

THE INVESTIGATION OF  
OCTAAMMINE- $\mu$ -NITRO- $\mu$ -AMIDODICOBALT(III) NITRATE  
AS AN ANALYTICAL REAGENT FOR SULFATE

by

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THE INVESTIGATION OF  
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INTRODUCTION

Sulfate analysis is one of the most common and widespread analyses in all analytical chemistry, and in one way or another has been carried out for many years. Increased use of organic and inorganic compounds containing sulfonyl or sulfate groups or radicals, as well as greater demands on the purity of substances in which sulfates exist as contaminants, has made necessary new and better methods for sulfate analysis. Modifications of old methods have also been made to meet the new requirements.

The oldest and most common method, found in any standard quantitative analysis text (7, 11, 54), uses the insolubility of barium sulfate as the basis for the gravimetric determination of sulfate. Used per se, the method is long and tedious, as almost any student of quantitative analysis can attest. Frequently the method lacks selectivity in that many ions are coprecipitated with the sulfate, and the analysis is in error. Nevertheless, it is something of a standard for sulfate analysis for macro samples, and the majority of all references on sulfate analysis in the literature makes use of the insolubility

of the barium sulfate.

Lead sulfate is also insoluble, and methods based on its insolubility have been used for sulfate analysis (38, 40), but since the sulfate is more soluble than the corresponding barium salt, and suffers from coprecipitation, too, the methods have never enjoyed the popularity of the barium sulfate precipitation methods for gravimetric analysis.

Benzidine (15) has been used to precipitate sulfate in several cases; following combustion in oxygen (12), Parr bomb (8) and Carius digestion (1). It has found little general use, however, because it is sensitive to interferences and is fairly soluble in water (56). The precipitated sulfate may be dissolved and the amount of benzidine present determined by volumetric or colorimetric methods. These techniques are much easier than the gravimetric, but one can not by-pass the limitations imposed by the precipitation step.

Hexaamminecobalt(III) bromide has been used by Mahr and Krauss (35) to precipitate the sulfate ion, but so far detailed data on the method are not available (3). More recently, a new cobalt complex reagent, octaammine- $\mu$ -nitro- $\mu$ -amidodicobalt(III) nitrate has been investigated (3). While the solubility of the sulfate precipitate is higher than for barium sulfate, it is not sensitive to nitrate or several other ions which cause errors

in the barium sulfate method.

According to Wilson (56), the best volumetric method is the titration of an 80% alcohol-water solution of the sulfate with barium perchlorate, using Thorin as the indicator. This method was proposed by Fritz and co-workers (13, 14). Sulfate analysis may also be carried out volumetrically by titrating with barium chloride, using either tetrahydroquinone (19, 20, 24) or dipotassium rhodizonate (18, 46) as the indicator. It is necessary to employ various expedients for both of the latter indicators to improve the endpoints (56).

Several methods have been proposed to carry out the analysis of sulfate indirectly. Belcher, et al., have suggested dissolving the barium sulfate precipitate in excess EDTA and back titrating with a magnesium solution (4). One may add barium chloride in excess to the sulfate solution and titrate the excess with EDTA (43, 55) or chromate (10, 53). A precipitated sample of the sulfate may be treated with an ion exchange resin in a batch process, in which the barium equilibrates with the resin, and the filtrate is titrated with a base (44). These methods are generally less tedious than the gravimetric determination, but are subject to the same coprecipitation errors.

In addition to the utilization of indicators, many instrumental methods have been developed for the detection

of the endpoint in titrimetric methods. Trace amounts of sulfate may be determined in this manner by titrating the sulfate with barium chloride and detecting the endpoint turbidimetrically (17, 22, 48) or nephelometrically (9, 16). The endpoint may also be detected conductometrically when the sulfate is titrated with barium chloride (39, 42). Recently, Jamieson has developed a high frequency conductometric method using octaammine- $\mu$ -nitro- $\mu$ -amidodicobalt(III) nitrate (26).

While the sulfate ion is not reducible at a dropping mercury cathode, and cannot be determined directly by polarographic techniques, it may be determined by measuring the decrease in the diffusion current of the barium ion when barium sulfate is precipitated (20, 21, 31). However, a better method for sulfate using polarographic techniques is to titrate the sulfate with lead nitrate, detecting the endpoint amperometrically (30, 36). Coprecipitation and the high solubility of the lead sulfate in the presence of strong salt solutions cause serious errors.

Sulfate analysis may be carried out colorimetrically or spectrophotometrically in several ways. For low level sulfate (15-200ppm), an insoluble thorium borate-dye compound releases the dye stoichiometrically when sulfate ions come into contact with it (33). Good agreement with gravimetric methods have been reported. In

another method, an excess of 4-ammino-4'-chlorodiphenyl (ACD) is added to the sulfate solution, and, after the precipitate is filtered, the excess ACD is determined colorimetrically (5, 28). It has been used successfully for sulfate in the presence of nitrates, but is unsuitable when a high concentration of neutral salts is present. The method may be carried out on submicro quantities of sulfate. Phosphate must be absent.

Iwasaki (25) has used the color developed by the  $\text{CrO}_4^=$  which is released when a  $\text{BaCrO}_4$  precipitate comes into intimate contact with a solution containing sulfate.

There have been numerous colorimetric methods based on the development of colored solutions when certain reagents are reacted with benzidine sulfate, after a benzidine sulfate precipitation. Some of the most important reagents that have been used are N-(1-naphthyl)ethlene-diammine (29), sodium B-naptho-quinone-4-sulfonate, (34) p-dimethylaminobenzaldehyde (45), and molybdotungstophosphoric acid (37). These methods are very sensitive, but since they are based on the benzidine sulfate precipitation, they are subject to the limitations of the gravimetric procedure.

A procedure has been used (27) wherein the sulfate is reduced to the sulfide and determined colorimetrically as methylene blue. The method is very sensitive, but the reduction is difficult. It is not widely used.

As stated previously, a new gravimetric reagent has been investigated by Belcher and Gibbons (3). This work grew out of the investigation of several Vortmann salts (50, 51, 52) which reportedly formed slightly soluble sulfates. These salts were the same substances on which Werner had conducted his classic molecular structure studies.

Of the Vortmann salts investigated, only one was sufficiently stable and sensitive, and whose sulfate salt solubility was comparable to that of barium sulfate.

Very good analytical results were obtained using this new reagent, octaammine- $\mu$ -nitro- $\mu$ -amidodicobalt(III) nitrate, and, furthermore, the presence of many ions that commonly interfere with the analysis of sulfate by other methods were not troublesome. The lack of interference is particularly valuable in the case of nitrates which usually must be removed prior to the precipitation of barium or benzidine sulfates but cause no error when the new reagent is used.

Upon reading the work of Belcher and Gibbons, one is almost immediately struck with the idea that the analysis could be carried out spectrophotometrically. Cobalt complex salts are usually highly colored since the cobalt atom has an incomplete d-orbital and the energy of electronic transition is usually low enough to absorb visible

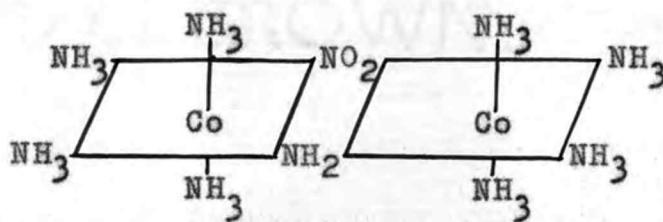
light. The prepared salts of the complex were reported to be colored. (3, 51) If the absorbance of the cobalt complex could be measured and the subsequent depletion or reduction of the absorbance could be attributed to the presence of sulfate in a sample, then the reduction could be used to determine, quantitatively, the amount of sulfate in the sample. An investigation was launched to determine the feasibility of this procedure.

PREVIOUS WORK WITH THE  
COBALT COMPLEX REAGENT

Belcher and Gibbons (3) selected five Vortmann salts which formed insoluble sulfates, and conducted an investigation into their gravimetric analytical properties. The salts chosen were (I) octaammine- $\mu$ -dihydroxodicobalt(III) chloride, (II) chloroaquoctaammine- $\mu$ -amidodicobalt(III) chloride, (III) octaammine- $\mu$ -peroxo- $\mu$ -amidocobalt(IV)cobalt(III) nitrate, (IV) octaammine- $\mu$ -nitro- $\mu$ -amidodicobalt(III) nitrate, and (V) octaammine- $\mu$ -hydroxy- $\mu$ -amidodicobalt(III) nitrate.

