

REMOVAL OF CALCIUM SULFATE DEPOSITS FROM
WASTE ACID TREATMENT FACILITIES

by

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I. INTRODUCTION

Sulfate ions in water and industrial wastes pose an important and often expensive problem with which to cope. In municipal water supply, the sulfate concentration is dependent upon the source of the water utilized in meeting the demand of the community. The sulfate concentrations of ground waters are generally higher than those of surface waters, owing to the fact that water, in percolating through earth and rock formations, dissolves minerals with which it comes into contact. Sulfate ions constitute a large part of the hardness which finds its way into water in this manner.

Waters high in sulfate concentrations have many undesirable qualities. Hard water is of poor quality for domestic use because of the nuisance effect. Hard water is also unsuited to the operations of many industrial processes. Consequently, water must often be treated to remove sulfate ions in order to render the water suitable for use.

The problem of sulfate concentrations in wastes is of considerable importance to some industries, since treatment to reduce sulfate concentrations in the wastes must be employed before the wastes are discharged into a public watercourse upon which communities downstream depend for their normal water requirements. Such a watercourse will often contain high concentrations of

sulfate ions, and the problem of water hardness must be dealt with by the downstream consumers.

High sulfate concentrations are present in wastes from such industries as pulp mills, textile mills, munitions manufacture, and from metal pickling processes. These industries must necessarily treat their wastes before discharging them into water-courses.

The problem of sulfation (the deposition of calcium sulfate) is of extreme importance to industries having large volumes of sulfuric acid wastes. Economic considerations usually call for the neutralization of sulfuric acid wastes with lime, the result being the formation of calcium sulfate. The calcium sulfate is deposited in treatment facilities, thereby reducing their operating efficiency. Such deposition, if allowed to continue, eventually requires extensive cleaning operations and possibly the replacement of certain units of the treatment facilities. This is especially true in the case of pipe lines which become so congested that the required flow no longer can be accommodated.

Valid analytical methods for the determination of sulfate concentrations in water and wastes are essential to an intelligent approach to the sulfation problem. Consequently, three methods of analysis were investigated preliminary to the study of the removal of calcium sulfate deposits from treatment

facilities. The standard gravimetric method of analysis, which is regarded as the standard for sulfate determination, was investigated first. The volumetric and turbidimetric methods of analysis were then investigated in an attempt to establish a comparison or correlation with the standard gravimetric method.

II. REVIEW OF LITERATURE

Calcium sulfate, in the form of gypsum, is present in most waters, causing non-carbonate (permanent) hardness⁽⁸⁾. If the hardness is determined excessive, treatment is required in order to render the water suitable for general use. The hardness caused by the presence of sulfate, however, is not the only objection to its presence. Odors and tastes are accompanied by high concentrations of sulfate⁽³⁾.

By necessity, industries which produce as a result of manufacturing processes wastes of high sulfate concentrations must employ treatment for the removal of sulfate before discharging the wastes into a public watercourse. If no such treatment were required, use of the water downstream as a potable water supply would be uneconomical⁽⁴⁾.

Sulfation

Industries discharging wastes with high concentrations of sulfuric acid must employ complete neutralization facilities. This is necessary to reduce the detrimental effect upon the receiving stream. Several patented processes are currently employed for neutralization⁽⁴⁾. It is in such treatment

facilities that sulfation occurs. If lime is employed as the neutralizing agent, calcium sulfate is the product of reaction during the mixing process. Deposition of the calcium sulfate results unless there is sufficient agitation to maintain the calcium sulfate in suspension until subsequent settlement is allowed in a lagoon or other type settling basin. Even under the most favorable conditions, a moderate amount of deposition occurs.

Sulfation is a common occurrence where lime is employed in waste acid neutralization, but, to the author's knowledge, there has been little success in its prevention and no success in the development of a method for the removal of the deposited material. An intensive literature survey in the Virginia Polytechnic Institute libraries revealed no information pertaining to research involving removal of sulfate deposits. A fifteen year index to Industrial and Engineering Chemistry makes no reference to the general problem.

The absence of information relative to the problem of sulfation necessitated the investigation and evaluation of analytical methods for the determination of sulfate concentration. Such evaluations may be used as indications of valid applications of the methods under consideration, and the proper analytical procedure can then be selected for analysis of the problem at hand.

Standard Gravimetric Method for Sulfate Determination

The gravimetric method for sulfate determination is a direct method and is employed in analytical work in which a high degree of accuracy is desired. "The gravimetric method is recognized as the primary procedure"⁽¹⁾. There are in current use many variations of the standard gravimetric method, but the method most widely accepted is that outlined in Standard Methods for the Examination of Water and Sewage⁽¹⁾. Theroux, Eldridge, and Mallman⁽¹¹⁾ list a procedure which varies considerably from the generally accepted method. Hoover⁽⁸⁾ presents a method which varies from the "Standard Methods" procedure only in the recommended volume of sample. Even where variations and alterations of the method are exercised, reasonably consistent results can be expected.

Although the gravimetric method is considered the most reliable analytical procedure available, it is not infallible. Sulfites must not be present in the sample analyzed gravimetrically. Silica and iron in high concentrations must, likewise, be absent⁽¹⁾.

Volumetric Method for Sulfate Determination

The volumetric method of analysis employs the principle of titration of an acid with a base. The principle involved is simple, but the time and manipulations entailed are disadvantages. Ordinarily, fairly good results are obtained, but care must be taken in the preparation of the sample to eliminate ferric iron, the cause of low results⁽¹¹⁾. If ferric iron is present in the sample, a reagent must be added to reduce the iron to the ferrous state, which does not interfere with results.

Turbidimetric Method for Sulfate Determination

The turbidimetric procedure for determination of sulfate concentration is similar, in effect, to the gravimetric method. The chief difference in the methods is that the barium sulfate is precipitated and weighed in the gravimetric procedure, whereas a barium sulfate suspension is produced in the turbidimetric method, and the intensity of the suspension is proportional to the sulfate concentration.

Various types of photometric instruments are used in the turbidimetric method of analysis. Photometers are employed not only in the determination of sulfate concentration, but in nitrate and phosphate concentration analysis as well.

The employment of the photometer in turbidimetric analysis involves the preparation of a curve based on readings made on standard solutions. Once established, the curve is referred to for the concentration of the unknown. This provides a rapid and convenient determination method in routine analysis.

Difficulty is encountered in establishing the curve from standard solutions because of the nature of the prepared suspension. For this reason, many precautions must be observed if reliable results are to be expected. Snell and Snell⁽¹⁰⁾ recommend the use of a suspension stabilizing agent for more consistent results. Peptone, gum ghatti, gelatine, or glycerine may be used for such a purpose.

The turbidimetric method is very sensitive to the presence, in solution, of many elements. Standardization work is performed with the use of distilled water to which only the desired sulfate concentrations are added. It is, therefore, imperative that care be exercised in the exclusion of such detrimental elements from the unknown analyzed. Also, the sulfate concentration should be low if the analysis is to be conducted turbidimetrically. Snell and Snell⁽¹⁰⁾ state that the sulfate concentration should be between 0.8 and 8.0 parts per million and that sodium, zinc, cadmium, mercury, and aluminum should not be present in the sample, since

they lead to high results. Magnesium and nitrogen compounds in solution cause low results. A uniform salt concentration (NaCl) is essential along with a uniform acid concentration (HCl). A pH of 3 to 4 is recommended⁽¹⁰⁾.

Because of the extreme limitations of the turbidimetric analysis, the most common application of the method is in the determination of sulfate in water, where the concentration is generally low⁽¹⁰⁾.

III. OBJECT OF INVESTIGATION

The investigation had two objectives. The first objective was to investigate and evaluate methods for the determination of sulfate concentration in order to select an appropriately accurate method which could be used in a complete analysis of the calcium sulfate deposits. The second objective was to develop a chemical medium through which the removal of calcium sulfate deposits could be effected. It was thought that if a feasible removal method could be developed, a general proposal for field application of the procedure could be presented. Such a proposal would be of value to industries harassed by the problem of sulfation.

IV. INVESTIGATION OF ANALYTICAL METHODS

General

Limitations of the various analytical methods of analysis are the prime factors leading to inconsistent results in routine laboratory work. All too often, the indiscreet analyst selects a particular procedure for his work without investigating such limitations as may exist for the method. For work of importance, an investigation and evaluation of the analytical procedure selected should be conducted in advance of any routine analytical work.

Factors pertinent to the applicability of a particular analytical method may be considered as follows: (a) time involved in preparation of samples, (b) time consumed in actual manipulations of the procedure and the number of such manipulations, (c) the concentration range over which the method is applicable, and (d) the consistency and accuracy which can be achieved. Because of these factors, the three methods of analysis were thoroughly investigated and evaluated as a guide to the selection of an accurate procedure to be used in analyzing the sulfation problem.

Standard Gravimetric Method for Sulfate Determination⁽¹⁾

"In an acid solution barium chloride precipitates only sulfates as barium sulfate."⁽¹⁾ The reaction which occurs is as follows:



The barium sulfate is precipitated and is filtered out. The precipitate is ignited at 800°C to constant weight, allowed to cool in an desiccator, and weighed. The equivalent weights of barium sulfate and sulfate are used to calculate the sulfate concentration as SO₄. A sample calculation is presented in appendix D.

Apparatus:

The apparatus for the investigation consisted of standard laboratory equipment. This included pipettes, graduated cylinders, Erlenmeyer flasks (500 ml. volume), a vacuum flask for filtering, and other incidental glassware. Gooch crucibles (appendix A) were used for filtering the samples. A furnace capable of producing heat at 800°C was required for igniting precipitates. Actually, a 1000°C capacity furnace was employed. A standard steam bath was used for digestion of the samples before filtering. Hot plates were utilized in heating the samples to boiling.

Reagents:

The reagents required for the procedure consisted of:
(a) a 10% barium chloride solution, (b) hydrochloric acid (1:1 solution), and (c) a silver nitrate-nitric acid wash solution. All reagents were prepared according to "Standard Methods"⁽¹⁾ (appendix A).

Preparation of Samples:

Duplicate samples* were prepared covering a concentration range varying from 40 p.p.m. through 360 p.p.m. SO_4 in order that an evaluation of accuracy could be made. Since 200 p.p.m. SO_4 (approximately) was the concentration recommended for best results⁽¹⁾, it was thought that such an investigation would bring about a more thorough understanding of the limitations of the gravimetric procedure. No precautions were necessary relative to the removal of sulfites, silica, and iron, since only standard concentrations were utilized in the preliminary phase of the investigation, and only distilled water and a standard sulfate solution were used.

The concentrations investigated were 40, 160, 200, 240, and 360 p.p.m. SO_4 . These values were selected in order that the

* Duplicate samples were not specifically recommended, but the author felt that more reliable results would be obtained through such a practice.

accuracy of the method could be investigated in both high and low concentrations and a comparison could be made with the accuracy at the 200 p.p.m. SO_4 concentration recommended for the procedure.

