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REAGENTS FOR DETERMINATIONS OF TRACE IMPURITIES IN WATER

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ABSTRACT

REAGENTS FOR DETERMINATIONS OF TRACE IMPURITIES IN WATER

Determinations of trace impurities, pollutants, in water are often complicated by a large number of factors which consume a great deal of time. Thus, ideal reagents --- sensitive, specific, stable, water-soluble reagents --- are needed for rapid, spectrophotometric determinations of trace impurities in water. Syntheses, purifications, and characterizations of the naphthol-mono-sulfonic acids are described. In addition, data essential to the quantitative evaluation of various naphtholsulfonic acids is presented. A new method for the determination of nitrate in water is described; the proposed method, which uses 2-nitroso-1-naphthol-4-sulfonic acid, is much more rapid than the presently accepted standard methods for determination of nitrate. Another method, which uses 1-naphthol-4-sulfonic acid for the determination of nitrate and proposed by another worker has been carefully and critically evaluated and found to be satisfactory only under very carefully controlled conditions. A new reagent, sodium 2-nitroso-1-naphthol-5-sulfonate, has been proposed for the rapid, specific, sensitive determination of cobalt in natural waters. Full development of water resources, and the control of pollutants returned to natural-water systems, are dependent upon methods of determining trace constituents; significant contributions toward meeting those needs have been accomplished in this work. The methods can readily be applied to such diverse systems as lakes where agricultural fertilizer run-off may be significant, to effluents from plants in the metallurigical industry, to natural-water systems in highly mineralized areas, and to run-off from strip-mined lands. Effective new research areas are readily identified as an extension of the work reported here; better methods for the determination of nitrate in water, and more sensitive methods for the determination of cobalt in water are envisioned.

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INTRODUCTION

Determinations of trace impurities in water are complicated in many instances, as anyone who has analyzed water samples knows, by the necessity of prior separations for removal of interfering substances, the use of prolonged evaporation steps to concentrate the impurities to concentrations above minimum detection levels, the use of non-aqueous-solvent extractions to enable use of water-insoluble reagents, the necessity of baking to dryness for example to allow nitrations to occur in concentrated acids, the careful regulation of time to control the decomposition of unstable chemical substances in the system, and by many other factors. The long-term objective of this research is to develop ideal reagents; sensitive, specific, stable, water-soluble reagents for rapid, spectrophotometric determinations of trace impurities in water.

The medium-term objective of the research is to study water-soluble, sulfonated *ortho*hydroxynitroso aromatic compounds, particularly sulfonated nitrosonaphthols.

It is believed that this typical group of chelating agents is one among which one or more such ideal reagents may be identified. The well known nitroso-R-salt is one example of this type of reagent. All these compounds react with Fe(II), Co(II), Ni(II), and Cu(II) and probably Pd(II), Pt(II), and Mn(II) in relatively dilute, aqueous solutions to form colored complexes. But as the substituents on the organic reagents are varied the complexes (1) have different stabilities in terms of

formation constants, pH, light sensitivity, and temperature; (2) form at various concentrations; (3) vary in intensity of color; (4) have different oxidation states of the metal atom present; and (5) are formed with various degrees of specificity. It is desired to relate these variations to the structures of the ligand molecules, and in so doing relate the specificity of the chelating functional group for a particular metal ion to the structure of the ligand molecule.

The structural correlations will then be extended to other systems, particularly to those exhibiting steric effects in chelation. Similarly, the development of more highly colored complexes than those presently known should be possible. The preparation and study of such compounds should lead to more sensitive, more specific, water-soluble reagents for the determination of trace impurities in the aqueous environment.

Several short-term problems were first studied believing that they would contribute several new determinations for trace impurities in water while laying the ground work for the medium-term and long-term objectives discussed above. The short-term projects that were proposed prior to the start of this effort were: A. The Spectrophotometric Determination of Nitrate in Water Using 2-Nitroso-1-naphthol-4-sulfonic Acid, B. The Spectrophotometric Determination of Nitrite in Water Using 1-Naphthol-4-sulfonic Acid, C. Effect of the Position of the Sulfonic Acid Substituent on Acidity of the Naphtholic Hydrogen, D. Sodium 2-Nitroso-1-naphthol-5-sulfonate as a Reagent for Cobalt in Water, E. 2-Nitroso-1-naphthol-7-sulfonic Acid, and F. Sodium 2-Nitroso-1-naphthol-8-sulfonic Acid.

During the term of this work, projects A, C, and D were studied in detail as presented in Chapters 1, 4, and, 3, respectively, later

in this report. The work on problem A led to the necessity of the work described in Chapter 2. Chapter 5, a general study of synthesis and characterization of the entire family of these types of compounds, contributed significantly to all six of the near-term objectives.