The result of their investigation revealed that only (IV) possessed the necessary properties to warrant its recommendation as an analytical reagent, although there was little difference in the sensitivity of the reagents to sulfate in neutral solutions. The other four Vortmann salts were generally unstable and decomposed during the standing time of the precipitated sulfate. Accordingly, octaammine- $\mu$ -nitro- $\mu$ -amidodicobalt(III) nitrate was subjected to further examination.

Cobalt(III) normally forms octahedral complex species, and the most likely formula of (IV), using conventional symbols, is shown below:



Belcher and Gibbons reported that the solubility of the sulfate of (IV) placed it at a disadvantage when compared to the solubility of barium sulfate, being 22.4 mg/l at 25° C. compared to 2.3 mg/l at 18° C. for barium sulfate; but that it is less soluble than benzidine sulfate (98 mg/l at 25° C.). The greater solubility of the sulfate of (IV) makes it necessary to work in small controlled volumes for accuracy equivalent to the barium sulfate method.

Perhaps the chief advantage of the new method is the lack of the coprecipitation errors that often accompany other methods. One common interference, already mentioned, is nitrate ion (3, 56). It has no effect upon the analysis when (IV) is used, which is, in fact, a nitrate salt. Other ions that were investigated for possible interfering effects are shown in Table 1. In the case of  $\text{PO}_4^{3-}$ , the pH was maintained slightly less than 5, so that the phosphate was actually in the monobasic and dibasic forms. EDTA was added to the aluminum and iron solutions to prevent their hydrolysis. When these steps were taken, no interferences were observed.

The authors found a standing time of four hours was suitable for crystal development under certain

conditions (final volume 50 ml of a 25% acetone-water precipitation solution) when the sample size was 20.17 mg. For smaller sample sizes, smaller volumes (20 ml for 2.02 mg of sulfate) were used, while for larger samples the standing time could be reduced to one half hour. The data obtained by Belcher and Gibbons in the investigation of the effect of standing time are shown in Table 2.

The recommended procedure for the use of the new reagent calls for the precipitation to be carried out in a 25% (v/v) acetone-water solution. The precipitate may be oven dried to anhydrous sulfate or washed with acetone and air dried. When the resulting precipitate is air dried, it contains two water molecules of crystallization. Although the investigation of the effect of the pH on the precipitation procedure was not conducted, it was found that an analysis carried out in a neutral or

Table 1  
Interferences

Ion	Recoveries (mg.)	Ion	Recoveries (mg.)
Na <sup>+</sup>	20.16, 20.16	F <sup>-</sup>	20.21, 20.20
K <sup>+</sup>	20.15, 20.17	NO <sub>3</sub> <sup>-</sup>	20.16, 20.16
Ca <sup>++</sup>	20.23, 20.20	O <sub>2</sub> <sup>--</sup>	20.16, 20.15
Al <sup>+++</sup>	20.19, 20.20	H <sup>+</sup>	20.18, 20.14
Fe <sup>+++</sup>	20.22, 20.21	H <sup>+</sup> , PO <sub>4</sub> <sup>---</sup>	20.16, 20.19
Cl <sup>-</sup>	20.20, 20.19		

In all cases the amount of sulfate added was 20.17 mg.

Table 2

## The Effect of Standing Time on Recoveries

Time (hr.)	Final Vol. (ml.)	Recoveries	Sulfate Added (mg.)
0.25	100	18.14, 17.98	20.17
2.0	100	18.42, 18.68	20.17
6.0	100	18.92, 18.08	20.17
24.0	100	19.97, 20.01	20.17
4.0	50	19.06, 19.12	20.17
24.0*	50	20.08, 20.04	20.17
6.0*	100	20.16, 20.12	20.17
24.0*	100	20.20, 20.14	20.17
2.0*	50	20.12, 20.06	20.17
4.0*	50	20.21, 20.14	20.17

\*Precipitated in a 25% (v/v) Acetone-water solution.

slightly acidic solutions resulted in no pH error. The recommended procedure called for an adjustment of the solution to neutrality unless phosphate was present, in which case some hydrochloric acid was added.

The new reagent was strongly recommended by Belcher and Gibbons as a means of carrying out an analysis of sulfur in organic compounds. The cobalt complex reagent is particularly valuable because, after an oxygen bomb combustion or peroxide fusion, the sulfur exists as the sulfate and the nitrogen as nitrate. The peroxide or nitrate need not be removed prior to sulfate analysis when the cobalt complex reagent is used.

Jamieson (26) compared four different titrants in

a titration of sulfate, using a high-frequency conductometric method. The four reagents were barium acetate, lead nitrate, hexaamminecobalt(III) bromide and octaammine- $\mu$ -nitro- $\mu$ -amidodicobalt(III) nitrate. The latter proved to be at least equal in accuracy to the other three, especially when nitrate was present.

ABSORPTION SPECTRA OF OCTAAMMINE- $\mu$ -  
NITRO- $\mu$ -AMIDODICOBALT(III) NITRATE

The cobalt complex reagent, octaammine- $\mu$ -nitro- $\mu$ -amidodicobalt(III) nitrate, is beautiful orange in color. When it is dissolved in water the color deepens, but otherwise remains unchanged. Since no investigation of the absorption spectrum had previously been published, such an investigation was clearly in order as a first step in the study of the reagent. Consequently, the absorbance was measured over the range of wavelengths from 200 m $\mu$  to 800 m $\mu$ .

The Beckman Model DK-1 Automatic Recording Spectrophotometer was employed for the absorbance measurements from 350 m $\mu$  to 800 m $\mu$ . Subsequent absorbance measurements from 200 m $\mu$  to 350 m $\mu$ , using more dilute solutions, were made using the Beckman Model DU Spectrophotometer, because it was convenient to the laboratory.

Instruments

Beckman Model DK-1 Spectrophotometer

Instrument settings

Radiation source	Tungsten lamp
Photomultiplier	IX
Scan time	3 minutes
Time constant	0.1 second
Sensitivity	50

Beckman Model DU Spectrophotometer

Reagents

Cobalt complex stock solution

The cobalt complex reagent, octaammine- $\mu$ -nitro- $\mu$ -amidodicobalt(III) nitrate, is not available commercially. It was prepared in this laboratory according to the methods of Werner and co-workers (50, 51, 52, 53), starting from cobaltous chloride. A stock solution was prepared by dissolving 8.393 grams of the recrystallized reagent into distilled water, followed by dilution to 500 ml in a volumetric flask. A few drops of nitric acid were added to insure stability, since the solutions were known to be somewhat unstable in basic solutions.

Procedure

A 5 ml aliquot of the 0.0279 M cobalt complex stock solution, described above, was transferred to a 50 ml volumetric flask and diluted to the mark with distilled water. After thorough mixing, a portion of the sample was transferred to a silica cell and placed in the Beckman DK-1 Spectrophotometer. The absorbance was measured from 800 m $\mu$  to 350 m $\mu$ , using water as the reference solution, or blank.

For the absorbance measurements below 340 m $\mu$ , the solutions used were prepared by diluting a sample of the

stock solution described above and by dissolving a weighed, dry sample of the reagent in water. Nitric acid was not added to the latter solution, as it had been to the stock solution.

### Discussion

The cobalt complex nitrate reagent has one single, simple absorbance peak in the visible portion of the spectrum, as shown in Figure 1. This peak, which has a relatively broad maximum at  $476 \text{ m}\mu$ , is responsible for the characteristic orange color of the solution. Figure 1 was obtained by transforming the non-linear plot from the spectrophotometer recorder and re-plotting on linear paper. The data used in the transformation are given in Table 3.

The absorbance below  $400 \text{ m}\mu$  appears to be much more intense, shown by the rapidly rising absorption spectrum in Figure 1. Two solutions of the cobalt complex nitrate,  $4.0 \times 10^{-5} \text{ M}$ . and  $1.0 \times 10^{-5} \text{ M}$ ., were prepared and the absorbance measurements were made from  $400 \text{ m}\mu$  to  $200 \text{ m}\mu$ . The absorption spectra for these two solutions are shown by curves 1 and 2 of Figure 2. The absorbance is small above  $250 \text{ m}\mu$ , and no absorbance peak was found.