Procedure:

The standard gravimetric procedure, as prescribed in Standard Methods for the Examination of Water and Sewage⁽¹⁾, is as follows:

1. Adjust a 250 ml. clear sample, by dilution or concentration, to approximately 200 p.p.m. sulfate as SO_4 .
2. Add 2 ml. 1:1 hydrochloric acid to the sample.
3. Heat the solution to boiling.
4. Add 10 ml. hot 10% barium chloride solution slowly, while stirring.
5. Digest the precipitate on a steam bath for 2 hours.
6. Filter in a tared crucible and wash the precipitate with warm distilled water until free of chlorides as determined by use of the silver nitrate-nitric acid wash solution.
7. Ignite the precipitate at 800°C to constant weight. Place the crucible in a desiccator to cool.
8. Weigh the crucible and precipitate and calculate the sulfate concentration.

Four series of analyses were conducted according to the prescribed procedure. The concentrations investigated, as previously stated, varied from 40 to 360 p.p.m. SO_4 , inclusive. The data were recorded, and an analysis of accuracy was conducted, taking into consideration the theoretical solubility losses for each concentration investigated⁽⁵⁾.

Upon completion of the preliminary phase of investigation of the gravimetric method, an investigation was made relative to the applicability of the method to the analysis of actual waste samples. The wastes were normally of high sulfate concentration, ranging as high as approximately 3,000 p.p.m. SO_4 . Because of the high sulfate concentration of the waste, it was necessary to employ dilution in order to obtain a sample of approximately 200 p.p.m., as recommended for the procedure.

The Hellige turbidimeter, which measures the turbidity of a solution, was employed to determine primarily the sulfate concentration of the undiluted waste. A barium sulfate suspension was produced in a portion of the full strength waste by use of barium chloride crystals and a salt acid solution. The turbidity of the barium sulfate suspension was determined, from curves prepared for use with the Hellige instrument, in terms of sulfate concentration. The sulfate concentration determined in this manner provided a guide for use in dilution

of the sample to approximately 200 p.p.m. for analysis by the gravimetric method.

The samples prepared by dilution for gravimetric analysis were not filtered because the prevailing turbidity of the samples resulted almost entirely from suspended particles of calcium sulfate. Removal of silica was not necessary since its concentration in the samples was less than the critical value of 1%. Sulfites and iron were not present in the samples.

Sixteen analyses of waste samples were conducted gravimetrically with preliminary turbidimetric analyses as guides to dilutions of the samples. The data were recorded and a statistical analysis conducted in the comparison of the turbidimetric results with gravimetric results.

Data and Results:

The data and results obtained in the investigation of the gravimetric method have been tabulated and are presented in Tables 1 and 2. The relationship of sulfate concentration to error in results obtained has been shown graphically in Figures 1, 2, and 3. A comparison of turbidimetric results with gravimetric results has been presented in Figure 4.

Figure 1 shows curves for the four series of analyses which were conducted using standard sulfate concentrations varying from 40 p.p.m. to 360 p.p.m., inclusive. Sulfate concentration is compared with total % error in results. Presented along with the four curves, for comparison of theoretical error with total error, is a curve showing the theoretical error resulting from solubility losses at each concentration investigated.

Figure 2 is a graphical presentation of the average, maximum, and minimum % error in results at each of the five sulfate concentrations. The general variation range (spread) of error is clearly indicated by the comparison of the maximum and minimum % error curves.

Figure 3 shows the deviation of actual % error from theoretical % error resulting from solubility losses at each of the sulfate concentrations investigated for the four series of analyses.

Figure 4 presents a graphical comparison of turbidimetric and gravimetric results from the analyses of sixteen actual waste samples. The curve of "best fit", determined by the method of lease squares (appendix F), is employed for the comparison of results. Variance of data (appendix G) and 90%

confidence limits (appendix H) are also shown for the purpose of evaluating the reliability of the data obtained from the sixteen analyses.

TABLE 1

Results of Gravimetric Method for Four Series of Analyses

Description of Table 1.

Column 1: SO₄ Recovered (p.p.m.SO₄) - Average of Duplicate Samples.
 Column 2: Total Error (%) of Recovery.
 Column 3: Theoretical Error (%) Due to Solubility Losses at 50°C.*
 Column 4: Deviation (%) of Total Error from Theoretical Error.
 Column 5: Average total error (%) for Four Series of Analyses.
 Column 6: Variation in Total Error (%) (Max. % Error - Min. % Error)

Observed Results	Column Numbers	Actual SO ₄ Concentrations of Prepared Samples (p.p.m.SO ₄)				
		40	160	200	240	360
Series #1	1	37.80	158.35	199.05	238.20	362.75
	2	5.40	1.03	0.48	0.75	0.76
	3	3.45	0.86	0.69	0.57	0.38
	4	56.50	19.80	30.40	31.50	99.90
Series #2	1	37.60	157.43	198.80	237.97	361.43
	2	6.00	1.60	0.60	0.85	0.40
	3	3.45	0.86	0.69	0.57	0.38
	4	73.90	85.80	12.80	49.10	5.50
Series #3	1	37.36	162.75	199.20	242.40	360.47
	2	6.60	1.75	0.40	1.00	0.13
	3	3.45	0.86	0.69	0.57	0.38
	4	91.30	100.00	42.00	33.60	65.80
Series #4	1	38.70	157.80	200.40	239.30	359.10
	2	3.30	1.40	0.20	0.30	0.25
	3	3.45	0.86	0.69	0.57	0.38
	4	4.30	63.00	71.00	47.00	34.00
	5	5.34	1.44	0.42	0.73	0.39
	6	3.30	0.69	0.40	0.70	0.63

* Samples were filtered at approximately 50°C

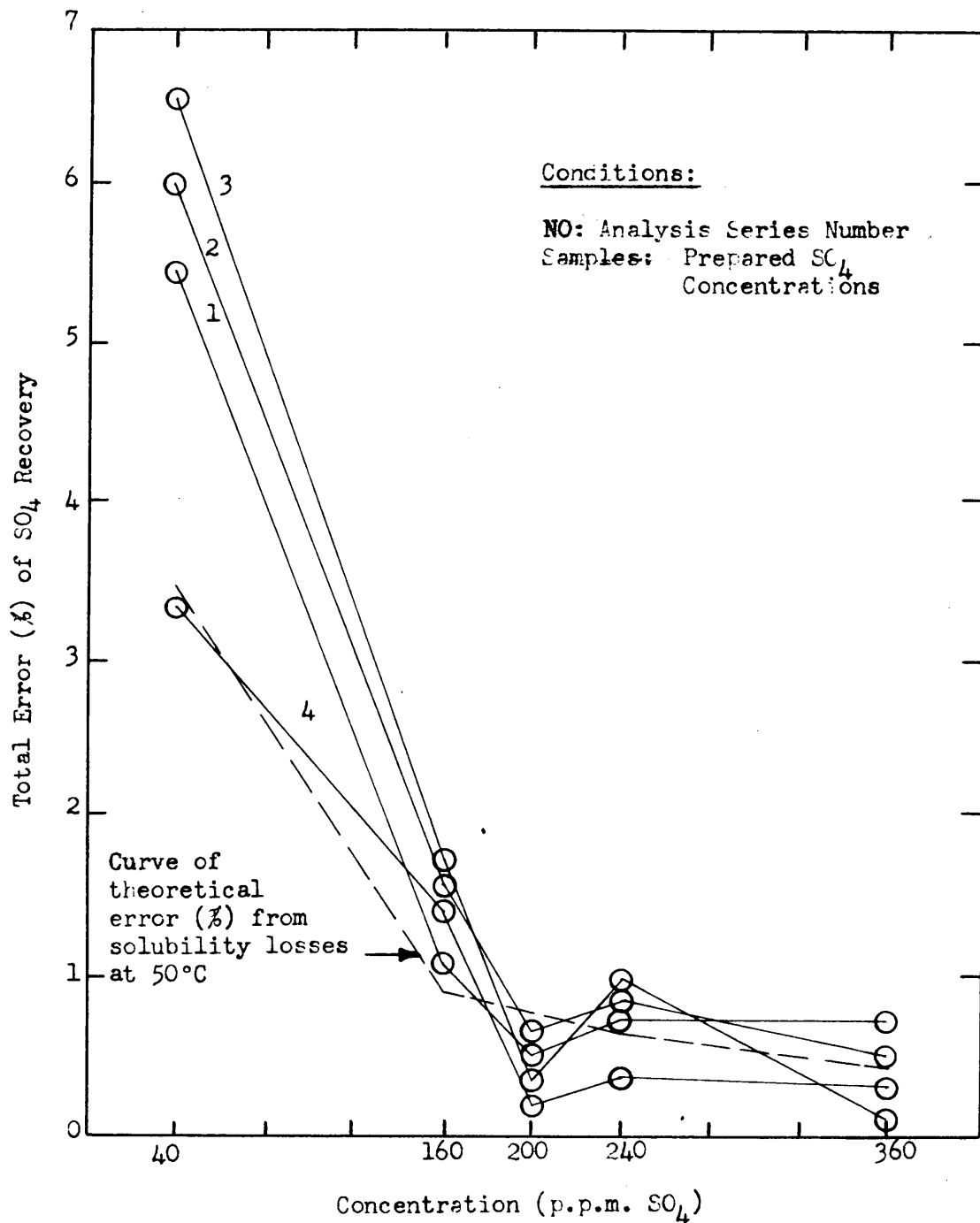


Figure 1.