The attention of the reader is directed to Chapters 1 thru 5 of this report where detailed presentation of the achievements of the project objectives are presented, as are summaries of the research procedures used and the specific results and conclusions that were reached.

The efficiency of assimilation and the long-range effectiveness of research are often related to the effectiveness of communication of the research results, not only to professional peers, but to professionals in other scientific disciplines and to the educated, reading public. In an attempt to facilitate effective communication, Chapter 6 was written to declare, in laymen's language and terms, the findings of the research described in this report.

Chapter 1

THE SPECTROPHOTOMETRIC DETERMINATION OF NITRATE IN WATER USING 2-NITROSO-1-NAPHTHOL-4-SULFONIC ACID

Frank N. Abercrombie* and Albert L. Caskey

I. INTRODUCTION

It has become increasingly apparent within the scientific community, as well as throughout society as a whole, that man must make a greater effort to protect his environment from the effects of natural and unnatural (technical) chemical contamination. Various inorganic-nitrogen compounds are capable of being advantageously utilized in the environment such as in soil fertilization in farming. However, because of their toxic nature, the occurrence of these same compounds, even at the trace impurity level in natural waters, presents an environmental problem of readily recognized importance.

The occurrence of nitrate in natural waters presents a health hazard to humans and livestock consuming this water. E. H. W. J. Burden (1) has reviewed the toxic properties of nitrate with a special emphasis

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given to the potability of water supplies. More than 45 parts per million (ppm) of nitrate-nitrogen is often fatal to infants. Over prolonged periods of time, 15 to 20-ppm nitrate-nitrogen is frequently fatal to livestock. Concentrations of nitrate in natural waters which will not cause death interfere with reproduction, weight gain, and milk production in dairy cattle.

The geographical distribution of nitrate pollution in well waters in the state of Illinois has been discussed by Larsen and Henly (2). They correlated nitrate concentration with well depth, and with geographical and geological areas. In wells of from 0-25 feet in depth, 28 % contained at least 10-ppm nitrate-nitrogen, and 13 % contained more than 23-ppm nitrate-nitrogen. Most of the data for the report by Larsen and Henly was obtained from about 9000 determinations of nitrate, conducted by the Illinois State Water Survey, with some duplication for individual wells. In the opinion of these authors, the Larsen and Henly report indicates that nitrate pollution occurs to such an extent in Illinois that there is reason for concern.

The occurrence of nitrate in natural waters is complicated by the unavailability of an accepted, reliable, rapid, accurate, simple method with which the concentration of nitrate can be determined. Methods suggested for the determination of nitrate concentrations in natural waters are nearly as varied as the chemistry of the element nitrogen. Several methods have utilized the properties of nitrogen(V); the nitrate ion in acidic aqueous media can function as an oxidizing agent and the nitronium ion can function as a nitrating agent. Other methods require the reduction of nitrate to nitrite; the nitrite then acts as an oxidizing, nitrosating,

or diazotizing agent. Nitrate ion can also be reduced to ammonia; the ammonia can be measured by distillation or Nesslerization.

There are a number of reviews which describe many of the proposed methods for the determination of nitrate (3-12). The American Public Health Association and the American Water Works Association have tentatively accepted (13) the phenoldisulfonic acid and brucine methods for use in determining nitrate concentrations. The phenoldisulfonic acid method requires extensive sample pretreatment, including evaporating the samples to dryness. The brucine method uses a poisonous alkaloid (similar to strychnine) which gives a non-linear concentration curve.

Knowing that 2-nitroso-1-naphthol-4-sulfonic acid reacts rapidly with excess nitrate ion in hot, acidic, aqueous media in near quantitative yields to form 2,4-dinitro-1-naphthol, the development of a simple method for the determination of nitrate was thought to be possible by Caskey and Abercrombie, who reported a preliminary study of the system in 1966 (14). Beer's law was shown to be obeyed, in terms of the nitrate added to the reaction mixture, when both the disappearance of the reagent and the formation of the "nitration product" were followed spectrophotometrically. Caskey and Abercrombie (14) speculated that the "nitration product" was 2-nitro-1-naphthol-4-sulfonic acid, when it was demonstrated to not be 2,4-dinitro-1-naphthol.

Further study revealed that 2-nitroso-1-naphthol-4-sulfonic acid, in significant excess, reacted with nitrate in aqueous perchloric acid to definitely form 2-nitro-1-naphthol-4-sulfonic acid, which yielded a system that obeyed Beer's law with respect to the concentration of nitrate originally present in the system (15). That work, including some refined

data, was described by Abercrombie and Caskey (16). Those findings have served as the basis for the research described in this chapter of this report and are summarized in the text immediately following.

