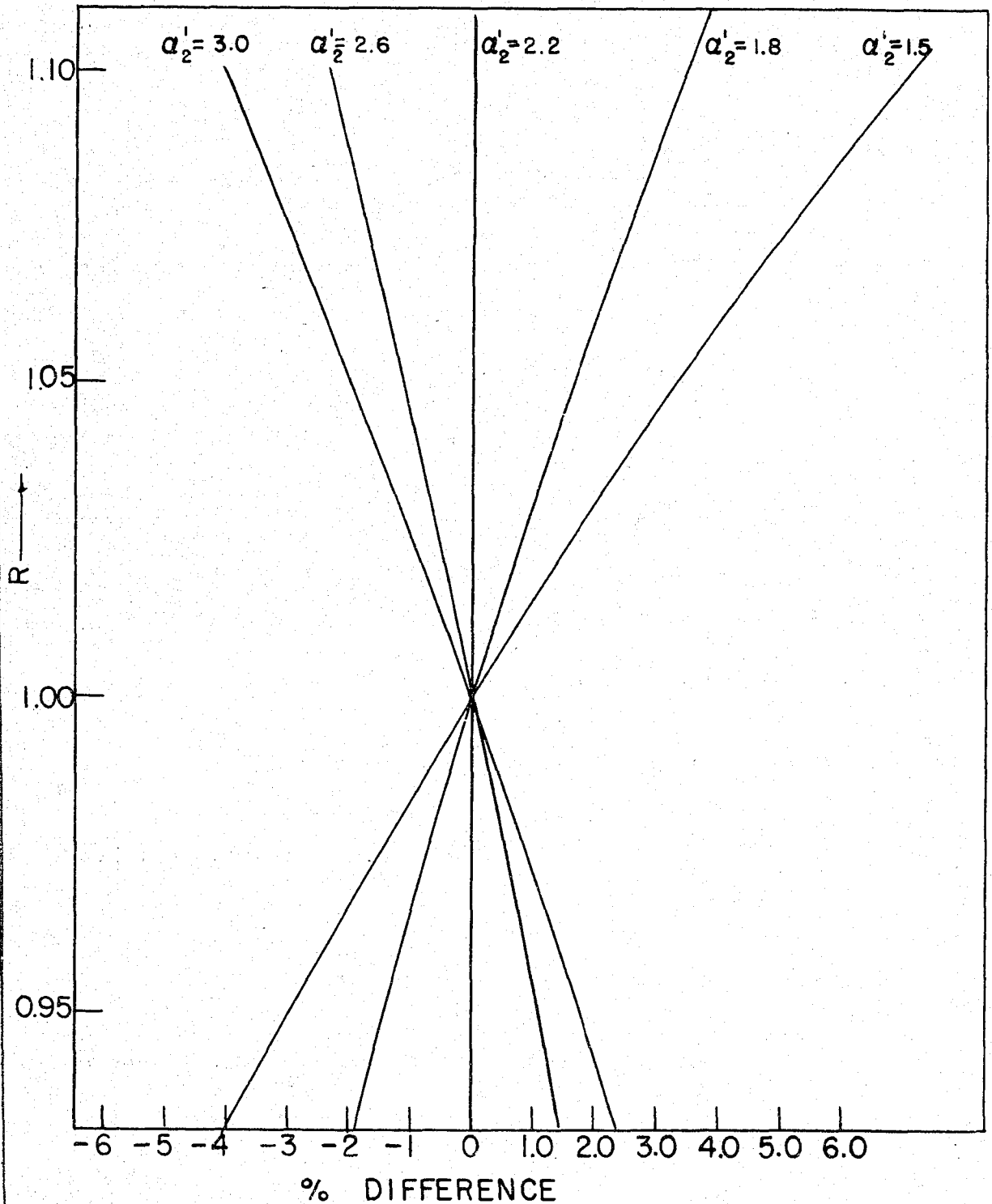


FIG.5 CALCULATED ERROR IN ANALYTICAL RESULTS WITH THE CUVETTE TRANSPARANCY RATIO FOR SELECTED VALUES OF α_2' EQUATION (17)

C_3 = Concentration of standard used to obtain A_1 and A_1'
 (assigned value of 2.2 for calculation of c_2)

$$\alpha_3 = \frac{C_3}{C_1}, \quad \alpha_2' = \frac{C_2'}{C_1}$$

A_1, β, C_2 = Values of absorptivity, length ratio and
 unknown concentration calculated with
 unmodified method.