Relation of Error of SO_4 Recovery to SO_4 Concentration for the Gravimetric Method

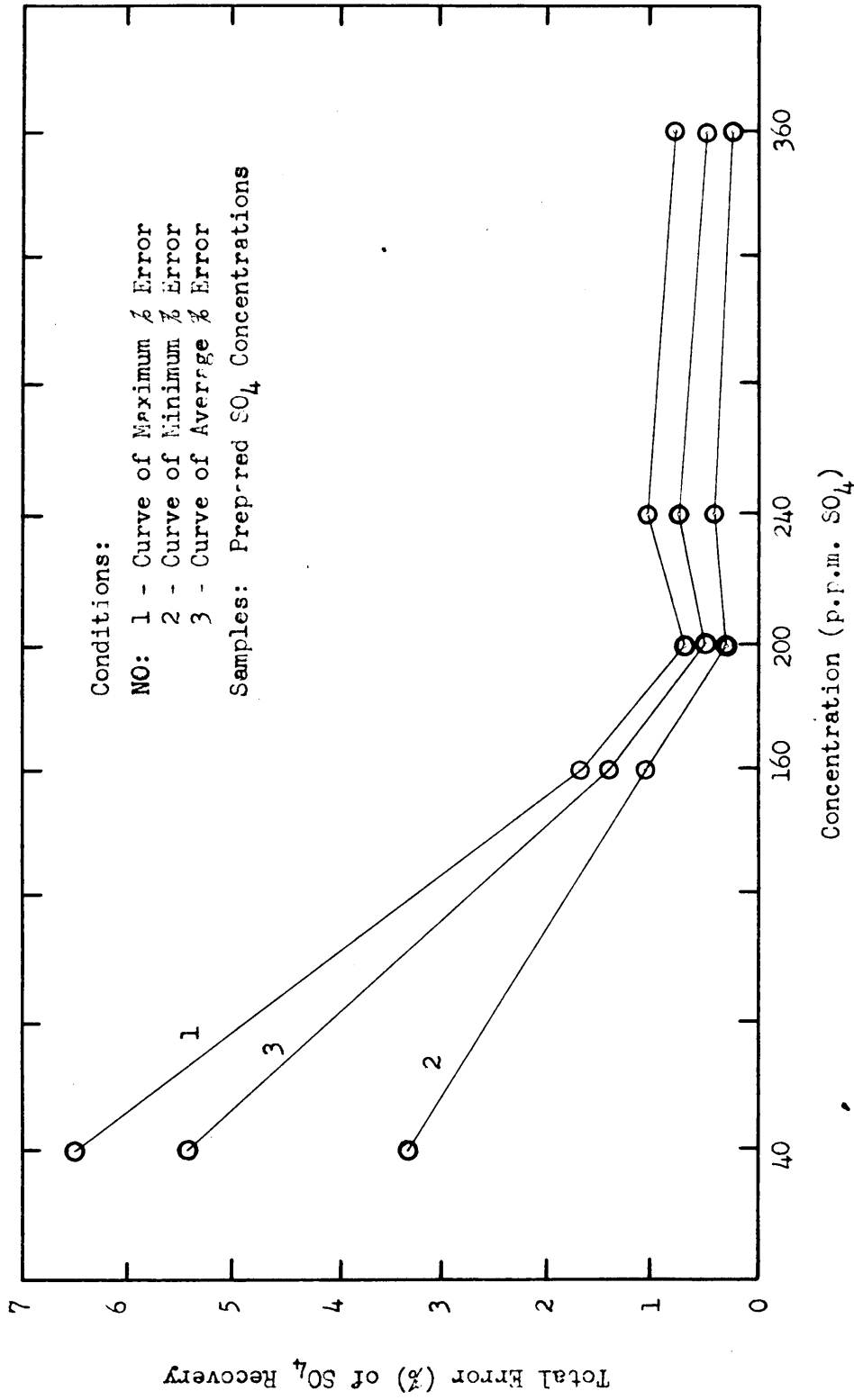


Figure 2.

Relation of Error of SO₄ Recovery to SO₄ Concentration Showing Curves of Maximum, Minimum, and Average % Error for Four Series of Gravimetric Analyses

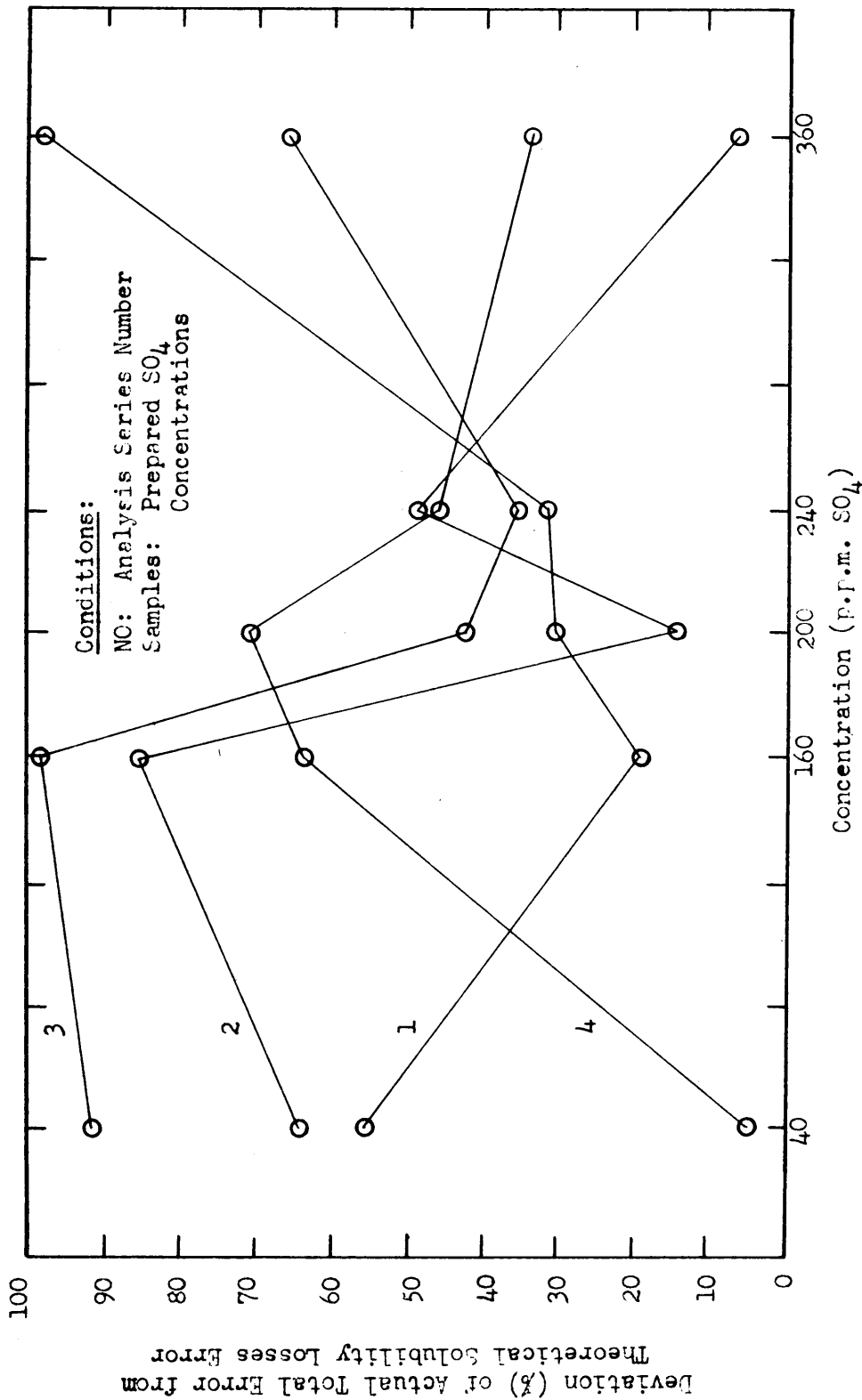


Figure 3.

Deviation in Error of SO₄ Recovery from Theoretical Error of Recovery (Solubility Losses) for the Gravimetric Method

TABLE 2

Results of Gravimetric and Turbidimetric
(Hellige*) Analyses of Waste Acid

Analysis Number	Turbidimetric Results (p.p.m. SO ₄)	Gravimetric Results (p.p.m. SO ₄)
1	1800	2098
2	500	680
3	1300	1563
4	1450	1713
5	1000	1126
6	1350	1636
7	2450	2790
8	1400	1654
9	1250	1617
10	1600	1708
11	2100	2403
12	1350	1692
13	900	1175
14	2250	2687
15	750	900
16	2100	2254

* The Hellige turbidimeter was used for preliminary determinations prior to adjustment of concentration of samples for gravimetric analysis.

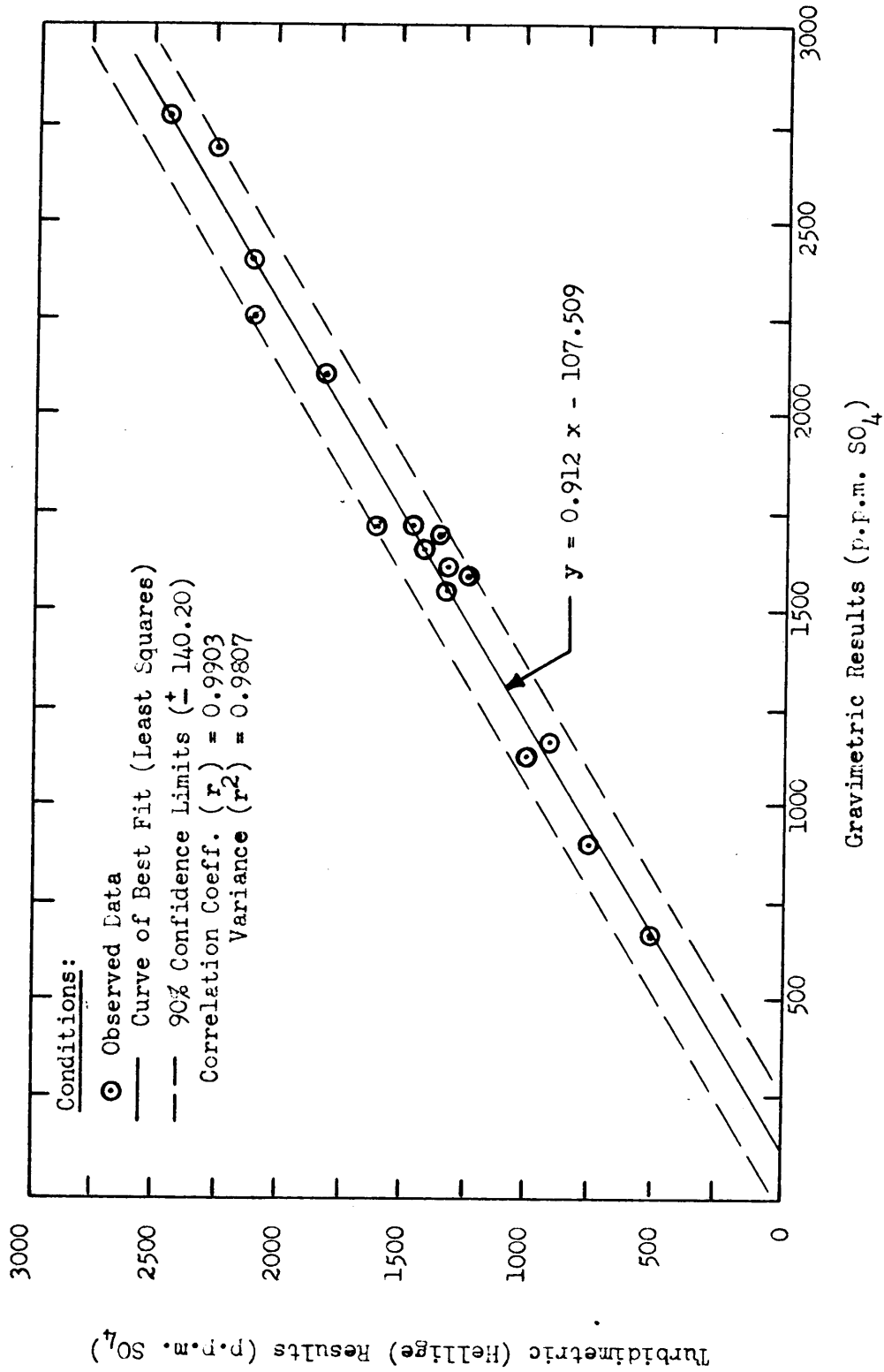
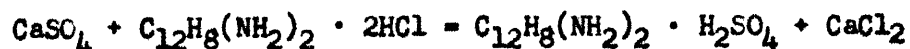


Figure 4.
Comparison of Turbidimetric (Hellige) Results with Gravimetric Results
for Waste Acid Analysis

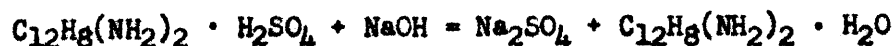
Volumetric Method for Sulfate Determination

If ferric iron is present in the sample analyzed volumetrically, low results will be obtained because of the reaction of ferric iron with benzidine hydrochloride. Ferrous iron does not, however, react in this manner. Hydroxylamine hydrochloride is, therefore, added to reduce the ferric iron to the ferrous state.