The spectra of the three compounds of interest in the study were sufficiently different that it was easy to follow the course of the nitration reactions spectrophotometrically. The spectral characteristics of these compounds are presented in Figure 1 and in Table 1. The symbols 2-NO, 2-NO_2, and 2,4-NO_2 represent 2-nitroso-1-naphthol-4-sulfonic acid, 2-nitro-1-naphthol-4-sulfonic acid, and 2,4-dinitro-1-naphthol, respectively.

The stability of the analytical chemical reagent, 2-nitroso-1-naphthol-4-sulfonic acid, was studied as a function of temperature, length of the heating interval, and perchloric acid concentrations. 2-Nitroso-1-naphthol-4-sulfonic acid does not significantly decompose when heated for less than 2 hours in concentrations of perchloric acid of less than 4.9 N and in temperatures of less than 50 ^{o}C. Increasing the temperature or perchloric acid concentration causes decomposition of 2-nitroso-1-naphthol-4-sulfonic acid.

The product formed by the reaction of 2-nitroso-1-naphthol-4-sulfonic acid with excess nitrate in hot, acidic, aqueous solutions was isolated, characterized, and clearly reaffirmed to be 2,4-dinitro-1-naphthol.

2-Nitro-1-naphthol-4-sulfonic acid was prepared by the "nitration" and oxidation of 2-nitroso-1-naphthol-4-sulfonic acid. The potassium salt of 2-nitro-1-naphthol-4-sulfonic acid was isolated, characterized, and reaffirmed to exist as a monohydrate.