Curves 3 and 4 of Figure 2 are for  $\text{NH}_4\text{OH}$  and  $\text{HNO}_3$ , respectively. Ammonium hydroxide has an appreciable

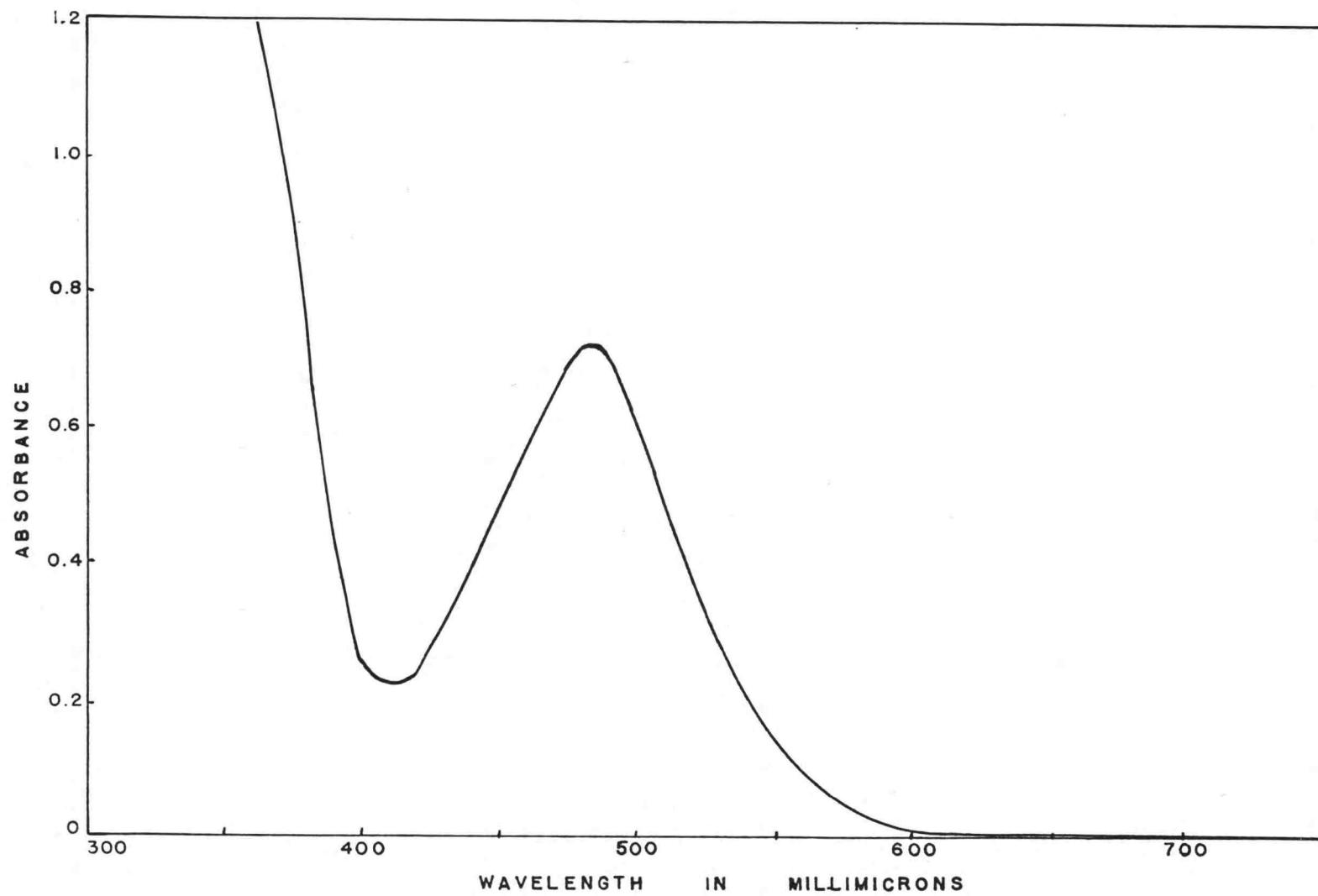


FIGURE I. ABSORPTION SPECTRA OF THE COBALT COMPLEX

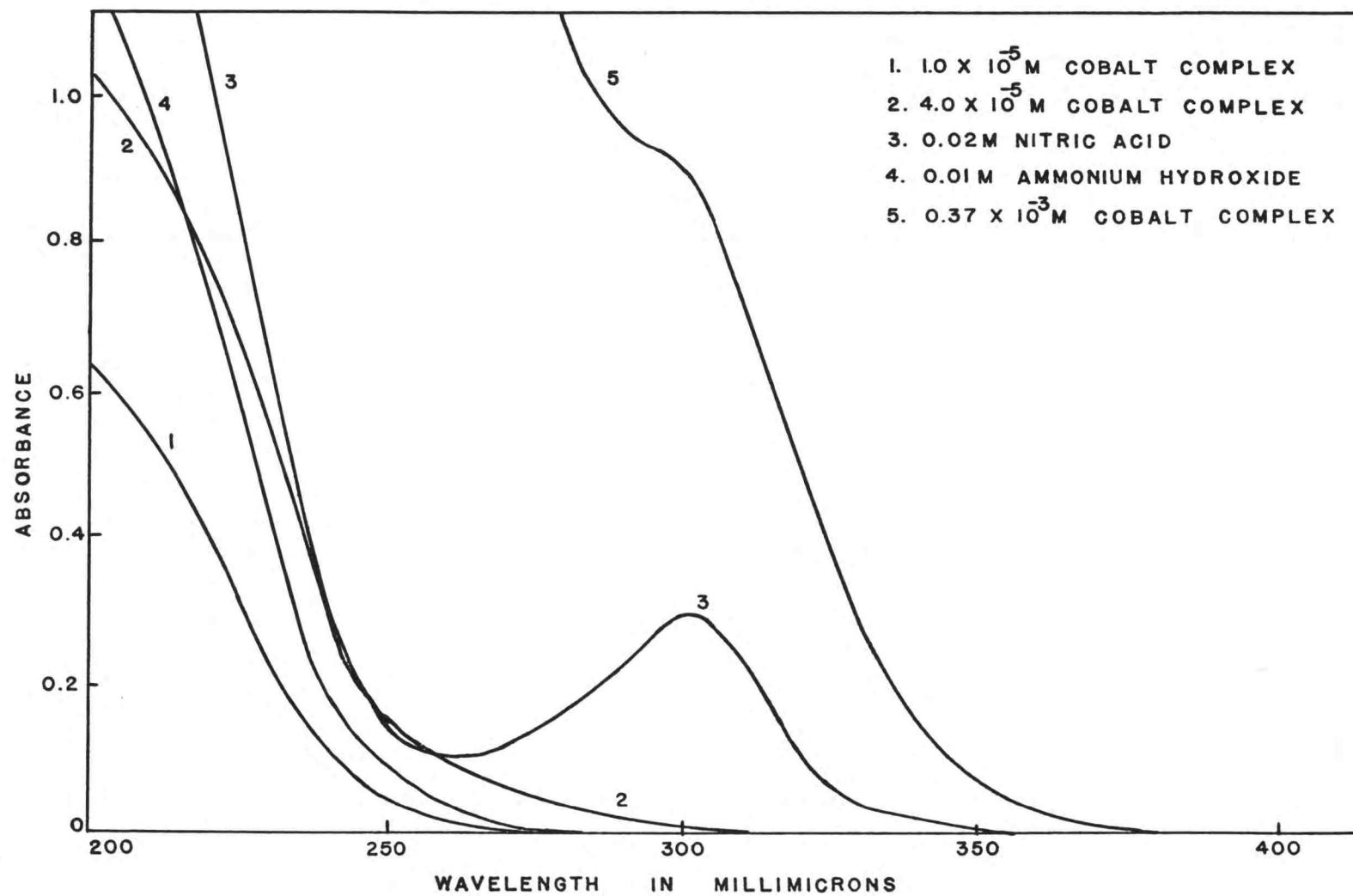


FIGURE 2. ABSORPTION SPECTRA OF THE COBALT COMPLEX

Table 3

## Absorption Spectrum of the Cobalt Complex

Wavelength (m $\mu$ )	Absorbance	Wavelength (m $\mu$ )	Absorbance
800	.000	475	.705
760	.000	470	.660
720	.002	460	.615
680	.002	450	.539
640	.005	440	.432
600	.015	420	.268
580	.046	410	.228
560	.100	400	.246
540	.226	390	.400
520	.406	380	.620
510	.519	370	.980
500	.580	360	1.25
490	.700	350	1.50
480	.710		

absorbance only below 250 m $\mu$ , but nitric acid absorbs at 302 m $\mu$ , as well as below 250 m $\mu$ . Curves 1 and 2 evidently show the absorbance due to the ammino and nitro groups in the cobalt complex, and also the absorbance due to the NO<sub>3</sub><sup>-</sup> ions. Curve 5 is an absorption spectrum for a solution of the cobalt complex nitrate which had been prepared from a dry sample of the reagent. A hump appears on the absorption curve at 302 m $\mu$ , probably due to the NO<sub>3</sub><sup>-</sup> ions and perhaps to the nitro group, but the overwhelming absorbance of the amido and nitro groups in the complex, and the NO<sub>3</sub><sup>-</sup> ions in solution, reduces its significance.