In a hydrochloric acid solution, a reaction occurs involving the sulfate and benzidine hydrochloride to form a slightly soluble compound of benzidine and sulfuric acid as follows:



All HCl must be washed from the precipitate before boiling or high results will be obtained, since the method involves titration of an acid with a base. Only the H_2SO_4 combined with the compound is to be titrated, if accurate results are to be obtained.



The volume of NaOH used in the titration is employed for calculation of the concentration of sulfuric acid as sulfate (SO_4). A sample calculation is shown in appendix E.

Apparatus:

The apparatus required for the procedure consisted of standard laboratory apparatus. The glassware required included pipettes, an automatic 10 ml. burette graduated in five-hundredths milliliters, several 400 ml. beakers, 6 small funnels, and a 25 ml. graduated cylinder. A funnel rack of 6 funnel capacity was used for filtering operations. Hot plates were used for heating the samples prior to titration.

Reagents:

The reagents required for the volumetric method were: (a) a 1% solution of hydroxylamine hydrochloride, (b) a benzidine hydrochloride solution, (c) a 0.05 normal sodium hydroxide solution, and (d) standard phenolphthalein indicator solution. All reagents were prepared according to the Laboratory Manual for Chemical and Bacterial Analysis of Water and Sewage⁽¹¹⁾. See appendix B for preparation of reagents.

Preparation of Samples:

The samples were prepared varying over a sulfate concentration range of 5 p.p.m. to 160 p.p.m. SO_4 , inclusive. This range was investigated for the purpose of overlapping the lower range of the gravimetric investigation. It was thought that if

the volumetric method proved reliable for the greater portion of the range investigated, an analytical method would then be available which would eliminate the process of concentrating samples for analysis by the gravimetric method, and the volumetric method could be used instead of the gravimetric procedure for samples of low sulfate concentrations.

Procedure:

The Laboratory Manual for Chemical and Bacterial Analysis of Water and Sewage⁽¹¹⁾ outlines the volumetric procedure as follows:

1. Measure exactly 250 ml. of the sample into a 400 ml. beaker.
2. Add 10 ml. of a 1% solution of hydroxylamine hydrochloride. (If the iron content is less than 0.5 p.p.m., this step may be omitted.)
3. Add to the sample 20 ml. of benzidine hydrochloride.
4. Stir the sample vigorously and allow the precipitate to settle.
5. Filter the solution through filter paper and wash the beaker and the paper with small portions of distilled water. (Whatman #42 filter paper is very satisfactory).

6. Pierce the filter paper in the funnel and wash the precipitate from the paper into the original beaker with approximately 200 ml. of distilled water. Heat to boiling to dissolve the precipitate.
7. Add 3 drops of phenolphthalein indicator and titrate with 0.05 normal sodium hydroxide solution until the first permanent pink color is obtained.
8. Place the filter paper in the solution and continue the titration to the first permanent pink color. Record the ml. of sodium hydroxide solution used.

Six series of analyses were conducted according to the procedure outlined. The sulfate concentrations of the prepared solutions varied from 5 p.p.m. to 160 p.p.m., inclusive. The data were recorded, and an accuracy analysis was conducted.

Data and Results:

The data and results obtained from the investigation of the volumetric method have been tabulated and are presented in Table 3. A study of accuracy is shown graphically in Figure 5, in which the maximum, average, and minimum % error in results for each of the six sulfate concentrations investigated can be found. The variation range (spread) of error is indicated by a comparison of the maximum and minimum % error curves.

TABLE 3

Results of Volumetric Method for Six Series of Analyses

Description of Table 3

- Column 1: SO₄ Recovered (p.p.m. SO₄).
- Column 2: Total Error (%) of Recovery.
- Column 3: Average Error (%) of Recovery.
- Column 4: Variation in Total Error (%) (Max. % Error - Min. % Error)

		Column Numbers	Actual SO ₄ Concentrations of Prepared Samples (p.p.m. SO ₄)					
			5	10	20	40	80	160
Observed Results	Series #1	1	5.12	11.23	19.44	34.79	73.68	148.39
		2	2.40	12.30	2.80	13.00	7.90	7.30
	Series #2	1	5.12	10.23	18.41	32.75	76.80	154.70
		2	2.40	2.30	8.00	18.10	4.00	3.50
	Series #3	1	5.12	10.23	21.49	66.52	77.78	155.55
		2	2.40	2.30	7.50	13.26	2.78	2.78
	Series #4	1	4.91	9.98	19.90	36.33	75.22	157.60
		2	1.80	0.20	0.50	9.18	5.98	0.15
	Series #5	1	5.12	9.72	19.96	34.79	76.75	147.88
		2	2.40	2.80	0.20	13.03	4.06	7.58
	Series #6	1	5.12	10.23	19.43	35.80	74.20	143.75
		2	2.40	2.30	0.29	10.50	7.25	10.15
		3	2.30	3.70	3.22	12.85	5.33	5.24
		4	0.60	12.10	7.80	8.92	5.12	10.00

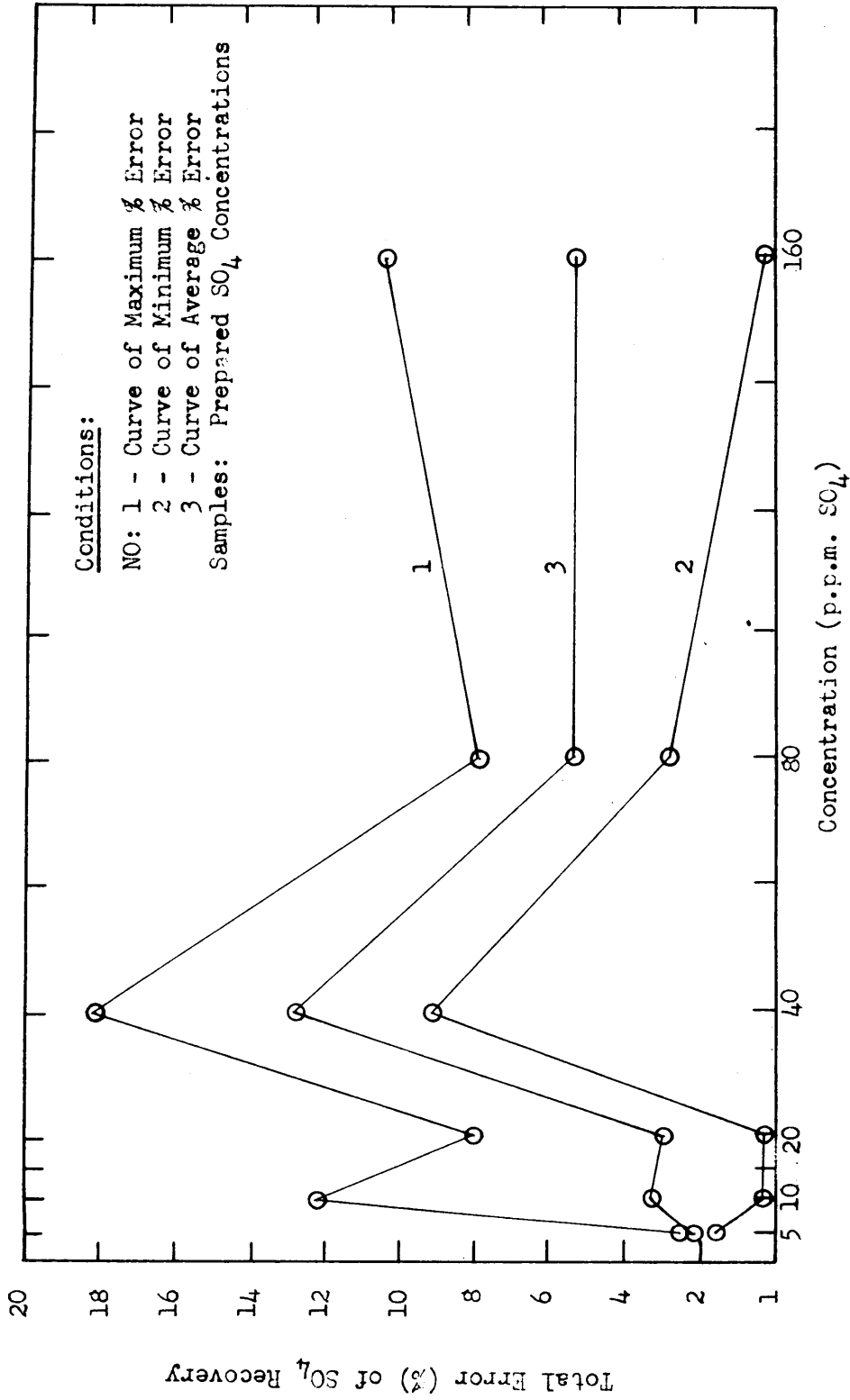


Figure 5.

The Relation of Error of SO₄ Recovery to SO₄ Concentration Showing Curves of Maximum, Minimum, and Average % Error for Six Series of Volumetric Analyses

Turbidimetric Method for Sulfate Determination

The investigation of the turbidimetric method was pursued in an attempt to obtain a standard curve which could be used rapidly and conveniently in determining sulfate concentration photometrically. The Lumetron, a very sensitive photometer which measures light transmittance through a given prepared sample, was utilized in the investigation of the method.

The principle involved in the turbidimetric method of analysis is similar to the gravimetric procedure in chemical reaction. In the gravimetric procedure, a barium sulfate precipitate is formed, filtered out of solution, and weighed; in the turbidimetric method, it is desired to produce a barium sulfate suspension and measure, photometrically, the light transmittance through the sample. The transmittance varies logarithmically as the sulfate concentration varies arithmetically (i.e., the transmittance increases with a corresponding decrease in sulfate concentration).

Apparatus:

The apparatus required for use with the Lumetron photometer were a selection of monochromatic light filters and a selection of cuvettes and cylindrical cells for holding the samples.

Fourteen short form Nessler tubes, calibrated at 50 ml. and 100 ml. volumes, were used for preparing the standards. Nessler tube racks were required for supporting the tubes. Pipettes and other incidental glassware were used in the preparation of the standards.