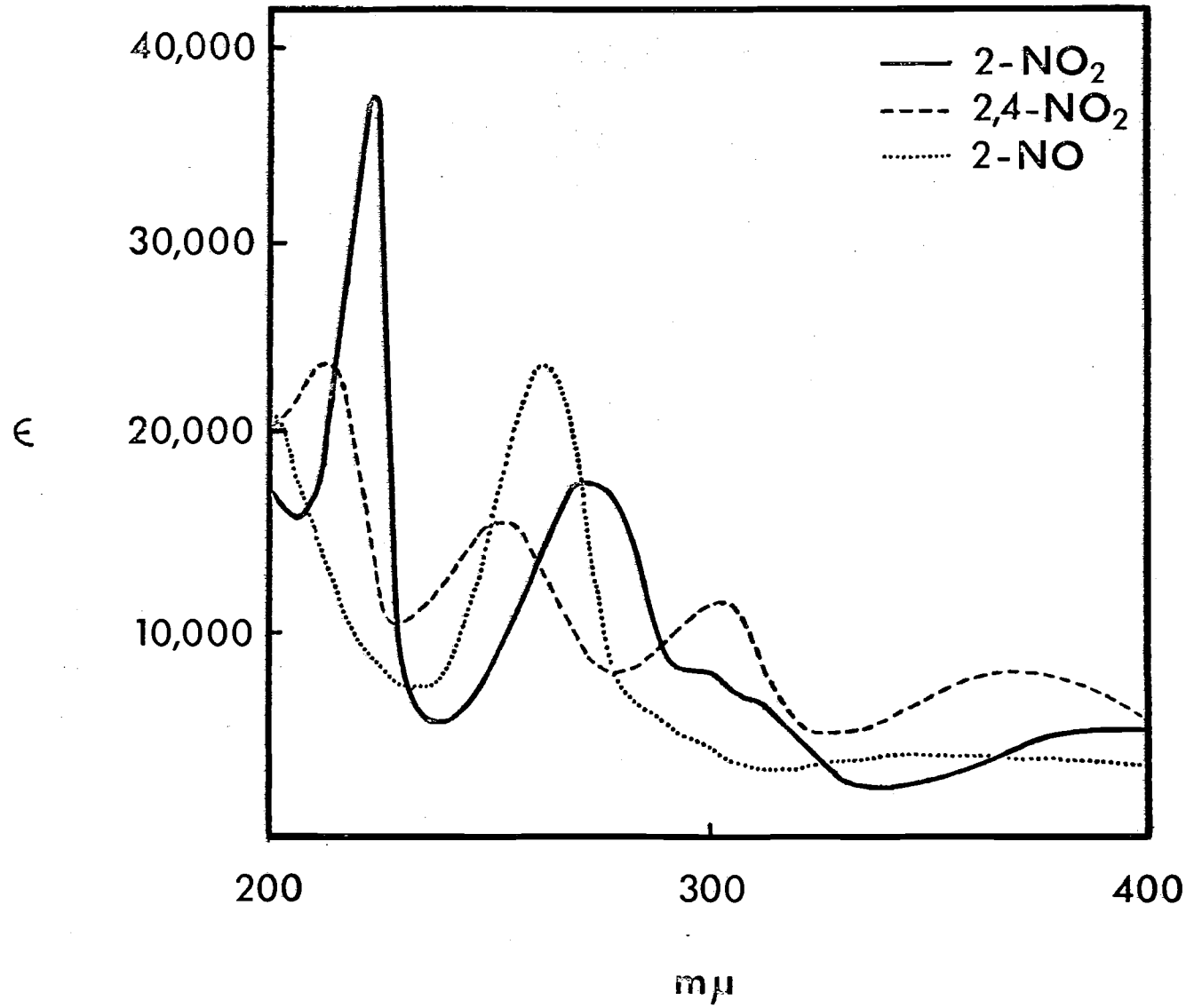


Figure 1. Ultraviolet spectra of 2-nitroso-1-naphthol-4-sulfonic acid, 2-nitro-1-naphthol-4-sulfonic acid, and 2,4-dinitro-1-naphthol

Table 1. Ultraviolet Absorption Spectra (16)

2-Nitroso-1-naphthol-4-sulfonic acid		2,4-Dinitro-1-naphthol		2-Nitro-1-naphthol-4-sulfonic acid	
λ_{max} (mμ)	ε	λ_{max} (mμ)	ε^a	λ_{max} (mμ)	ε^a
261	27,000	210	22,400	221	38,700
347	5,000	249	16,800	270	21,300
		299	12,300	295	9,610
		375	8,450	387	5,280

[a]From slopes of Beer's law plots, calculated via IBM 1620 computer from the original data.

Excess 2-nitroso-1-naphthol-4-sulfonic acid reacted with nitrate ion in 8.44 N perchloric acid at 50.5 °C within 45 minutes to form 2-nitro-1-naphthol-4-sulfonic acid. The absorbance values at the most intense absorption maxima of 2-nitroso-1-naphthol-4-sulfonic acid and 2-nitro-1-naphthol-4-sulfonic acid were shown to be linearly dependent upon the amount of nitrate present. Beer's law was obeyed over a range of 0.3-13 ppm nitrate-nitrogen under the conditions of absorbance measurements.

The main objective of the research reported here was to develop a practical, reliable, sensitive, accurate method for the determination of nitrate using 2-nitroso-1-naphthol-4-sulfonic acid as the analytical reagent. The new method was to be superior to the methods which have been tentatively accepted by the American Water Works Association (13). A secondary objective of the research was to investigate the chemistry of the reaction between nitrate and 2-nitroso-1-naphthol-4-sulfonic acid in aqueous perchloric acid and thus be better able to understand the system and to more readily be able to identify and eradicate possible interferences with the method. Both of these objectives have been successfully satisfied through an extensive study (17) of the chemical system; a portion of these studies have been presented in this chapter of this report. In order to facilitate the acceptance of the method and to better communicate to water and sewage treatment plant personnel, Abercrombie and Caskey (18) have previously presented the practical aspects of the method.

II. EXPERIMENTAL

A. Reagents

Reagent-grade chemicals meeting American Chemical Society specifications were used whenever available. Additional chemicals used were the highest grade available.

The 2-nitroso-1-naphthol-4-sulfonic acid was previously prepared and described by Caskey (19). This compound is also commercially available from the G. Frederick Smith Chemical Company.

The water used was deionized water which had been prepared from distilled water by passing the water through 45 x 400-mm and 38 x 400-mm columns of monobed, self-indicating, ion-exchange resin, Rohm and Haas Amberlite MB3 (Mallinckrodt 322 G). The deionized water was stored free from carbonate.

B. Equipment

A Corning Model 12 pH meter, equipped with a general-use glass electrode, and a fiber-type, saturated-calomel electrode was used to measure the pH of the solutions. The electrode system was calibrated using commercially available buffers.

Beckman Model DB (1401) and DK-1A recording spectrophotometers and a Cary Recording Spectrophotometer, Model 11, were used for the absorbance measurements, along with matched, silica, absorption cells of either 1.00-, 2.00-, or 10.00-cm path length.

Three different types of constant temperature bath controller units were used. They included a Precision Scientific Co. Porta-temp. regulator (Sargent 84875), a Sargent Thermonitor Controlled Water Bath

(Sargent S-84810), and a Sargent Thermonitor Model ST Water Bath (Sargent S-82052).