The use of the absorbance at any wavelength below

400 m $\mu$  is not attractive for several reasons. These are: (1) the peak at 302 m $\mu$  is useless, or nearly so, because the NO<sub>3</sub><sup>-</sup> ions will remain in solution after the precipitation of the sulfate, (2) other wavelengths used for analysis will be sensitive to any variation of wavelength being used, and (3) substances containing amino or nitro groups will interfere with the sulfate analysis. Many other substances which have an absorbance at these lower wavelengths will also interfere. It is possible to shift to other salts of the reagent, thus eliminating NO<sub>3</sub><sup>-</sup> ions from the solution, but it is still more appealing to use the visible absorbance peak. Consequently, the absorbance peak at 476 m $\mu$  was used for all subsequent investigations.

## STABILITY OF THE REAGENT AT VARIOUS pH VALUES

Belcher and Gibbons (3) found that octaammine- $\mu$ -nitro- $\mu$ -amidodicobalt(III) nitrate, the cobalt complex reagent, was stable and that the precipitated sulfate had not changed after one week. The same authors also found that they could oven-dry the sulfate at 100° C. with no apparent change in the precipitate.

In an effort to prepare a higher purity stock solution, a re-crystallized sample of the complex was dried overnight in this laboratory in an oven at 110°-120° C. and subsequently dissolved in distilled water. After standing a few days, the solution turned dark and yielded a black-brown precipitate. The pH of the solution was found to be 8.2, indicating that perhaps a basic decomposition had occurred. Previous preliminary investigations had shown the reagent to be unstable in mildly basic solutions. Apparently either the anhydrous reagent or its decomposition products hydrolyzed upon dissolution in water, and raised the pH. Further decomposition then took place.

To determine the extent of the limitation imposed upon the reagent by the basic instability, it was decided that a scan over the visible spectrum should be made at various acid concentrations. Emphasis also was placed upon determining whether there is a shift in the

wavelength of the peak of maximum absorbance with changes in the pH of the solution because of the importance of having an absorbance peak that is independent of pH over a considerable wide range.

#### Instruments

Beckman Model DK-1 Spectrophotometer

Beckman Zeromatic pH meter

#### Reagents

##### Cobalt complex stock solution

An 0.0279 M stock solution was prepared by dissolving 8.393 grams of the reagent in water and diluting to 500 ml.

##### Sodium hydroxide solution

An 0.1 N sodium hydroxide solution was made by dissolving 4 grams of carbonate-free sodium hydroxide in boiled distilled water. This solution was diluted to approximately one liter.

##### Nitric acid solution

An 0.1 normal nitric acid solution was prepared by diluting reagent grade nitric acid.

#### Procedure

A solution was prepared by transferring 10 ml of the cobalt complex stock solution into a 50 ml volumetric

flask. The solution was then quickly diluted to the mark and thoroughly mixed by shaking. A portion of the solution was transferred to a silica cell and the absorbance scan was made on the Beckman Model DK-1 Spectrophotometer, using the same instrument settings listed previously.

Following completion of the absorbance scan, another solution was made up in exactly the same fashion except that a small portion of sodium hydroxide was added to adjust the pH to the desired value. The absorption spectrum was then measured as before. This procedure was repeated for solutions containing either sodium hydroxide or nitric acid until absorption scans were obtained for solutions with pH ranging from 10.8 to 1.6.

After each absorption scan, the pH of the solutions were measured using a Beckman Zeromatic pH meter. Buffer solutions, prepared according to Bates (2) were used to calibrate the pH meter.

#### Discussion

A plot of absorbance versus wavelength has been prepared by the same method described in the previous section. This plot is shown in Fig. 3. Only three absorption spectra are shown, since there was essentially no difference between the absorption spectra of all the solutions of intermediate pH; the spectrum of each

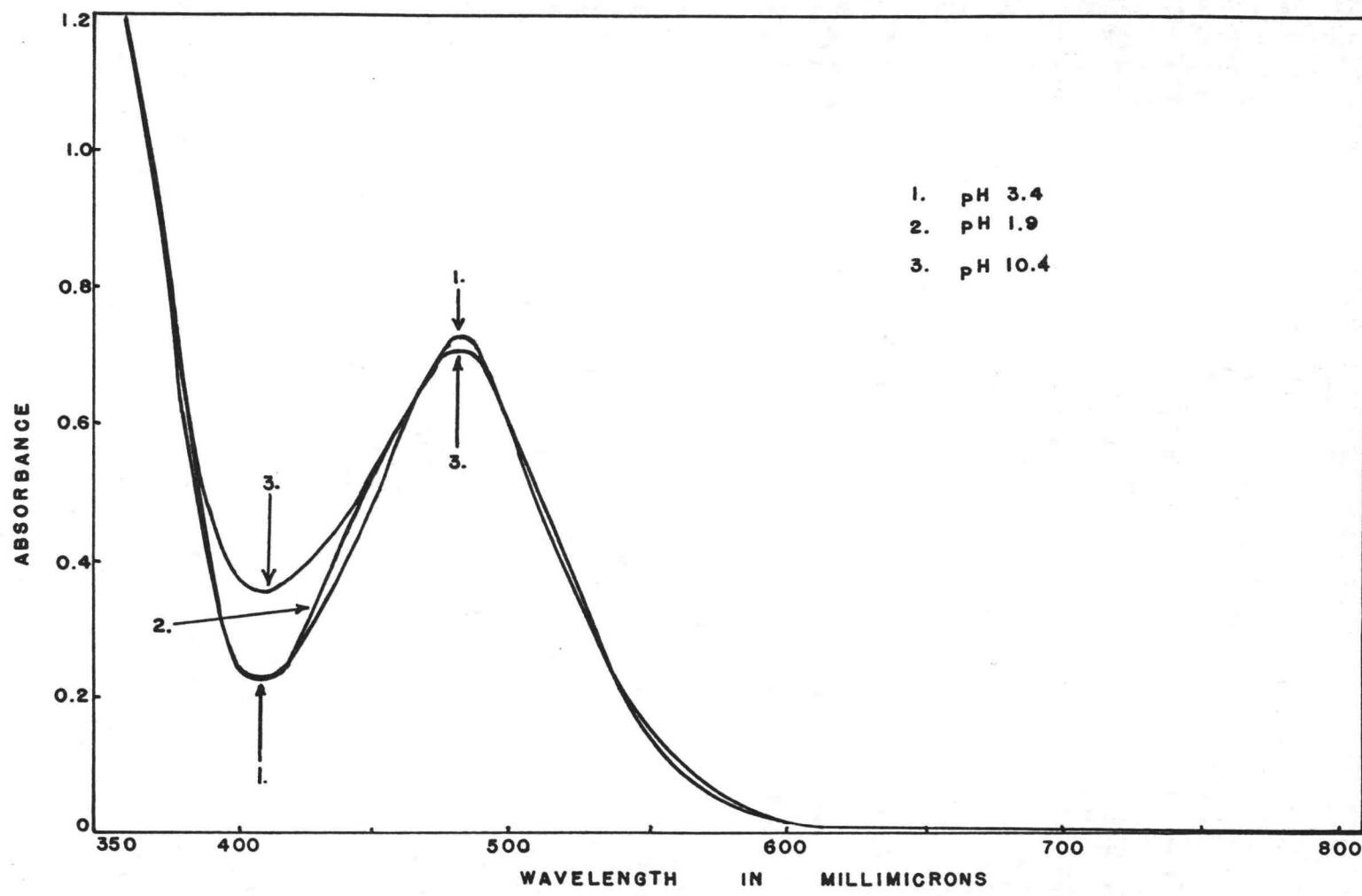


FIGURE 3. ABSORPTION SPECTRA OF THE COBALT COMPLEX AT VARIOUS pH VALUES

Table 4

## Absorption Spectra at Various pH Values

Wavelength m $\mu$	Absorbance				
	pH 1.6	pH 1.9	pH 3.4	pH 7.7	pH 10.8
800	.000	.000	.000	.000	.000
760	.000	.000	.000	.000	.000
720	0.002	.001	.003	.000	.001
680	0.002	.002	.004	.000	.003
640	.005	.008	.007	.003	.011
600	.015	.015	.016	.012	.032
580	.046	.046	.049	.036	.065
560	.100	.106	.115	.095	.133
540	.226	.227	.238	.213	.248
520	.406	.397	.427	.388	.416
510	.519	.490	.513	.474	.510
500	.580	.588	.620	.538	.618
490	.700	.678	.682	.670	.670
480	.710	.710	.705	.699	.704
475	.705	.712	.690	.699	.705
470	.660	.710	.672	.699	.690
460	.615	.629	.604	.640	.652
450	.539	.550	.512	.568	.567
440	.432	.440	.412	.430	.500
420	.268	.286	.259	.280	.373
410	.228	.245	.227	.233	.347
400	.246	.254	.243	.243	.385
390	.400	.335	.393	.350	.466
380	.620	.545	.593	.542	.708
370	.980	.822	1.060	.843	.957
360	1.250	1.200	1.280	1.235	1.390
350	1.500	--	1.520	1.420	--

solution with pH between 1.9 and 7.7 closely resembled that shown for pH 3.4. The data for Fig. 3 are given in Table 4.