These calculations indicate that the following conditions
 will give the best values for Hiskey's method:

- (1) Cuvettes should be as closely matched as possible for
 all operations.
- (2) The best value of β should be obtained at a high
 absorbancy.
- (3) The best value of A_1 should be obtained at a large
 value of α_3 .
- (4) The unknown concentration should be as close as
 possible to the concentration of the standard used
 to measure A_1 .

Conditions (1) and (2) are followed in existing procedures.
 It is interesting that (3) and (4) indicate a best analysis
 at large values of α_3 whereas Hiskey's consideration of the
 instrumental error predicted the most accurate analysis at
 values of α_3 close to one. It seems that the practical value
 will lie somewhere between one and $\frac{1.343}{A} + 1$.

Assumptions Used

Beer's law obeyed by peroxy-vanadium

The assumption was used that this system obeys Beer's law. This was based on previous investigations (93, 94). The system does obey Beer's law insofar as the usual absorbancy versus concentration plot will reveal the deviations. This was corroborated in a preliminary experiment. However, the difference noted in the value of K' (page 71) has been noted consistently during this work. The value of K' increases slightly with the concentration of vanadium. This deviation cannot be explained by the increasing slit width nor by the effect of the aluminum on the peroxy-vanadium complex. It has been noted by Wright and Mellon (93) and has been confirmed in preliminary experiments that larger amounts of hydrogen peroxide decrease the absorptivity of the peroxy-vanadium solutions. This may be the cause of the increasing value of K' , since increasing the vanadium concentration does decrease the vanadium to hydrogen peroxide ratio. This effect does not significantly affect the analysis results given here because the standards for the calculation of K' were of about the same concentration as the unknown. Due to the construction of the analysis equation, error in K' affects only the difference in concentration between the blank standard and the sample concentration. Due to this and also because the variation in K' is not large, this error is not

serious. If the accuracy warrants it, a working plot of K' versus concentration may be made. This plot would make it unnecessary to determine K' with each set of samples.

Transmittance of cuvette walls

The assumption that the per cent transmittance of a cuvette can be represented by $P_0 x$ does not affect the analytical method because the value of $\log R$ is considered to be a variable correction factor which must be determined at the time of the analysis and at the slit width of the analysis. The only reservation is this: This postulated relation should not be accepted as true without further testing. The only tests which depended on this relation in this work were the experiments to determine β' . The only acceptable negative evidence for these experiments would have been definitely curving lines. This would have occurred only if the relation was very definitely different than the one postulated.

Repositioning cuvettes

An experimental assumption which was made was that the cuvettes were repositioned exactly when the measurements were made for the calculation of $\log R$. This assumption seems to be borne out by the deviations which occurred in the values of K' within each set on page 71. The deviations are almost exactly the amount which would be expected from an error of 0.1% in the transmittance reading.

Advantages and Disadvantages

The analysis portion of the method is convenient and simple, however the preparative work which is necessary is a marked disadvantage. This definitely limits the use of the method to accurate analyses for vanadium when a more convenient method is not available and to control type analyses in which the preparation time is not so much a disadvantage. Some of the preparative work could be avoided if glass standards were available to take the place of the standard blank. This would also eliminate the necessity of keeping a standard vanadium solution on hand. It would also be convenient if cuvettes could be made so that the sample could be dissolved and treated in the cuvette.

The Effect of Aluminum

The values obtained for K' , which are given in table 12 show that aluminum does not interfere significantly.

Further Applications

Vanadium method

This analysis should be applicable to any mixture containing vanadium in which the other constituents do not absorb at 460 $m\mu$. Wright and Mellon's (93) work may be consulted for a listing of 23 ions which did not interfere in their method and would not be expected to interfere in this method.

High precision spectrophotometric analysis

The application of Reilley and Crawford's (88) theoretical treatment to the more precise analysis of components present in limited quantity should be of major importance to spectrophotometric analysis. It is hoped that the discussion of cuvette characteristics which is given here may be of help in this development.

Suggestions for Further Study

This investigation has revealed many avenues for interesting research. Those which are adjudged to be of the most practical importance are given below.

The experimental investigation of Reilley and Crawford's theoretical conclusions is not a direct outgrowth of this investigation, but should be an interesting and rewarding task.

The manufacture and testing of glass standards and solution cuvettes which is mentioned above should be feasible and would further spectrophotometric analysis.

The use of colored systems to study the designing of cuvettes might lead to better and less expensive cuvettes.

If the variation of K' with concentration was studied further in order to prove that the variation was or was not due to a deviation from Beer's law, the high precision method might prove a very sensitive test for this deviation.

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