Borosilicate glassware was used exclusively. All volumetric glassware used was NBS Class A quality. The glassware was cleaned by rinsing seven times with distilled water and drying at 120 ^{o}C. Occasionally, the glassware was washed in a hot-water, Alconox solution prior to the distilled water rinse.

Repipets (Labindustries 3010-A) were also used for delivering solutions in accurate volumes. For one-volume settings, the repipets were found to deliver volumes of distilled water with standard deviation (ml) of 4 x 10^{-4} (2.00), 8 x 10^{-4} (2.00), and 1.7 x 10^{-3} (1.00) for six trials.

C. Experimental Procedure for the Proposed Analytical Method for the Determination of Nitrate in Natural Waters

1. Special Stock Solutions

a. 2-Nitroso-1-Naphthol-4-Sulfonic Acid Reagent

Dissolve 0.1534 g 2-nitroso-1-naphthol-4-sulfonic acid and dilute to 200.0 ml with deionized water to prepare a 2.358 x 10^{-3} M 2-nitroso-1-naphthol-4-sulfonic acid solution. (Distilled water may be substituted if deionized water is not available.)

b. Stock Nitrate Solution

Dissolve 0.3609 g anhydrous potassium nitrate and dilute to 1000.0 ml with deionized water. This solution contains 50.0 mg N/l.

c. Standard Nitrate Solution

Carefully dilute 10.00 ml of the stock nitrate solution to 100.0 ml with deionized water; 1.00 ml = 5.00 x 10^{-3} mg N or 22.2 x 10^{-3} mg NO_3.

d. Cobalt Chloride Solution

Dissolve 0.714 g cobalt(II) chloride hexahydrate in deionized water and dilute to 1000.0 ml to prepare a 2.00×10^{-3} M cobalt solution.

e. Standard Silver Solution

Dissolve 5.89 g silver perchlorate monohydrate or 4.40 g silver sulfate in deionized water and dilute to 1000.0 ml; 1.00 ml is equivalent to 1.00 mg Cl.

f. Potassium Thiocyanate

Dissolve 9.7 g potassium thiocyanate in deionized water and dilute to 1 liter.

To determine the titer of the potassium thiocyanate solution, titrate 25.00 ml of the standard silver solution, 3 drops of Volhard indicator solution, and 3 drops of nitrobenzene with the potassium thiocyanate solution to a faint yellow, orange, or brown color of the end point. The chloride titer [units: mg Cl/ml potassium thiocyanate] is 25.00/ml potassium thiocyanate.

g. Ferric Alum

Place 20 ml deionized water and 0.5 ml nitric acid over ferric alum. Stir intermittently for 8 hours. Decant the supernatant liquid for use as a Volhard indicator.

h. Aluminum Hydroxide Floc

Dissolve 125 g potassium or ammonium alum in 1 liter deionized water contained in a 2-liter (or larger) beaker. Warm to 60 ^{o}C; add 55 ml ammonium hydroxide slowly, with stirring. Wash the floc with 1-liter portions of deionized water by stirring thoroughly, settling, and decanting until the supernatant liquid is free from ammonia, chloride, nitrate, and nitrite.

i. Sulfuric Acid Solution, 1 N

Add 28 ml sulfuric acid to 750 ml deionized water and dilute to 1 liter after cooling.

j. Sodium Hydroxide Solution, 1 N

Dissolve 40 g sodium hydroxide in deionized water and dilute to 1 liter.

k. Potassium Permanganate, 0.1 N

Dissolve 0.316 g potassium permanganate in deionized water and dilute to 100 ml.

2. Assay of Perchloric Acid for Redox Impurities

Place 1.00 ml of the 2-nitroso-1-naphthol-4-sulfonic acid solution in two 100-ml volumetric flasks. Add 2.00 ml of the standard nitrate solution to one of the flasks and sufficient deionized water to each flask to make the volume of liquid in each flask 7.5 ml. Add 10.00 ml of the perchloric acid from the bottle being assayed and heat each flask at 50 ^{o}C for 70 minutes. Add approximately 50 ml cold deionized water to each flask and dilute to volume after equilibration to room temperature. (The cold deionized water is obtained by burying the water bottle in ice. If ice is not available, this can be omitted.) Measure the absorbance of each solution at either 261 or 222 mμ against a deionized water-acid blank containing 10.00 ml perchloric acid/100 ml of volume. If the acid is acceptable for use in this procedure, the absorbances of a 1-cm path of the solution containing nitrate should be 0.51 ±0.03 at 222 mμ and 0.49 ±0.01 at 261 mμ. Also, the absorbances of a 1-cm path of the solution without nitrate should be 0.25 ±0.05 at 222 mμ and 0.57 ±0.02 at 261 mμ, if the acid is acceptable. Perchloric acid from G. Frederick Smith Chemical Co. was found to consistently meet these requirements.