The data obtained indicate that there is no evident decomposition of the reagent below pH 7, and that the height and wavelength of the peak is not affected by changing the pH, provided decomposition does not occur.

In the course of the investigation, periodic experiments, not shown here, were made to determine if the nature of the absorbance of the reagent had changed. As far as could be determined, one solution of the reagent remained unaltered at pH 3.5 for an interval of more than two years.

### THE ABSORBANCE OF THE REAGENT AT VARYING CONCENTRATIONS

Further absorbance measurements of the cobalt complex reagent were required to determine whether the relationship given by the Beer-Lambert Law was valid. It is necessary to have a substance whose absorbance is a linear function of the concentration not only for extrapolation purposes, but also in order that the subsequent transformation of absorbance, plotted against the amount of sulfate that has been added, is a linear function. In addition, when a linear plot is obtained there is additional assurance that the absorbing species is stable when the concentration is varied, and not subject to change throughout the concentration levels investigated.

#### Procedure

A series of solutions were prepared by taking samples of varying volumes from the cobalt complex stock solution. These aliquots were transferred to 50 ml volumetric flasks and diluted to the mark with distilled water. The absorbance measurements of the prepared solutions were made with a Beckman Model B spectrophotometer.

#### Discussion

The results of the absorbance measurements are

shown in Figure 4. No detectable deviation from the Beer-Lambert Law is evident. The straight line gives a value of 240 for the molar absorbancy index.

More than one cobalt complex solution were prepared in the course of the investigation. To test the solutions for purity, the new solutions were subjected to the same examination described above. The data from these examinations are given in Table 5.

Table 5

## Beer's Law Plot for the Cobalt Complex Stock Solution

Solution No. 1	Concentration (moles/l.)	Absorbance
	$11.7 \times 10^{-3}$	2.36
	$8.35 \times 10^{-3}$	1.69
	$5.75 \times 10^{-3}$	1.19
	$2.87 \times 10^{-3}$	0.579
	$1.33 \times 10^{-3}$	0.545
	$2.71 \times 10^{-3}$	0.276
	$0.23 \times 10^{-3}$	0.062
Solution No. 2	Concentration (moles/l.)	Absorbance
	$7.25 \times 10^{-3}$	1.74
	$4.34 \times 10^{-3}$	1.04
	$3.62 \times 10^{-3}$	0.867
	$2.92 \times 10^{-3}$	0.699
	$1.48 \times 10^{-3}$	0.354
	$0.76 \times 10^{-3}$	0.182
Solution No. 3	Concentration (moles/l.)	Absorbance
	$4.16 \times 10^{-3}$	1.00
	$2.50 \times 10^{-3}$	0.600
	$1.66 \times 10^{-3}$	0.401
	$0.83 \times 10^{-3}$	0.199

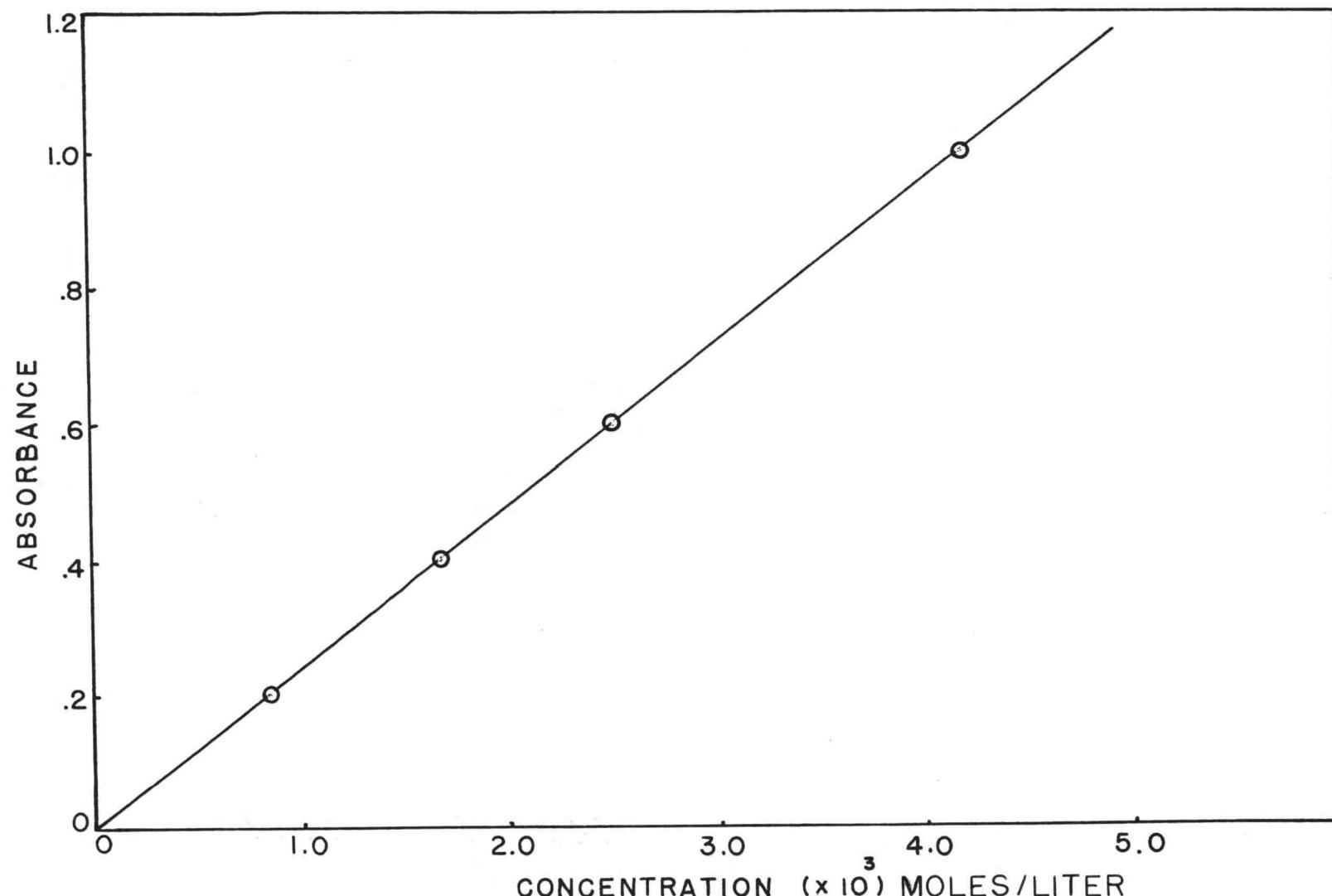


FIGURE 4. BEER'S LAW PLOT OF THE COBALT COMPLEX

The slopes obtained from plotting the data in Table 5 give three values for the molar absorbancy index. Since the reagents were impure, containing mostly absorbed nitric acid and water vapor, the calculated molar concentrations are in error and will cause the slopes to vary. The largest value for the molar absorbancy index will normally be more nearly correct because, as the purity increases the calculated concentration will decrease, causing the slope of the plots to increase. Therefore, the measurement of molar absorbancy index is quite analogous to the use of the highest melting point of a substance to check its purity. The highest value obtained for the molar absorbancy index so far has been 254. The molar absorbance indices for the solutions in Table 5 are 202, 240 and 240.

Impurities have no deleterious effect upon the performance of the reagent unless the impurities are also interferences, because, as the later procedures will show, one always adds an excess of the reagent to the precipitating solutions.

The procedures for the different stock solutions were identical except that for the first solution the Beckman Model B Spectrophotometer was used, while the Beckman Model DU Spectrophotometer was used for the later ones.

### PRECIPITATION PROCEDURE FOR THE SPECTROPHOTOMETRIC ANALYSIS

The following work was undertaken to determine the amount of soluble sulfate present in a solution as a function of the absorbance of the reagent and, consequently, to obtain a calibration plot for the sulfate analysis.