Reagents:

The reagents required for producing the barium sulfate suspension were a 10% barium chloride solution, and Hellige salt acid solution. A standard sulfate solution was prepared in such a manner that 1 ml. of the solution contained 0.1 mg. of sulfate as SO_4 . This standard solution was employed in the preparation of solutions of various concentrations for standard curve work.

In an attempt to produce a more stable barium sulfate suspension, the Hellige salt acid solution was altered by the addition of fullers' earth and hydrochloric acid. The altered salt acid solution was filtered to remove the excess turbidity resulting from the addition of fullers' earth. Glycerine was mixed with the filtrate for additional stability promotion. It was anticipated that the addition of fullers' earth would provide, in a sense, nuclei to which the particles of barium sulfate could adhere. The hydrochloric acid was added to

prevent the precipitation of barium phosphate in the analysis of actual waste samples⁽¹⁰⁾. The procedures for preparation of all reagents used in this analytical method are presented in appendix C.

Preparation of Standards:

The standards were prepared in short form Nessler tubes. The standard solution, 1 ml. of which was equivalent to 0.1 mg. SO_4 , was added to the Nessler tubes in such volumes as to represent sulfate concentrations, as SO_4 , varying from 0 p.p.m. to 52 p.p.m., inclusive, when the samples were made up to 50 ml., including the reagents. The concentrations were pared in intervals of 4 p.p.m. SO_4 .

After the correct volume of standard solution was added to each Nessler tube, 10 ml. of altered salt acid solution and 5 ml. of 10% barium chloride solution were added. The samples were made up to a volume of 50 ml. with distilled water and allowed to stand for 10 minutes. Next, the samples were shaken thoroughly and allowed to stand an additional 5 minutes. The samples were then ready for analysis.

Procedure:

In a preliminary investigation of the use of the Lumetron photometer, it was learned that the 420 m. monochromatic filter was satisfactory for sulfate determination. The investigation revealed, also, that the use of a 50 m.m. cylindrical cell provided a greater ordinate variation on a curve and was, therefore, more appropriate than other available cells and cuvettes for sulfate determination.

The photometer was allowed to "warm-up" for 10 minutes before the analysis of the standards was begun. The 420 m. filter was then cleaned and placed into its retainer. The galvanometer was adjusted to the zero position, and the instrument was in readiness for use.

The procedure for reading the transmittance of light through the barium sulfate suspensions was as follows:

1. The 0 p.p.m. SO_4 standard (blank) was poured into the 50 m.m. cylindrical cell and the cell placed into the instrument.
2. The sensitivity deflection of the galvanometer was adjusted to 10 units.
3. The transmittance was adjusted to 100%.
4. Each standard was then shaken gently, poured into the cell, and the transmittances read.

Four series of analyses of standard sulfate concentrations varying from 0 p.p.m. to 52 p.p.m. SO_4 , inclusive, were conducted and the results recorded for comparison.

Data and Results:

The data and results obtained in the investigation of the turbidimetric (photometric) method for sulfate determination have been tabulated and presented in Table 4. A graphical presentation of the results has been made in Figure 6.

Table 4 presents the data obtained from the four series of analyses along with a list of instrument particulars which were maintained throughout the investigation.

Figure 6 shows graphically the relationship between light transmittance, and sulfate concentration. The sulfate concentration is plotted arithmetically while the % transmittance is plotted logarithmically. The curve is of best fit "by eye"; a statistical analysis would be of little significance because it is desirable that the analyst re-check the data occasionally with standards when using such a curve in analytical work. A curve which cannot be reproduced constantly and reasonably is of questionable value in photometric analysis.

TABLE 4

Data for Obtaining a Standard Curve for the Lumetron Photometer

Concentrations of Prepared Standards (p.p.m.SO ₄)	Instrument Particulars: Sensitivity Deflection --- 10 units Type Filter --- 420 m. Type Cell --- 50 m.m. cylindrical			
	Observed Dial Readings			
	Series #1	Series #2	Series #3	Series #4
	Transmittance (%)	Transmittance (%)	Transmittance (%)	Transmittance (%)
0	100.00	100.00	100.00	100.00
4	95.75	95.00	95.00	95.50
8	91.00	92.25	91.50	92.00
12	88.00	87.75	89.00	90.00
16	84.25	84.25	84.50	85.00
20	81.50	81.75	81.75	82.25
24	78.00	77.50	75.00	76.50
28	74.00	74.00	72.25	73.75
32	71.00	71.75	71.50	71.00
36	67.75	68.25	69.00	70.00
40	66.00	66.25	63.25	65.00
44	63.25	63.00	63.00	62.25
48	59.25	60.00	59.50	59.50
52	57.50	56.75	57.00	56.00

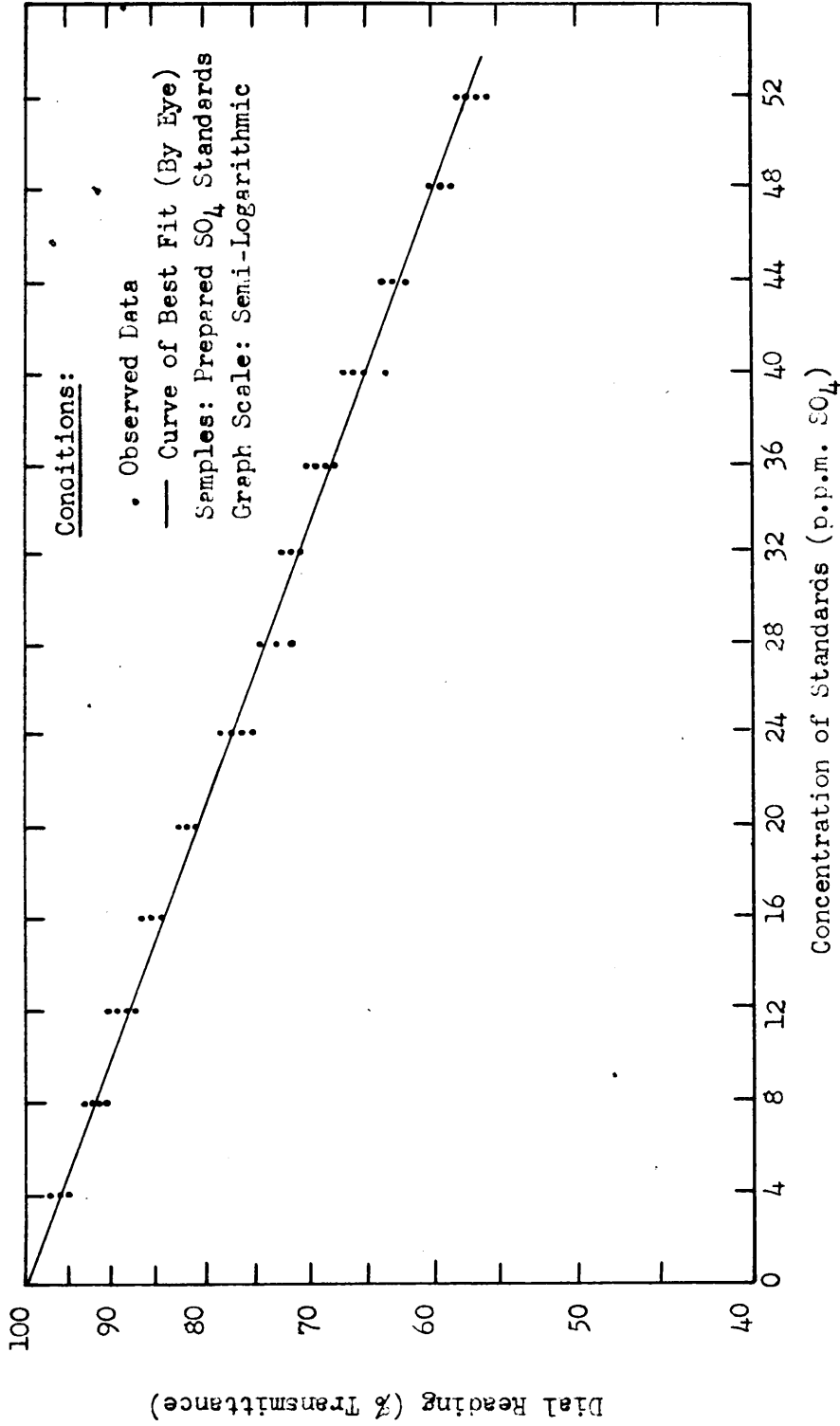


Figure 6.

Relation of Lumetron Dial Readings (% Transmittance) to SO₄ Concentration
for Four Series of Turbidimetric (Photometric) Analyses

Discussion of Results

The results obtained in the investigation of the three methods were, in general, satisfactory and gratifying. The graphical analyses were of particular significance in that certain facts relative to reliability, applicability, and limitations of the methods were indicated.

From the investigation of the gravimetric method it was revealed that a general trend toward lower % errors prevailed at the 200 p.p.m. sulfate concentration (Figure 1). This was interpreted by the author as firm support to the recommendation that samples be adjusted to approximately 200 p.p.m. sulfate concentration for analysis by the gravimetric method⁽¹⁾. Also of significance were the graphical analyses which revealed less variation in total % error at the 200 p.p.m. sulfate concentration (Figure 2) and lower deviations of actual total % error from theoretical % error at sulfate concentrations of 200 p.p.m. and 240 p.p.m. (Figure 3).

From the investigation of the use of the Hellige turbidimetric method as a guide in adjustment of actual waste samples to the recommended 200 p.p.m. sulfate concentration, it was learned, from a statistical analysis of the data obtained, that there exists a high correlation of turbidimetric results with gravimetric results (Figure 4).

Results arising from the investigation of the volumetric method indicated that the applicability of the method to analysis of water and wastes of very low sulfate concentrations would be most appropriate. The trend in total % error with increased sulfate concentration was not definite. The lowest % errors, however, were obtained, generally, at very low sulfate concentrations (Figure 5). The data obtained indicate that the volumetric method could be used where the time consuming concentration of a sample by evaporation in preparation for gravimetric analysis is not permitted.

The results obtained in the investigation of the turbidimetric (photometric) method were, in general, unsatisfactory. Much difficulty was experienced in efforts to produce a stable barium sulfate suspension. Considerable time was spent in experimentation with reagents in an effort to develop the desirable stability of suspension. The attempt was unsuccessful, however, in that such a curve as could be constructed from any of the four sets of data presented in Table 4 would be unreliable; the data are inconsistent and without definite trend in their inconsistency.

Conclusions

The object of the investigation of the three methods for sulfate determination was to evaluate the results obtained by each method from the standpoints of accuracy and applicability. It was anticipated that the results of such an evaluation could be utilized in the selection of an accurate method for a complete analysis of the problem of removal of calcium sulfate deposits from treatment facilities.

From the accuracy analysis of the gravimetric method results, it was determined that a total error of less than 1% prevailed at the recommended sulfate concentration of 200 p.p.m., and that the variation in error (spread) was a minimum at that concentration. Likewise, the deviation in total % error from theoretical % error was relatively small at the recommended concentration. It was, therefore, concluded that the recommendation that the sample be adjusted to approximately 200 p.p.m. was of sound basis and probably represented extensive experimentation.