3. Pretreatment of Water Samples

The necessity of using the following procedures must be determined by the nature of the individual water sample.

If iron(II) is present, add 1.00 ml 1 N sodium hydroxide to 75.00 ml of the water sample and stir the solution while bubbling air or oxygen through the solution for 5 minutes. Neutralize the solution to pH 7 ±1 with the 1 N sulfuric acid if the solution is to be treated for color, or add 1.00 ml 1 N sulfonic acid if nitrite is to be removed. An alternate procedure for the removal of iron(II) is discussed later in conjunction with the removal of nitrite.

Decolorize the water sample as necessary by adding 3 ml aluminum hydroxide floc to the treatment sample and stirring for 5 minutes. Filter the slurry through a long-stem 60° funnel fitted with a wash cone of Whatman 40 filter paper. A liquid column in the stem will accelerate the filtration process.

If nitrite or iron is present, add 1 ml 1 N sulfuric acid to the treatment sample and stir. Add dropwise while stirring the 0.1 N potassium permanganate until a faint pink color persists for at least 15 minutes. (A slight excess can be removed by heating and stirring the solution after adding a few pieces of filter paper.) Make the proper deduction at the end of the nitrate determination for the nitrite concentration as determined by the method described in "Nitrogen (Nitrite)" in "Standard Methods for the Examination of Water and Wastewater" (13). Adjust the pH of the solution to 7.

If chloride is present, add with stirring 3 drops of the Volhard indicator solution, 3 drops of nitrobenzene, and a known excess of standard

silver solution to a separate 25.00 ml portion of the water sample. Titrate the solution with the potassium thiocyanate solution to a faint yellow, orange, or brown color of the end point. The volume of silver solution consumed by the chloride present is given by: ml Ag consumed = ml Ag added - ml KCN x KCN titer. The ml of silver solution multiplied by a factor of 3 is the volume of silver solution necessary to remove the chloride from the treatment sample. (If it is necessary to add more than 10 ml of silver solution, prepare a more concentrated silver solution and adjust the volume to be added accordingly.) If the solution contains only a trace of chloride, add 0.1 ml standard silver solution. After stirring, filter the solution through a Whatman 40 filter paper cone in a long-stem 60° funnel pretreated as follows: add 3 ml of the aluminum hydroxide floc to 25 ml of deionized water and after stirring, filter the slurry through the filter paper cone to be used, or use the filter paper cone used previously in the removal of color.

Dilute the sample to 100.0 ml with deionized water if any of the pretreatment procedures were necessary. If pretreatment was not necessary, do not dilute the sample.

4. Treatment of Water Sample and Standard Solutions for Ultraviolet Absorbance Measurements

Place accurately-measured, equal volumes (1.0-6.5 ml) of the pretreated water sample in two 100-ml volumetric flasks. The samples should contain 0.3-20 μg of N; dilute if necessary.

Prepare a series of standard solutions by placing 0.00, 0.20, 0.40, 0.50, 0.75, 1.00, 1.50, 2.00, 2.50, 3.00, 3.50, 4.00, 4.50, and 5.00 ml of the standard nitrate solution in 100-ml volumetric flasks.

Add 1.00 ml of the 2-nitroso-1-naphthol-4-sulfonic acid solution to one flask in each pair of samples and all flasks in the series of standard solutions. Add sufficient water to all flasks to make the volume of solution in each flask 7.5 ml. Add 10.00 ml perchloric acid to each flask, stopper, shake well, and place the flask in a 50 ^{o}C bath. Remove each flask after a time interval of 30-70 minutes and add 50 ml cold deionized water. All flasks should be heated the same length of time $\pm$1 minute. The Beer's law curves will have the greatest slope if the heating time is 70 minutes. After the flasks have equilibrated to room temperature, dilute to volume.

Measure the absorbances, preferably within 1-2 hours at 222 mμ and/or 261 mμ. Use a blank of 10.00 ml of perchloric acid diluted to 100.0 ml with deionized water and 1-cm cells for the standard series solutions. Use the water sample in each pair which does not contain 2-nitroso-1-naphthol-4-sulfonic acid as the blank for the other solution in the pair. The use of the water sample heated in acid can be omitted if the history of the water sample is such that the absorbance at 222 mμ or 261 mμ is insignificant. The water sample blank may then be replaced with the deionized water-perchloric acid blank.