At this point only the colorimetric character of the reagent had been investigated. Since the sulfate is precipitated by the reagent, the removal of the sulfate should lead to a decrease in the absorbance of the solution. If a stock solution is used to obtain a standard curve, and the same stock solution used for a subsequent analysis, then one may determine the amount of sulfate present in a sample by direct transformation. In this case, the absorbance of the solution from which the insoluble sulfate has been precipitated is plotted against the quantity of sulfate known to be present in the sample.

In order to be successful the amount of sulfate must be the only variable in this procedure and it must be controllable. Consequently, the effect of variables such as temperature, standing time, pH of the solution, etc. must be made negligible. Belcher and Gibbons (4) were able to obtain accurate quantitative results by the

gravimetric precipitation of the sulfate under the following conditions: the temperature variation was slight, the precipitation solution was neutral or slightly acidic, the standing time (time required to reach virtual equilibrium) was four hours, and the precipitation was carried out in a controlled volume of solution. By adhering to these conditions one should be able to obtain a procedure suitable for spectrophotometric analysis, and then to proceed to determine the effect of each of the individual variables listed, as well as other variables that influence the results of the procedure adopted.

It initially seemed probable that a fast method, based on centrifuging the precipitate, followed by decantation of the supernatant liquid, could be developed. The precipitate consists of small particles which are definitely crystalline and a centrifuging procedure should be feasible. However, some small crystals continued to float on the top of the liquid after centrifuging and somewhat painstaking care was required to prevent their transfer to the absorbance cell. With the advantage of speed gone, a more reliable procedure, a filtration process, was adopted for the subsequent investigation.

In the quantitative investigation of the cobalt complex reagent by Belcher and Gibbons, the recommended procedure called for a 25% (by volume) acetone-water

solution for the precipitation step. Acetone was added to reduce the solubility of the sulfate. In an attempt to follow the procedure, several experiments were conducted in which acetone solutions were used, but acetone bubbles formed on the walls of the absorbance cell causing erratic absorbance readings. Acetone solutions were not used subsequently, nor was any other high vapor pressure liquid. A limited search for other water miscible solvents that would reduce the solubility was conducted. The most promising solvent found was 1, 8-dioxane, but this, too, proved to be unsatisfactory. When the dioxane was mixed with the cobalt complex reagent, a dark brown precipitate formed. Consequently, further efforts in this direction was discontinued since the effect of the solubility of the sulfate for this type of analysis causes no significant error, merely serving to lower the limits of minimum sample size.

#### Reagents

##### Cobalt complex stock solutions

Stock solutions with concentrations of 0.02796 M and 0.0117 M were used in this investigation. The method of preparation has been described previously.

##### Standard sulfate stock solution

A standard sulfate stock solution was prepared by dissolving 5.3989 grams of dried analytical grade sodium

sulfate in distilled water and diluting to one liter. The concentration was .03800 moles/liter or 3.651 milligrams of  $\text{SO}_4^{2-}$  per milliter of solution.

#### Procedure

5 ml of the cobalt complex stock solution were transferred by pipette into a 25 ml volumetric flask, diluted to about 18 ml, and an aliquot of the standard sulfate was added. Several solutions were prepared in this way. Each contained a different quantity of sulfate, varying from 7 mg. to 25 mg. of  $\text{SO}_4^{2-}$ . The solutions were then diluted to the mark in the volumetric flask.

The solutions were left standing, with frequent shaking, for four hours. At that time, each was filtered through Whatman 41 filter paper and a portion of the filtrate was transferred to the absorbance cell. The absorbance of the solution was measured with the Beckman Model DU Spectrophotometer.

#### Discussion

The plot in Figure 5 reveals how the absorbance changes as a function of the amount of sulfate added. The slope of the plot is a function not only of the amount of the reagent and sulfate present, but also of the final volume of the precipitation solution. Curve 1 represents the calibration curve in which the final volume was

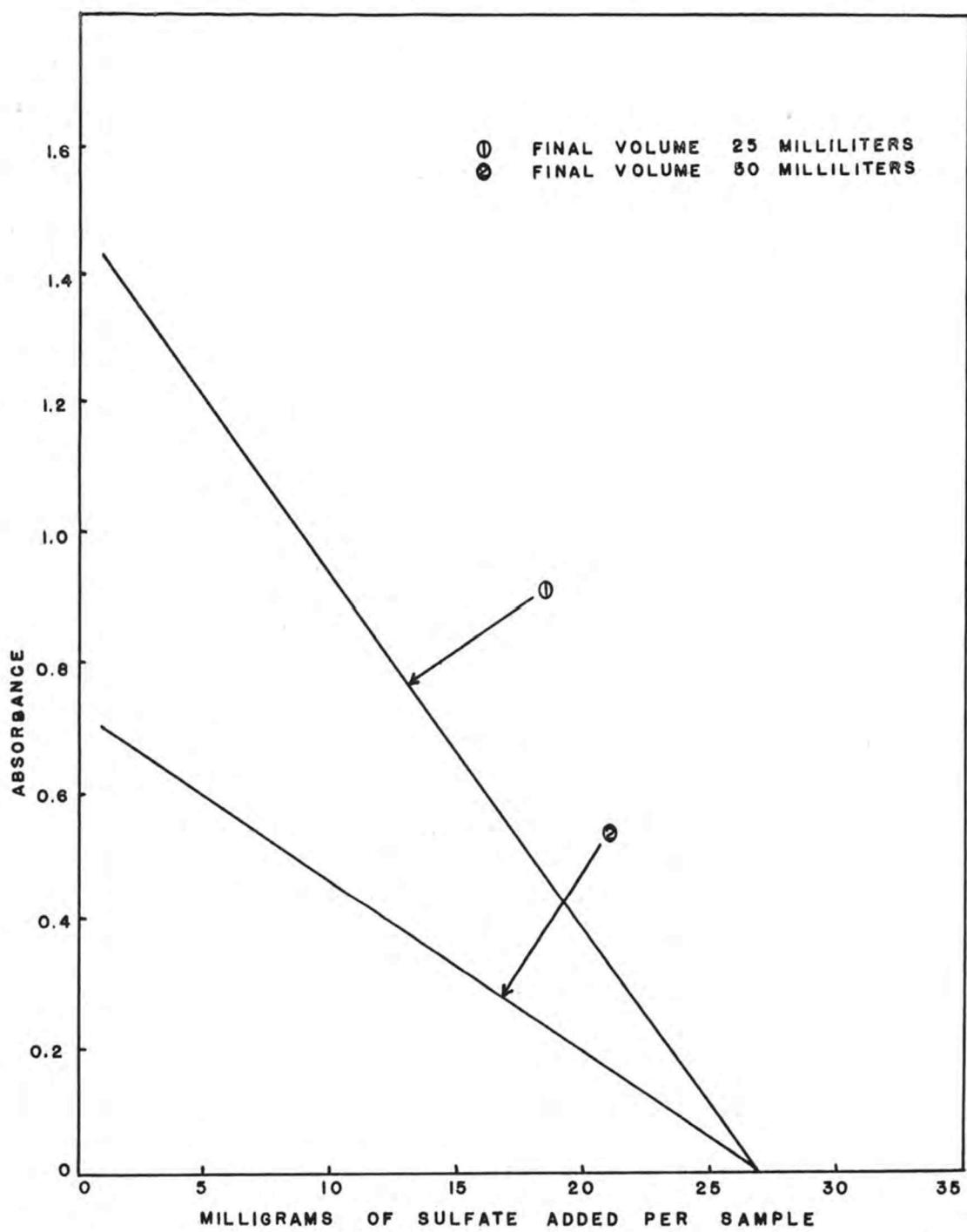


FIGURE 5. CALIBRATION CURVE FOR SULFATE SAMPLES

25 ml, while the final volume for Curve 2 was 50 ml.

When the amount of cobalt complex reagent added to a given precipitation flask is increased, the precipitation capacity, or capacity for precipitating the sulfate, will increase by a stoichiometric amount, but the slope will remain unchanged. Further, if the final volume of the precipitation solution is also increased, the slope will actually decrease. In other words, the slope is a constant for any given precipitation flask, and one may increase the sensitivity only by diluting the reagent less in the precipitation flask. This is pointed out in an effort to clarify why the final volume must not only be controlled closely, but must also be kept small.

The plot obtained from the measurements does not intersect the ordinate, but is discontinuous at the point where the amount of sulfate added is just large enough to cause the precipitation of the cobalt complex reagent to begin. If the line is extrapolated to where the sulfate added is equal to zero, the intercept absorbance one gets from the plot is greater than it actually is when no sulfate is added. This is a reasonable phenomenon, since the absorbance of the solution should remain constant until the precipitation of the sulfate causes a decrease to occur.