The statistical analysis of data collected in the investigation of the use of the Hellige turbidimetric method as a guide in adjustment of waste samples to the recommended sulfate concentration for gravimetric analysis indicated a high correlation of the two methods. It was seen that the turbidimetric results

could be used, with a high degree of confidence, in selecting the corresponding gravimetric concentrations from the curve (Figure 4).

The investigation of the volumetric procedure indicated that the method could more appropriately be applied in analysis of samples of very low sulfate concentrations. Such an application of the procedure would eliminate the necessity of concentrating, by evaporation, a sample for analysis by the gravimetric method.

Investigation of the turbidimetric (photometric) method of analysis revealed that inconsistencies were much too prevalent. The curves could not be constantly reproduced, and, therefore, were not reliable.

Since wastes which result in the deposition of calcium sulfate in treatment facilities are very high in sulfate concentration, it was concluded that the gravimetric method of analysis would be the most appropriate method for the analysis of the deposited sulfate.

V. INVESTIGATION OF THE REMOVAL OF CALCIUM

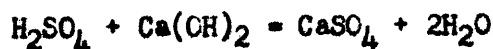
SULFATE DEPOSITS

General

Calcium sulfate, a product of chemical reaction in the neutralization of waste sulfuric acid with lime $\text{Ca}(\text{OH})_2$, is deposited upon the walls and bottoms of reaction chambers and upon the internal surfaces of pipe lines. The deposits are a hard, resistant material resembling well-stratified sandstone or limestone. Such deposition, if allowed to continue its course, eventually reduces the efficiency of the treatment facility to a point that remedial measures must be employed. The remedy, in the case of a pipe line, may possibly involve replacement of the entire line. Therefore, it is readily seen that a method for the removal of the deposited material is desirable.

Analysis of the Deposited Material

A sample of the material was analyzed prior to the investigation of a method for the deposit removal. The material consisted largely of calcium sulfate, the result of the neutralization of waste sulfuric acid:



The gravimetric method for sulfate determination was used in the primary analysis. In preparation for the sulfate analysis of the material, 3.8146 grams of the dry sample were dissolved in distilled water, with the aid of hydrochloric acid, and diluted to one liter. This yielded a 3,814.6 p.p.m. concentration of the material in solution. The gravimetric sulfate analysis was then conducted.

Results:

Concentration of the material in solution = 3814.6 p.p.m.

Sulfate concentration of the solution

(gravimetric) = 2109.4 p.p.m. SO_4

Equivalent weight of SO_4 = 48.03

Equivalent weight of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ = 86.09

Sulfate concentration of solution as

$$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = (2109.4) \left(\frac{86.09}{48.03} \right) = 3780.0 \text{ p.p.m.}$$

$$\% \text{CaSO}_4 \cdot 2\text{H}_2\text{O} = \frac{3780.0}{3814.6} = 99.2$$

The results of the analysis of the deposit sample revealed that the material consisted almost entirely of sulfate, expressed as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

Media Employed in the Primary Investigation

Small portions of the deposit were immersed in various solutions in an effort to determine which chemical agents, if any, would react with the material. The solutions used in the preliminary investigation were of various concentrations and consisted of the following:

- (1) Ferrous ammonium sulfate
- (2) Ferric ammonium sulfate
- (3) Stannous chloride
- (4) Calgon (a commercial metaphosphate)
- (5) Hydrochloric acid
- (6) Glycerine and alcohol
- (7) Ammonium chloride
- (8) Ammonium molybdate
- (9) Sodium hydroxide and alcohol

The sodium hydroxide and alcohol solution was the only one among those listed that indicated any significant tendency toward disintegration of the sample. The results were encouraging, however, and led to further investigation of the effect of the sodium hydroxide-alcohol solution upon samples of the material.

Development of the Successful Medium

Twelve solutions containing various concentrations of sodium hydroxide, alcohol, and water were prepared. Material samples were immersed in these solutions in order to determine the most effective concentration. Time of immersion and conditions of the immersed samples at the different time intervals were recorded. The results of the primary investigation were interpreted and used as a guide to further investigation of a concentration which apparently was most effective in the disintegration of the sample. The concentration of sodium hydroxide was held constant and the water and alcohol concentrations were varied in the second series of five solutions prepared. The results of the second investigation were of no consequence in that the results of the previous investigation were not reproduced. In a third series of four solutions, the water and alcohol concentrations were varied while the sodium hydroxide concentration was held constant but at a greater value than that employed in the second series of five solutions. The results of the third investigation were completely satisfactory in that one sample completely collapsed overnight.

Throughout the three primary investigations, the solutions were mixed by weight percentages. For this reason, it was thought, difficulty was experienced in reproducing the results of each preceding investigation. It was decided that inconsistencies in mixing could be eliminated by using titration as a guide in adjusting the solutions to the desired sodium hydroxide concentrations.

The sodium hydroxide concentration of the most effective solution used in the primary investigation was checked by titration. The actual concentration was found to be 5% greater than was indicated by the weight percentage mixture. This information was used in selecting the proper concentrations for mixture as adjusted by titration.

A series of four solutions were then mixed and adjusted, as determined by titration, to the desired concentrations. Alcohol was added next, in various concentrations, by per cent of total initial volume of the sodium hydroxide-water solution. The material samples were immersed in the prepared solutions, and the progress of the investigation was recorded at various time intervals. The results obtained were satisfactory.

A second investigation of the effective concentration, adjusted as determined by titration, was conducted in an effort to determine the effect of the solution upon different types of

samples (i.e., samples taken from pipe lines and from reaction chambers). The sodium hydroxide concentration was held constant in a series of six solutions, and the alcohol concentrations were varied in an effort to determine the effect of different alcohol concentrations on the reaction. Duplicate material samples were immersed in the prepared solutions, and the observations were recorded at different time intervals. Results of the previous investigation were reproduced.

Data and Results:

The data and results obtained in the development of the successful medium (sodium hydroxide-water-alcohol solution) have been recorded and presented in Tables 5 to 10, inclusive.

Tables 5 and 6 show the results of the primary investigation in the development of the sodium hydroxide-water-alcohol solution. The results obtained indicated that the effective concentrations were 10, 20, and 30% sodium hydroxide solutions with 5% alcohol concentration.

Table 7 presents the data obtained in further investigation of the 10% sodium hydroxide solution with varying concentrations of alcohol. The results of Tables 5 and 6 were not reproduced.

Table 8 shows the results of the investigation of a 15% solution of sodium hydroxide with the alcohol concentration varying. Good results were obtained, but they were not consistent with results of the previous investigations.

The results shown in Tables 6, 7, and 8 indicated that the preparations of the solutions were inconsistent and that titration should be used as a guide in adjustment of the solutions to the desired sodium hydroxide concentrations. All subsequent mixing was performed in this manner and the alcohol was added as % of the initial total volume of the sodium hydroxide-water solution.

Table 9 presents the data obtained in the investigation of 15% and 25% sodium hydroxide solutions with alcohol concentrations of 0% and 3%. The results indicated a 15% sodium hydroxide solution with 3% alcohol as the effective solution. For the other solutions, the results were relatively insignificant.

Table 10 shows the results of further investigation of the effective solution (15%) with varying alcohol concentrations. Pipe samples and pit samples were immersed, in duplicate, in the prepared solutions. All previous investigations were conducted with pit samples only. It was desired, therefore, to determine the effect of the solution upon pipe samples, which were apparently slightly different in that they contained

foreign matter not present in the pit samples. It was seen that the 15% sodium hydroxide solution was the most effective solution but that the effective alcohol concentration was higher for pit samples (3%) than for pipe samples (1%). The results shown in Table 10 were conclusive, since the results shown in Table 9 were reproduced.

TABLE 5
Results of Primary Investigation of the Effect of Various Concentrations
of the Sodium Hydroxide-Water-Alcohol Solution Upon Pit Samples

Solution*			Condition of Sample		
NaOH (%)	H ₂ O (%)	Alc. (%)	After 72 Hrs. Immersion	After 24 Hrs. "Air Drying"	After Additional 24 Hrs. Immersion in Supernatant
2	96	2	Surface softened	No change	No change
5	90	5	Surface softened	No change	Softened to 1/8" depth
7	86	7	Surface softened	No change	Softened to 1/8" depth
5	85	10	Surface softened	Very porous and crumbly	Crumbled with slight pressure
5	75	20	Surface softened	Very porous and crumbly	Crumbled with slight pressure
5	65	30	Surface softened	Very porous and crumbly	Crumbled with slight pressure

* Mixtures are by weight percentages.

TABLE 6
Results of Primary Investigation of the Effect of Various Concentrations
of the Sodium Hydroxide-Water-Alcohol Solution Upon Pit Samples

Solution*		Condition of Sample			
NaOH (%)	H ₂ O (%)	Alc. (%)	After 72 Hrs. Immersion	After 24 Hrs. "Air Drying"	After Additional 24 Hrs. Immersion in Supernatant
10	85	5	Softened deeply. Peeling and flaking apparent.	Very porous and crumbly	Completely dissolved
20	75	5	Softened deeply. Peeling and flaking apparent.	Very porous and crumbly	Completely dissolved
30	65	5	Surface softened	Very porous but still firm	Completely dissolved
8	8	84	No change	No change	No change
12	12	76	No change	No change	No change
16	16	68	No change	No change	No change

* Mixtures are by weight percentages.

TABLE 7
Investigation of the Effective Concentration Range as Indicated by
Results of Primary Investigation

Solution*		Condition of Sample				
NaOH (%)	H ₂ O (%)	Alc. (%)	After 24 Hrs. Immersion	After Additional 24 Hrs. Immersion	After 24 Hrs. "Air Drying"	After Additional 48 Hrs. Immersion in Supernatant
10	80	10	Softened to moderate depth	Softened to greater depth	Buoyant and very crumbly	No change
10	82	8	Softened to moderate depth	Softened to greater depth	Buoyant and very crumbly	Softened to degree flow would erode material
10	85	5	Softened to moderate depth	Softened to greater depth	Buoyant and very crumbly	Softened to degree flow would erode material
10	88	2	Surface mushy	Surface considerably softer	Buoyant and very crumbly	Softened to degree flow would erode material
10	90	0	Surface softened	No change	Slightly crumbly	No change

* Mixtures are by weight percentages.

TABLE 8

Investigation of the Effective Concentration Range as Indicated by
Results of Primary Investigation

Solution*		Condition of Sample			
NaOH (%)	H ₂ O (%)	Alc. (%)	After 24 Hrs. Immersion	After Additional 48 Hrs. Immersion	After Additional 72 Hrs. Immersion
15	80	5	Softened to moderate depth	Parted in layers but not completely dissolved	"Flushing condition"***
15	82	3	Completely collapsed. "Flushing condition"	Only fine precipitate remained	
15	84	1	Softened to moderate depth	Softened to greater depth	"Flushing condition"
15	85	0	Softened to moderate depth	Softened to greater depth	No change

* Mixtures are by weight percentages.