Construct a working curve by plotting absorbance vs. micrograms of nitrogen. Draw the best straight lines through the two linear regions and approximate the curvature at the higher concentrations of nitrate. The intersection of the two, straight-line regions, if both are present, at lower nitrate concentrations is the lower limit for the detection of nitrate for a given sample of perchloric acid. (If a reagent blank correction is necessary for a given lot of perchloric acid, the correction

may be made chemically by adding sodium nitrate [at 1 % excess of the amount equivalent to the blank] to the 2-nitroso-1-naphthol-4-sulfonic acid solution. A new working curve must be prepared if the chemical correction is used.) Only one series of standard solutions is necessary for each bottle of perchloric acid if the variables of temperature and time are the same for subsequent water samples studied at later dates with the same spectrophotometer. If two bottles of perchloric acid are mixed in a gallon container, it is possible to analyze in excess of 350 samples, irrespective of blanks, using the same working curve.

Read the micrograms of nitrogen from the graph for each sample. If a sample of 75 ml was diluted to 100 ml, multiply the amount of nitrogen read from the graph by 1.333; if the original sample was not diluted, omit this operation. The concentration of the nitrogen in the sample is then:

$$\text{mg/l nitrate } \underline{N} = \mu\text{g nitrate-N} \times 1/\text{ml sample}$$

$$\text{mg/l nitrate} = \text{mg/l nitrate-N} \times 4.43.$$

5. Treatment of Water Sample and Standard Solution for Visible Absorbance Measurements

The procedure is the same as that in part 4., except where noted. Use 50-ml volumetric flasks for all solutions. It is not necessary to use paired samples in order to have a blank in this procedure, unless the water sample absorbs at 525 mμ. After preparing the solutions as described in part 3., add 20 ml of ice-cold deionized water to each flask at the end of the heating interval. Empty the contents of each flask and two 1-ml rinsings into a 50-ml beaker; discard the third and fourth rinsings. Add 1.00 ml of the cobalt chloride solution. With stirring, add sodium hydroxide pellets to each beaker until the bright yellow or orange color

persists; add three sets of five pellets and then add the pellets individually after each preceding pellet has dissolved. Adjust the pH of the solution to 7.0 and quantitatively transfer the solution to the original flask. Keep the flask stoppered to exclude carbon dioxide. After equilibration to room temperature, dilute to volume with deionized water. Using a blank of 10.00 ml of perchloric acid diluted to 50.00 ml with deionized water, measure the absorbance of each solution at 525 mμ using a cell path appropriate with the accuracy desired. Construct the standard curve and calculate the nitrogen concentrations as directed in part 4.

D. Titrimetric Studies

The concentration of the perchloric acid was obtained using standard, carbonate-free sodium hydroxide as the titrant, and phenolphthalein as the indicator. A 1.00-ml portion of the concentrated (70 %) acid was transferred to a 100-ml volumetric flask and diluted to volume with deionized water. After the diluted acid was thoroughly shaken, 25.00-, 30.00-, or 40.00-ml aliquots were titrated. When more than one titration trial was reported for a bottle of acid, a different dilute acid solution was prepared from the concentrated acid for each trial. The bottles of concentrated acid were numbered sequentially for reference purposes. This is the number which follows the term "perchloric acid" in the following presentation.

E. General Laboratory Procedures

In all experiments, the following procedures were used: the flasks were shaken after the addition of a solution. This was done to insure mixing. Then the flasks were stoppered. When the flasks were removed from the bath for the addition of a reagent, each flask was returned to the bath before another flask was removed.

The reaction time interval in the constant temperature bath was considered to be the time which elapsed from the addition of the last reactant solution to the addition of the cold deionized water. The cold, deionized water was obtained by immersing a wash bottle in ice, utilizing some care to prevent contamination of the deionized water. All solutions were allowed to equilibrate to room temperature before diluting the solution to volume. All solutions were diluted to volume and shaken before obtaining ultraviolet spectra or absorbance values.

Stock solutions containing sodium nitrate or sodium nitrite were reprepared, using the methods described, when the solutions were depleted or when a solution containing nitrate or nitrite was more than four weeks old in terms of its initial preparation from solid material.