The abscissa intercept represents the total depletion of the cobalt complex reagent in the solution. This

point governs the maximum sample size, just as the point of discontinuity previously mentioned determines the minimum sample size.

It is now easily seen how the reduction of the solubility of the cobalt complex sulfate has little effect on the accuracy of the analysis, serving only to decrease the minimum sample size.

The purity of the cobalt complex reagent was initially unknown because the re-precipitation product of the reagent from a nitric acid solution could contain absorbed nitric acid. The plot of absorbance versus sulfate provides a means of calculating the degree of purity. The abscissa intercept corresponds to 26.85 mg. of sulfate added. This represents  $0.2795 \times 10^{-3}$  moles of sodium sulfate. Since two moles of sulfate is precipitated by one mole of the reagent,  $0.1398 \times 10^{-3}$  moles of the reagent have been precipitated. The concentration of the stock solution, by back calculation, is 0.0280 moles per liter. The value obtained by direct calculation is 0.02796, which gives very good agreement. The molar absorbancy index calculated for this solution was 254, the highest value obtained so far. Assuming the reagent to be pure, as evidenced above, the value 254 should be a constant for the cobalt complex reagent at 476  $\mu\text{m}$ .

Only the data of solutions 2 and 3 of Table 6 are plotted in Figure 5 since the plot of solution 1

Table 6

## Calibration Curve for Sulfate Samples

Solution	1	2	3
Concentration of Stock Solution	.0097M	.0279M	.0279M
Final Volume	25ml	25ml	50ml
	Wt SO <sub>4</sub> <sup>-2</sup> per sample (mg)	A	Wt SO <sub>4</sub> <sup>-2</sup> per sample (mg)
	1.58	0.955	7.25
	3.17	0.810	9.06
	6.34	0.619	10.87
	9.50	0.459	14.50
	12.67	0.293	16.31
			18.12
			19.93
			21.79
			25.37
			.015
			10.87
			14.50
			18.12
			25.37
			.457
			.346
			.247
			.047

would look quite similar to that of solution 2. A calibration curve must be prepared for each cobalt complex stock solution before it can be used for sulfate analysis.

### THE EFFECTS OF FOREIGN SUBSTANCES ON THE ANALYSIS

The methods used in conventional sulfate analysis are often subject to coprecipitation errors, as it was pointed out previously in the cases of the barium sulfate and benzidine sulfate methods. According to Belcher and Gibbons (3), a chief advantage of the use of the new reagent was that it could be used in the presence of nitrate and the peroxide ions which must be removed when the barium sulfate method is used. The authors also investigated other common ions in an attempt to determine the extent of their interference, if any. The result of the investigation, shown in Table 1, has been discussed previously.

Many substances in addition to those investigated by Belcher and Gibbons are often present in sulfate samples and may interfere with the analysis of sulfate, either gravimetric or spectrophotometric, when the cobalt complex method is used. Several such ions were investigated by adding them directly to the precipitation flask, and subsequently carrying out the analysis by the usual procedure.

#### Reagents

The foreign ion solutions were prepared by dissolving reagent grade chemicals in water and diluting to

the specified volume. The chemicals, weight of the chemical, and solution volume are indicated in Table 7 below.

Table 7

## Composition of the Foreign Ion Solutions

Foreign Ion	Weight (g)	Solution Volume (ml)
$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$	0.3265	250
$\text{Mg}(\text{NO}_3)_2$	0.4884	250
$\text{K}_2\text{SO}_3$	0.3644	250
$\text{CaCO}_3$	0.6090	100
$\text{Fe}(\text{NO}_3)_3$	0.4847	250
$\text{Al}(\text{NO}_3)_3$	0.6290	100
$\text{KH}_2\text{PO}_4$	1.3780	100

## Procedure

Aliquots of the prepared solutions were transferred to a 25 ml volumetric flask by calibrated pipette. Next, 5 ml of the 0.0279 M cobalt complex reagent were transferred by pipette into the flasks and the solutions were diluted to about 18 ml. Then 4 ml of the 3.651 mg/ml sulfate solution were added to each flask. The flasks were diluted to the mark and shaken thoroughly.

The solutions were kept at room temperature, about 20° C., for 4 hours, shaken well and filtered through Whatman 41 filter paper. A sample of each solution was collected, transferred to a silica cell which had been rinsed with the solution, and the absorbance was measured with the Beckman Model DU Spectrophotometer. The absorbance measurements and recoveries are given in Table 8.

#### Discussion

Interferences in this analysis could come from two sources. If a species absorbs at 476 m $\mu$  or if either the sulfate or the cobalt complex is precipitated from solution by a foreign ion, the analysis will be in error. Iron interferes by having a slight absorbance at 476 m $\mu$  while in solution and also by hydrolyzing and effectively blocking light transmission. Other substances which form hydrous oxide precipitates at hydrogen ion concentrations normally encountered will also interfere. The ions may often be complexed by various complexing agents and rendered harmless, as Belcher and Gibbons were able to do by complexing iron and aluminum with EDTA.

Sulfite apparently precipitates the cobalt complex reagent quantitatively, probably under nearly the same conditions that sulfate does. This ordinarily will not be a problem since it is rather easy to conduct a separate analysis on sulfite, and perhaps convert the sulfite

Table 8

## Interferences

Foreign ion	Wt SO <sub>4</sub> <sup>2-</sup> present	Wt SO <sub>4</sub> <sup>2-</sup> found
Fe <sup>+++</sup>	14.50	10.25
NH <sub>4</sub> <sup>+</sup>	14.50	14.50
Al <sup>+++</sup>	14.50	14.50
K <sup>+</sup>	14.50	14.25
Mg <sup>++</sup>	14.50	14.50
Ca <sup>++</sup>	14.50	14.52
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	14.50	14.50
CO <sub>3</sub> <sup>2-</sup>	14.50	14.50
F <sup>-</sup>	14.50	14.55
SO <sub>3</sub> <sup>2-</sup>	14.50	21.00
C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	14.50	14.58

to the sulfate for total sulfur determination.

### THE PRECIPITATION STANDING TIME FOR THE INSOLUBLE SULFATE

The recommended procedure of Belcher and Gibbons (3) specifies four hours standing time for the precipitation of the cobalt complex sulfate. Data were given for a shorter precipitation standing time with an apparent high degree of accuracy, but the feasibility of using a shorter standing time was not further discussed. If a shorter precipitation time could be used, it would clearly be advantageous.

With the spectrophotometric method it is possible to extract portions of a well mixed solution without disturbing the remainder, or upsetting the rate at which the solution approaches equilibrium. The following work was performed to establish the required standing time of the precipitate.

#### Procedure

Twenty-five ml of the cobalt complex stock solution were transferred to a 50 ml volumetric flask. An aliquot of the standard sulfate solution was added and the precipitating solution was quickly diluted to the mark. This procedure was repeated for several different aliquots of the sulfate solution.

The solutions were shaken frequently and representative samples of the precipitate solution mixture were

drawn off at intervals by pipette. The withdrawn samples were quickly filtered through Whatman 41 filter paper and the absorbance was measured on a Beckman Model B Spectrophotometer.

#### Discussion

The data obtained, shown in Table 9, indicate that higher levels of sulfate will come to equilibrium more quickly than the lower levels. This conclusion is also supported by the data of Belcher and Gibbons. At four hours the sulfate precipitation has not completely reached equilibrium, especially for low levels of sulfate, but at this point the change is sufficiently slow that the error caused by insufficient standing time is quite small. If the sulfate samples are small and the accuracy requirements are great, then a longer standing time may be necessary, and the calibration plot must be made accordingly. An attempt was made to use a shorter time of two hours, but the errors were too large.

Based on the data shown in Table 9, and upon the work of Belcher and Gibbons given in Table 2 in all subsequent work in which the precipitation step was involved, a standing time of four hours was employed.

Table 9

The Change of Absorbance With  
Standing Time

Time (min.)	#1	#2	#3	#4	#5
0	1.215	1.215	1.215	1.215	1.215
15	0.975	0.954	0.685	0.471	0.273
45	0.971	0.916	0.635	0.608	0.261
105	0.955	0.895	0.608	0.416	0.245
4 hours	0.935	0.855	0.578	0.400	0.244
3 days	0.921	0.830	0.564	0.393	0.244
Run	Milligrams $\text{SO}_4^{2-}$				
#1	4.69				
#2	9.39				
#3	23.47				
#4	32.86				
#5	42.25				

### THE EFFECT OF pH ON THE PRECIPITATION OF THE SULFATE

The stability of the cobalt complex reagent has been described on preceding pages. The investigation has shown that only in basic solutions is the cobalt complex reagent unstable. Above pH 8 a slow decomposition takes place. However, no information has been given to indicate how soluble a sulfate precipitate is in acid solutions.