** The term "Flushing condition" indicates that the material could be removed with normal flow.

TABLE 9
Investigation of Concentrations Determined by Titration in Mixing

Solution*		Condition of Sample		
NaOH (%)	Alc. (%)	After 24 Hrs. Immersion	After Additional 24 Hrs. Immersion	After Additional 48 Hrs. Immersion
15	0	No change	No change	Surface softened only slightly
15	3	Disintegration in progress	Completely collapsed. "Flushing condition"	Only flaky precipitate remained
25	0	No change	Surface softened slightly	No change
25	3	Surface softened	Softened to greater depth	Surface flaking

* NaOH concentrations are volume percentages as determined by titration.
 Alcohol concentrations are percentages of initial NaOH-H₂O solution volumes.

TABLE 10
Investigation of Effect of the Solution Upon Duplicate Pit and Pipe Samples

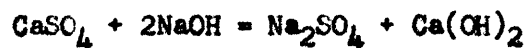
Solution*		Condition of Samples		
		After 24 Hrs. Immersion	After Additional 24 Hrs. Immersion	After Additional 48 Hrs. Immersion
Pit Samples	NaOH (%)			
	Alc. (%)			
	15	0	Surfaces softened only slightly	No change
	15	1	Surfaces softened only slightly	No change
Pit Samples	15	3	Completely collapsed. "Flushing condition"	Only fine precipitates remained
	15	5	No change	No change
Pipe Samples	15	0	No change	No change
	15	1	Disintegration in progress	"Flushing condition"
	15	3	No change	No change
	15	5	No change	No change
				Only fine precipitates remained
				No change
				No change
				No change

* NaOH concentrations are volume percentages as determined by titration. Alcohol concentrations are percentages of initial NaOH-H₂O solution volumes.

Analysis of the Products of Reaction

For the purpose of determining the nature of the chemical reactions which occurred when material samples were immersed in the sodium hydroxide-alcohol-water solutions, complete analyses of the products of the reactions (precipitate and supernatant) were conducted.

Because the relative activities of Ca^{++} and Na^+ are doubtful⁽⁵⁾, it was desired to determine, by analyses of the products of reactions, whether the reactions were analogous to the chemical equations,



where:

CaSO_4 is the main constituent of the deposited material and CaCO_3 represents impurities in the lime used in neutralization of acid wastes. Such impurities naturally would be deposited along with the calcium sulfate, the normal product of neutralization.

From inspection of the two equations, it could be seen that if the reactions followed the two equations, sodium sulfate and sodium carbonate, both of which are highly soluble, would be present in the supernatant solution. According to the two equations, calcium hydroxide would be present in the precipitate.

Analysis of Supernatant:

A sulfate analysis (gravimetric) of the supernatant was conducted. Following the sulfate analysis, the hydroxide (OH) and carbonate (CO₃) concentrations were determined by titration. The results were as follows:

SO ₄ as Ca(OH) ₂	= 23.07 %
OH as Ca(OH) ₂	= 21.87 %
CO ₃ as Ca(OH) ₂	= <u>1.86 %</u>
Total	46.80 %

The remainder of the supernatant was assumed to consist of water.

Analysis of Precipitate:

The analysis of the precipitate was conducted by the same methods used in the analysis of the supernatant. It was necessary, however, to prepare a solution by dissolving a quantity of dry precipitate, by boiling, in distilled water. Since

boiling was required to dissolve a small portion of the precipitate, it was anticipated that the precipitate contained calcium sulfate, which is moderately insoluble at low temperatures. The presence of calcium sulfate in the precipitate could be explained by incompleteness of the chemical reactions of the sodium hydroxide-alcohol-water solution with the calcium sulfate. The results of the analysis were as follows:

SO ₄ as Ca(OH) ₂	=	17.83 %
OH as Ca(OH) ₂	=	75.43 %
CO ₃ as Ca(OH) ₂	=	<u>10.44 %</u>
Total		103.70 %

Error in analysis = 3.70 %

From the results of the analyses of the supernatant and precipitate, it was concluded that the chemical reactions which occurred in disintegration of the material were of the nature indicated by the two chemical equations presented.

Final Investigation of the Medium

In preparation for a final test of the effect of the developed sodium hydroxide-alcohol-water solution upon calcium sulfate deposits, large bulk samples were immersed in the prepared solution. The material selected for the investigation was different, in the manner of deposition, from the two types of samples previously employed. The chemical composition was similar, however, for all of the material samples employed in the entire investigation. The selected sample had been formed on a test plate and its supporting member, over a period of time, while the plate was submerged in a reaction chamber during the process of neutralization of waste acid. The deposited material was hard and very dense.

Prior to the final test, a preliminary test was conducted in order to determine the most effective solution concentration for the type material selected for the final test. Small portions of the material were immersed in various concentrations of the solution, and it was seen that the most effective concentration was a 30% sodium hydroxide solution. Good results were obtained where alcohol concentrations varied from 1% to 3%, but the rates and degrees of reactions were different for the solutions of different alcohol concentrations.

The final test was begun by preparing two 30% sodium hydroxide solutions, one of 1% alcohol concentration and the other of 3%. One bulk sample of the selected material (approximately 50 cubic inches) was immersed in each of the prepared solutions. The conditions of the samples at various time intervals were recorded. The test was successful and conclusive.

Data and Results:

The data and results obtained from the final investigation of the medium have been recorded and presented in Table 11.

The records of progress of the test show that the solution containing 1% alcohol was very effective in the first immersion period, whereas the solution containing 3% alcohol seemed only mildly effective. The results of the second immersion period, however, revealed that the activity in the solution containing 3% alcohol had accelerated. At the end of the second immersion period, the disintegration of the sample in the solution containing 3% alcohol was more complete than in the solution containing 1%. The results, however, were very satisfactory in both instances.

TABLE 11
Investigation of Effect of the Solution Upon Large Bulk Samples

Volume of Bulk Sample (cu.in.)	Solution*		Condition of Sample		
	NaOH (%)	Alc. (%)	After 72 Hrs. Immersion	After 24 Hrs. "Air Drying"	After Additional 72 Hrs. Immersion in Supernatant
50	30	1	Cracked and crumbly. Considerable precipitate present. Rate of reaction decreased after second day of immersion.	Surfaces of remaining solid portions flaking and peeling.	"Flushing condition." Rate of reaction very slow in second immersion period.
50	30	3	Surface softened. No cracking or flaking apparent.	Surface "blistered" and peeling to considerable degree.	"Flushing condition." Only fine precipitate remained. Results most apparent in second day of second immersion period.

*NaOH concentrations are volume percentages as determined by titration. Alcohol concentrations are percentages of initial NaOH-H₂O solution volumes.

General Proposal for Application of the Method

From the results obtained in the investigation of the removal of calcium sulfate deposits from treatment facilities, the author feels that a general proposal for field application of the method can be presented. It is earnestly suggested, however, that an intensive investigation of the prevailing conditions be made and a complete analysis of the deposited material be conducted prior to any attempt to apply this method in the field. The entire investigation was conducted in the laboratory and is intended to be used only as a guide in the analysis of any existing problem.

The general proposal for application of the method is outlined as follows:

- (1) Conduct a complete laboratory analysis of the deposited material in an effort to determine its chemical composition.
- (2) Conduct a series of laboratory tests, under controlled conditions in order to determine the most effective solution for use.
- (3) Determine the required volume of solution for treatment, and prepare the solution.
- (4) Remove from service the treatment facility.

- (5) Completely fill the treatment facility with the prepared solution, and allow the solution to remain, undisturbed, for 72 hours. The facility must, of course, be by-passed during application of the solution.
- (6) Withdraw and retain the supernatant solution, flush out the facility with water or any other suitable liquid, and inspect the facility.
- (7) If the desired removal of deposits has not been achieved, allow the facility to "air dry" for 48 hours.
- (8) Refill the facility with the supernatant solution, previously withdrawn, and allow the solution to remain, undisturbed, for an additional 72 hours.
- (9) Withdraw the supernatant solution, as before, and flush the facility.
- (10) Inspect the facility. If the desired removal has not yet been achieved, repeat the "air drying" and refilling procedures of (7) and (8). Complete removal should, however, be realized within eight days of treatment.

Cost Studies

In general, the economic considerations in the application of the proposed method for the removal of calcium sulfate deposits should compare favorably with the costs involved in replacement of any unit of a treatment facility.

The latest prices of the required materials are as follows:

- (1) Sodium hydroxide flakes (76%) - - - \$ 80.00/ton
- (2) Alcohol (commercial) - - - \$ 0.40/gal.

Assuming a 30% sodium hydroxide solution with 3% alcohol added is required, then the required sodium hydroxide is approximately 2.35 pounds added to one gallon of water (determined by laboratory experiment). The total volume, 30% sodium hydroxide solution with 3% alcohol added, yielded by 2.35 pounds of sodium hydroxide flakes is calculated as follows:

x = initial volume of sodium hydroxide-water solution

$.03x$ = volume of alcohol added

$1.03x$ = total volume

then:

$$\text{Total Volume (gal.)} = 1.03 \left(\frac{2.35}{17.73} + 1 \right) = 1.03 (1.1325) = 1.168 \text{ gal.}$$

$$\text{Volume alcohol (gal.)} = (.03)(1.1325) = .034 \text{ gal.}$$

$$\begin{aligned} \text{Cost of the solution (per gal.)} &= \frac{(.04)(2.35) + (.034)(.40)}{1.168} \\ &= \$.075/\text{gal.} \end{aligned}$$

$$\begin{aligned} \text{Cost of the solution (per cu. ft.)} &= (.075)(7.5) \\ &= \$.5625/\text{cu. ft.} \end{aligned}$$

Since 1 sq. ft. cross-section area with a 1 ft. depth equals 1 cu. ft., it follows that the cost of the required solution is \$0.5625 per sq. ft. of effective cross-section area per ft. depth of the treatment facility.

From the data presented, it can be seen that the cost of application of the method would, in the case of pipe lines, be generally 5%, or less, of the expense of replacement of the facility.

VI. CONCLUSIONS

The investigation and evaluation of the methods for determination of sulfate revealed that the gravimetric procedure is the most accurate and valid of the methods examined. The volumetric method proved reliable for very low concentrations of sulfate but is of questionable value in the analysis of samples containing large sulfate concentrations. The study revealed that the turbidimetric (photometric) method of analysis is very inconsistent, since the barium sulfate suspension produced is relatively unstable. Efforts to develop reagents for stabilization of the suspension were fruitless.

The study of the removal of calcium sulfate deposits was successful and conclusive in that a sodium hydroxide-alcohol-water solution was developed which will remove the deposited material from treatment facilities. The chemical reaction and the rate and degree of reaction were found to be dependent upon such factors as (a) the physical and chemical compositions of the material, (b) the sodium hydroxide concentration of the solution, (c) the alcohol concentration of the solution, and (d) the time of immersion of the material in the solution.

The author has stressed the importance of a complete preliminary study of prevailing conditions prior to any attempt at application of the proposed method of removing calcium sulfate deposits. It is believed, however, that the general proposal presented in this work can be used as a guide in field application of the method.

VII. SUMMARY

The object of this research was to investigate and evaluate three methods for determination of sulfate and to use the obtained information as a guide in selecting an accurate analytical method with which to conduct a complete analysis of calcium sulfate deposits.

The investigation of the analytical methods revealed that the gravimetric method is most accurate for high sulfate concentrations. This method was selected for all analytical work conducted in the study of the deposited material and in the development of a sodium hydroxide-alcohol-water solution for the removal of the calcium sulfate deposits.

The initial phases of the development of the sodium hydroxide-alcohol-water solution were discouraging in that the results were inconsistent and could not be reproduced. It was believed that such inconsistencies resulted, primarily, from the method of mixing the solutions, since all mixing was done by weight percentages. The method of mixing was revised, and all subsequent mixing was governed by titration of the solution in order to determine the sodium hydroxide concentration. The alcohol was added after the solution was adjusted to the desired sodium hydroxide concentration.

The investigation revealed that, following the immersion period, "air drying" the material had an effect upon the behavior of the sample during the second immersion period. It was seen that the disintegration of more resistant materials could be facilitated by employing such a period for drying the material before a second immersion period.

A cost study revealed that application of the proposed method for removal of calcium sulfate deposits from treatment facilities is economically sound and that the cost of application of the method is very small compared to the cost of replacement of facilities.

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XI. APPENDICES

APPENDIX A

Preparation of Reagents for the Gravimetric Method⁽¹⁾

(1) Barium Chloride Solution:

A 10% (by weight) solution was obtained by dissolving 100 grams of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ crystals (20-30 mesh) in 900 milliliters of distilled water.

(2) Hydrochloric Acid Solution:

A 1:1 solution was prepared by mixing equal parts (by volume) of concentrated HCl and distilled water.

(3) Silver Nitrate-Nitric Acid Wash Solution:

To 500 milliliters of distilled water were added 8.5 grams of AgNO_3 and 0.5 milliliter of concentrated HNO_3 .

(4) Preparation of Gooch Crucibles:

Fine, acid washed asbestos was used for preparing the crucibles. A quantity of the asbestos was immersed in distilled water and allowed to stand overnight before use. Each crucible was then prepared, with the aid of the vacuum apparatus for filtering, by pouring portions of the thoroughly agitated asbestos-water mixture into the crucible and

allowing the suction, produced by the vacuum, to draw the asbestos to the bottom of the crucible, thus forming a firm filter mat. Care was taken to produce a tightly-packed mat of from one-eighth to three-sixteenths inch thickness to prevent loss of the barium sulfate precipitate. "Fiberglas" was not used as a primary layer in the filter mat, the reason being that the crucibles were ignited at 800 °C, which is a higher temperature than the melting point of "Fiberglas." After ignition at 800 °C, the crucibles were allowed to cool and were placed in a desiccator until which time they were tared prior to use in filtering the samples.

APPENDIX B

Preparation of Reagents for the Volumetric Method⁽¹⁾

(1) Hydroxylamine Hydrochloride Solution:

Ten grams of hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$) were dissolved in one liter of distilled water.

(2) Benzidine Hydrochloride Solution:

Eight grams of benzidine ($\text{NH}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{NH}_2$) were placed in an agate mortar and ground to a paste with addition of distilled water. The paste was washed into a liter volumetric flask. Ten milliliters of concentrated hydrochloric acid were then added, and the contents of the flask were made up to one liter with distilled water.

(3) Sodium Hydroxide Solution:

A standard 0.05 Normal solution was prepared from a stock sodium hydroxide solution and checked by titration with 0.02 Normal sulfuric acid.

(4) Phenolphthalein Indicator Solution:

The phenolphthalein solution normally used in the laboratory is suitable for this purpose and was used in the investigation.

APPENDIX C

Preparation of Reagents for the Turbidimetric Method

(1) Barium Chloride Solution:

A 10% solution was used. See appendix A for the preparation procedure.

(2) Altered Salt Acid Solution:

To 500 milliliters of Hellige salt acid solution, 25 milliliters of concentrated HCl were slowly added. The solution was mixed well, and 0.5000 gram of pulverized fullers' earth was added. The solution was agitated and allowed to settle for 20 minutes. The solution was then filtered through Whatman #41 filter paper. To the filtrate, 100 milliliters of C.P. grade glycerine were added while the solution was stirred.

(3) Standard Sulfate Solution:

In preparing standard sulfate concentrations, it was desired to prepare a solution such that 1 milliliter of the solution was equivalent to 0.1 milligram of sulfate as SO_4 . Sulfuric acid of specific gravity 1.84 and purity 96.6% was used for preparing the standard solution. Five and seventy-four one hundredths milliliters of the

concentrated H_2SO_4 were diluted to one liter with distilled water. This provided a solution such that 1 milliliter of the solution was equivalent to 10.0 milligrams of sulfate as SO_4 . Ten milliliters of the first prepared solution were diluted to one liter with distilled water to obtain the desired solution (1 ml. = 0.1 mg SO_4).

APPENDIX D

Calculation of Sulfate as SO₄ (Gravimetric Method)

The barium sulfate precipitate was weighed and the weight (grams) used in calculating results in sulfate concentration as SO₄. The equivalent weights of BaSO₄ and SO₄ were used to convert the weight of the BaSO₄ to weight of SO₄. The method of calculation was as follows:

$$\text{Equivalent weight of BaSO}_4 = 116.71$$

$$\text{Equivalent weight of SO}_4 = 48.03$$

$$(\text{grams BaSO}_4) \left(\frac{48.03}{116.71} \right) = \text{grams SO}_4$$

$$(\text{grams}) \left(\frac{1,000,000}{\text{ml. sample}} \right) = \text{p.p.m.}$$

Then:

$$(\text{grams BaSO}_4) \left(\frac{48.03}{116.71} \right) \left(\frac{1,000,000}{\text{ml. sample}} \right) = \text{p.p.m. SO}_4$$

$$(\text{grams BaSO}_4) \left(\frac{411,500}{\text{ml. sample}} \right) = \text{p.p.m. SO}_4$$

APPENDIX E

Calculation of Sulfate as SO₄ (Volumetric Method)

The calculation of sulfate was based upon results of titration. The sulfuric acid, which existed in a compound with benzidine as a result of chemical reaction, was titrated with 0.05 Normal sodium hydroxide. The results were calculated as follows:

$$\text{Equivalent weight (E.W.) SO}_4 = 48.03$$

$$(\text{ml. NaOH})(\text{Normality NaOH})\left(\frac{\text{E.W. SO}_4}{1,000}\right)\left(\frac{1,000,000}{\text{ml. sample}}\right) = \text{p.p.m. SO}_4$$

$$(\text{ml. NaOH})(0.05)\left(\frac{48.03}{1,000}\right)\left(\frac{1,000,000}{250}\right) = \text{p.p.m. SO}_4$$

$$(\text{ml. NaOH})(9.606) = \text{p.p.m. SO}_4$$

APPENDIX F

Equation for the Curve of Best Fit by the Method of Least Squares (9)

y = p.p.m. SO₄ by Hellige turbidimetric method

x = p.p.m. SO₄ by gravimetric method

n = number of analyses

m = slope

b = the "y" intercept

First normal equation,

$$(1) \sum y = M \sum x + n b$$

Second normal equation,

$$(2) \sum xy = M \sum x^2 + b \sum x$$

For the data presented in Table 2,

$$\sum y = 23,550$$

$$\sum x = 27,696$$

$$\sum xy = 45,714,050$$

$$\sum x^2 = 53,365,866$$

$$n = 16$$

Substituting values in the normal equations,

$$(1) \quad 23,550 = 27,696 m + 16 b$$

$$(2) \quad 45,714,050 = 53,365,866 m + 27,696 b$$

Solving simultaneously,

$$(1) \quad 652,240,800 = 767,068,416 m + (16)(27,696) b$$

$$(2) \quad \underline{731,424,800 = 853,853,856 m + (16)(27,696) b}$$

$$79,184,000 = 86,785,440 m + 0$$

$$\frac{79,184,000}{86,785,440} = m = 0.912$$

Substituting $m = 0.912$ in normal equation (1)

$$23,500 = (27,696)(0.912) + 16 b$$

$$\frac{23,500 - (27,696)(0.912)}{16} = b = -107.509$$

Curve of best fit

$$y = m x + b$$

$$y = 0.912 x - 107.509$$

APPENDIX G

Calculation of the Correlation Coefficient for the Data of Table 2

y = p.p.m. SO₄ by Hellige turbidimetric method

x = p.p.m. SO₄ by gravimetric method

n = number of analyses

r = the correlation coefficient

r² = variance

For the data analyzed,

$$\sum y = 23,500$$

$$\sum x = 27,696$$

$$\sum xy = 45,714,050$$

$$\sum x^2 = 53,365,866$$

$$n = 16$$

The equation for the correlation coefficient,

$$\sum \bar{xy} = \frac{(\sum x)(\sum y)}{n}$$

$$r = \frac{\sum \bar{xy} - \frac{(\sum x)(\sum y)}{n}}{\sqrt{\left[\sum x^2 - \frac{(\sum x)^2}{n} \right] \left[\sum y^2 - \frac{(\sum y)^2}{n} \right]}}$$

Substituting values in the equation

$$45,714,050 - \frac{(23,550)(27,696)}{16}$$

$$r = \frac{\sqrt{\left[53,365.866 - \frac{(27,696)^2}{16}\right] \left[39,267,000 - \frac{(23,550)^2}{16}\right]}}{\dots}$$

$r = .9903$ (indicates strong, dominant relationship)

$$r^2 = \frac{.9903^2}{.9903} = .9807 \quad \therefore 98.07 \% \text{ of data are related.}$$

APPENDIX H

Calculation of Confidence Limits for the Curve of Best Fit

y = p.p.m. SO_4 by Hellige turbidimetric method

x = p.p.m. SO_4 by gravimetric method

n = number of analyses

r = coefficient of correlation

r^2 = variance

(σ_r) = standard deviation of data from curve of best fit

For the data analyzed,

$$\sum y = 23,550$$

$$\sum y^2 = 39,267,000$$

$$n = 16$$

$$r^2 = .9807$$

The equation for standard deviation

$$(\sigma_r)^2 = (1 - r^2) \left[\sum y^2 - \frac{(\sum y)^2}{n} \right] \left(\frac{1}{n - 2} \right)$$

Substituting values in the equation

$$(\sigma_r)^2 = (1 - .9807) \left[39,267,000 - \left(\frac{23,550}{16} \right)^2 \right] \left(\frac{1}{16 - 2} \right)$$

$$(\sigma_r)^2 = 6344$$

$$(\sigma_r) = \pm 79.65$$

For 90% confidence and 14 degrees of freedom (2), t = 1.76

$$\text{confidence limits} = (\pm 79.65)(1.76) = \pm 140.2.$$