In a solution with pH 2, the ratio of sulfate ion concentration to that of the bisulfate ion is approximately unity. The solubility of the sulfate precipitate should have increased by about 10% at pH 3 and to about 50% at pH 2, if the bisulfate ion does not form a precipitate with the reagent. These calculations are based upon the value for the second ionization constant being about 0.01. This value is not known with a great deal of accuracy, and certainly not under these experimental conditions.

The following work was designed to establish the lower limit of pH in the precipitating solution.

#### Procedure

10 ml of the 0.0098 M cobalt complex stock solution were transferred to a 25 ml volumetric flask and diluted to about 15 ml with distilled water. A small

amount of nitric acid or sodium hydroxide was added to adjust the pH to the desired value. 2 ml of the standard sodium sulfate stock solution were added and the solution diluted to the mark.

The solution was shaken frequently for 4 hours and kept at about 25° C. The solution was then well mixed and filtered through Whatman filter paper. The absorbance of the filtrate was measured using a Beckman Model B Spectrophotometer. A Beckman Model H-2 pH meter was used to measure the pH of the solution. Other solutions were treated similarly, with varying amounts of  $\text{HNO}_3$  and NaOH being added to adjust the pH.

#### Discussion

The results of the experiment described, given in Table 10, indicate that the lower limit of the pH range is at least as low as pH 2. The increased solubility is just beginning to be evident at pH 2, and is not appreciable even at pH 1.5. A second experiment, under the same conditions as the one described except that new stock solutions, a Beckman DU Spectrophotometer and a Beckman Zeromatic pH meter were used, gives essentially the same conclusions. The data from the second experiment are given in Table 11.

The instability of the cobalt complex reagent is evident at pH 9 and above. This same effect was observed

Table 10

## The Effect of pH on the Absorbance

pH	Absorbance	pH	Absorbance
1.50	.381	3.63	.371
1.50	.380	3.74	.378
1.68	.380	3.77	.370
1.69	.377	6.35	.377
3.29	.371	6.92	.379
3.30	.371	8.30	.380
3.37	.366	9.16	.381
3.58	.372	9.55	.403

Table 11

## The Effect of pH on the Absorbance

pH	Absorbance
2.0	.366
2.8	.360
2.9	.364
3.5	.363
8.6	.362

previously for solutions containing no sulfate.

From these experiments it is possible to conclude that the pH range for the precipitation step of the sulfate analysis is pH 2 to pH 7, limited only by the solubility of the sulfate precipitate on the one hand and the instability of the cobalt complex reagent on the other.

### TEMPERATURE EFFECTS ON THE PRECIPITATION OF THE SULFATE

Temperature variations often have considerable effect on the solubility of slightly soluble salts, usually causing the salts to be more soluble as the temperature rises. In addition, the absorbance of the solution may change due to a change in the absorbing species itself. During the investigation it appeared that those were potential sources of error that should be investigated. No information concerning the temperature effects had previously been published.

#### Procedure

Five ml of the 0.020 molar cobalt complex solution were added to each of four 25 ml volumetric flasks and diluted to about 15 ml with distilled water. 2 ml of the 0.03800 M standard sulfate stock solution were added to the flasks. Each solution was diluted to the mark, shaken well, and placed in a constant temperature bath.

The temperature baths were maintained at 17.5° C., 25.0° C., 32.5° C., and 40.0° C. with an accuracy of 0.5° or better.

The solutions were shaken frequently for four hours while in the temperature baths. They were then removed

from the baths, filtered through Whatman 41 filter paper and quickly brought to room temperature. The absorbances were measured with the Beckman Model DU Spectrophotometer.

#### Discussion

Since laboratory work is most often carried out with some variation in temperature, it is important that these variations do not become troublesome. Most of the variations one would ordinarily expect would be included in the range 20-30° C. The tabulated results of this experiment indicate that the precipitation of the sulfate is practically temperature insensitive and a 10° temperature range would not cause any difficulty. In fact, it is quite possible that a much wider range of temperatures could be tolerated. The data in Table 12 indicate that only when the temperature rises above 32-40° C. will an error be caused by the increasing solubility of the sulfate.

Table 12

Temperature Variation Effects  
on the Absorbance

Milligrams $\text{SO}_4^{--}$ Added	mg Recovered	Temperature (Degrees C.)	Absorbance
10.87	10.88	17.5	0.563
10.87	10.92	25.0	0.561
10.87	10.84	32.5	0.566
10.87	10.70	40.0	0.573

## ANALYSIS OF THE SULFATE

Once the calibration curve had been obtained, it was possible to run an analysis of a sulfate sample. A regular student sample was used. The results were then compared with those obtained using the standard barium sulfate gravimetric analysis (7, 11, 54).

## Procedure

A sample of the unknown sulfate sample was weighed on an analytical balance and dissolved in distilled water. The solution was transferred quantitatively to a 500 ml volumetric flask and diluted to the mark. A 10 ml aliquot was transferred to a 25 ml volumetric flask containing 10 ml of the 0.0117 M cobalt complex stock solution and diluted to the mark. Four samples were treated in this manner. They were shaken frequently for 4 hours then filtered through Whatman No. 41 filter paper. A portion of the filtrate was transferred to a silica cell and the absorbance was measured using a Beckman DU Spectrophotometer. The amount of sulfate per sample was obtained from the standard curve.

The same unknown was subjected to an analysis by the barium sulfate gravimetric precipitation method outlined in a quantitative analysis text (54).

### Discussion

The results of the experiments have been tabulated and appear in Table 13. The results of another set of experiments, using the same procedure but different solutions and a different calibration curve, are given in Table 14. The accuracy and precision of the two methods compared are nearly the same. The precision of the gravimetric procedure appears to be slightly superior, but too few experiments have been performed to evaluate completely the comparative merits of the two methods on the basis of accuracy and precision. Furthermore, the conditions under which the analysis was carried out were optimum for the gravimetric method, but not for the spectrophotometric method. For example, the sample sizes were optimum and the percentage of sulfate per sample was high.

Being in an unfavorable comparison position notwithstanding, the precision and accuracy of the spectrophotometric method compares well with the corresponding gravimetric method. The spectrophotometric method consumes far less time per analysis than the corresponding gravimetric method. While the time required to complete an analysis is about the same for both methods, the time actually spent doing the work in the spectrophotometric method is no more than one half the time used in the

Table 13

## Spectrophotometric Analysis

Weight of Sample	0.4302	0.6616	0.5967
Absorbance	0.788	0.554	0.579
Mg SO <sub>3</sub> found	150.4	270.5	241.0
% SO <sub>3</sub>	40.50	40.89	40.39
Average % SO <sub>3</sub>			40.59
Standard Deviation			0.263

## Gravimetric Analysis

Weight of Sample	0.9457	0.8838	0.4238	0.7709
Weight of BaSO <sub>4</sub>	1.1075	1.0319	0.4963	0.9029
% SO <sub>3</sub>	40.17	40.05	40.16	40.17
Average % SO <sub>3</sub>	40.14			
Standard Deviation	.059			
Manufacturer's Value				40.18

Table 14

## Spectrophotometric Analysis

Weight of Sample (mg)	22.16	22.16	31.03	44.32
Weight of SO <sub>3</sub> found				
% SO <sub>3</sub>	39.56	39.56	39.76	39.95
Average % SO <sub>3</sub>				39.70
Standard Deviation				.188

## Gravimetric Analysis

Weight of Sample (mg)	.4432	.4432	.4432
Weight of BaSO <sub>4</sub> (g)	0.5183	0.5124	0.5138
% SO <sub>3</sub>	40.11	39.65	39.76
Average % SO <sub>3</sub>			39.84
Standard Deviation			0.199
Manufacturer's Value			39.76

gravimetric method. For instance, the new method requires only one hour and forty-five minutes, or less, of time actually spent on the analysis, compared to over five hours for an accurate gravimetric analysis.

Nevertheless, the new method is indirect and must be checked occasionally by running a known sulfate sample through the procedure, and the calibration must be prepared for each instrument, if not for each individual. These difficulties may be overcome, as they have for other methods based on the same or similar principles.

This investigation gives strong support to the original contention of Belcher and Gibbons that this new reagent can be usefully employed for low level sulfates. This is particularly true for sulfur-containing organic compounds, and for samples containing substances which interfere with other methods. It is suggested that the spectrophotometric analysis of sulfates using the new reagent, may be carried out efficiently and accurately, and that the analysis offers advantages not common to other methods.

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