F. General Procedure Used in Preparation and Manipulation of Reaction Solutions

The nitration system was studied under various conditions by preparing series of solutions holding all variables, but one, constant. The absorbance values of the diluted solutions were obtained to determine the effect of the varied independent variable upon the progress of the nitration reaction. The solutions were prepared in volumetric flasks by adding the reagent solutions with a pipet, Repipet, or buret; the flasks were stoppered and shaken after the addition of each reagent solution. Similarly, deionized water was added. The total volume of solution added to each flask in a series was maintained at a constant value by varying the volume of deionized water, when the volume of a reagent solution was varied. Concentrations reported pertain to the resulting solutions. The flasks were equilibrated for 15 minutes in a constant temperature bath, when this was necessary; after equilibration, 2-nitroso-1-naphthol-4-sulfonic

acid solutions were added. The observation of time commenced at the addition of the last reagent solution. At the end of the measured time intervals, ice-cold water was added, the solutions diluted to volume, and the ultraviolet spectral measurements obtained.

III. RESULTS AND DISCUSSION

To develop a reliable, accurate, and precise method for the determination of nitrate, it was considered necessary to study the effects of temperature, time and perchloric acid concentration in order to delimit the optimum conditions for the formation of 2-nitro-1-naphthol-4-sulfonic acid, while minimizing the decomposition of 2-nitroso-1-naphthol-4-sulfonic acid. The decomposition has been shown by Abercrombie (15) to occur at the conditions of temperature and acidity which were necessary for the formation of 2-nitro-1-naphthol-4-sulfonic acid from sodium nitrate and 2-nitroso-1-naphthol-4-sulfonic acid.

A. A Study of the Effect of Time on the Formation of 2-Nitro-1-Naphthol-4-Sulfonic Acid at 50.5 ^{o}C to Determine the Proper Length of Time to Use in Subsequent Studies

The effect of time on the formation of 2-nitro-1-naphthol-4-sulfonic acid from 4.29×10^{-4} M sodium nitrate and 4.29×10^{-4} M 2-nitroso-1-naphthol-4-sulfonic acid in 7.94 N $HClO_4$ has been presented in Table 2. The relatively constant values at the absorption maxima of 2-nitroso-1-naphthol-4-sulfonic acid and 2-nitro-1-naphthol-4-sulfonic acid indicated that the reaction was complete within 5 minutes. A time interval of 15 minutes was selected as the minimum time interval for use in all following studies in which the reaction time was not the independent variable. This was considered to be the minimum time interval which could be reproduced within the limit of error of the spectrophotometers.

Table 2. The Effect of Time on the Formation of 2-Nitro-1-Naphthol-4-Sulfonic Acid from 4.286×10^{-4} M Sodium Nitrate and 2-Nitroso-1-Naphthol-4-Sulfonic Acid at 50.0 °C in 7.94 N Perchloric Acid

Solution Number	Time (min.)	A @ 222 mμ	A @ 261 mμ
327	5.0	1.157	0.482
328	10.0	1.132	0.476
329	15.0	1.156	0.474
330	20.0	1.147	0.472

B. A Study of the Effect of Varied Perchloric Acid Concentrations on the Formation of 2-Nitro-1-Naphthol-4-Sulfonic Acid at Various Temperatures to Determine the Minimum Perchloric Acid Concentration Necessary to Cause Maximum Product Formation

The effect of varied perchloric acid concentrations on the formation of 2-nitro-1-naphthol-4-sulfonic acid from equal-molar, 7.50×10^{-5} M sodium nitrate and 2-nitroso-1-naphthol-4-sulfonic acid at 20-90 °C for 15.0 minutes is presented in Figures 2 and 3. The relatively slight increase in absorbance at 222 mμ indicated that very little 2-nitro-1-naphthol-4-sulfonic acid was formed at 20.0 and 30.0 °C in perchloric acid which was less than 9.5 N. At 40.2 °C, in perchloric acid concentrations of 6-8 and 9.5-11 N, the increase in absorbances at 222 mμ indicated that 2-nitro-1-naphthol-4-sulfonic acid was formed. The greatest amount of 2-nitro-1-naphthol-4-sulfonic acid was formed at 50.0, 50.7, and 71.8 °C in the perchloric acid concentration range of 7-8 N, as indicated by the high absorbance values at 222 mμ. Similar conclusions were drawn by following the decrease in the concentration of 2-nitroso-1-naphthol-4-sulfonic acid at its 261 mμ absorption maximum. The system was studied extensively, and the values presented were a representative sampling of the total study.

The relatively small amount of 2-nitro-1-naphthol-4-sulfonic acid formation in the perchloric acid concentrations of 8.5-9.0 N has been studied in sufficient detail to indicate that a region of acidity does exist where the rate of reaction is much slower than at higher, or lower, concentrations. The reproducibility of the low absorbance values at 222 mμ and higher absorbance values at 261 mμ, for solutions whose acid concentrations fall in this region, show that the results as presented in Figures 2 and 3 were not due to random error.

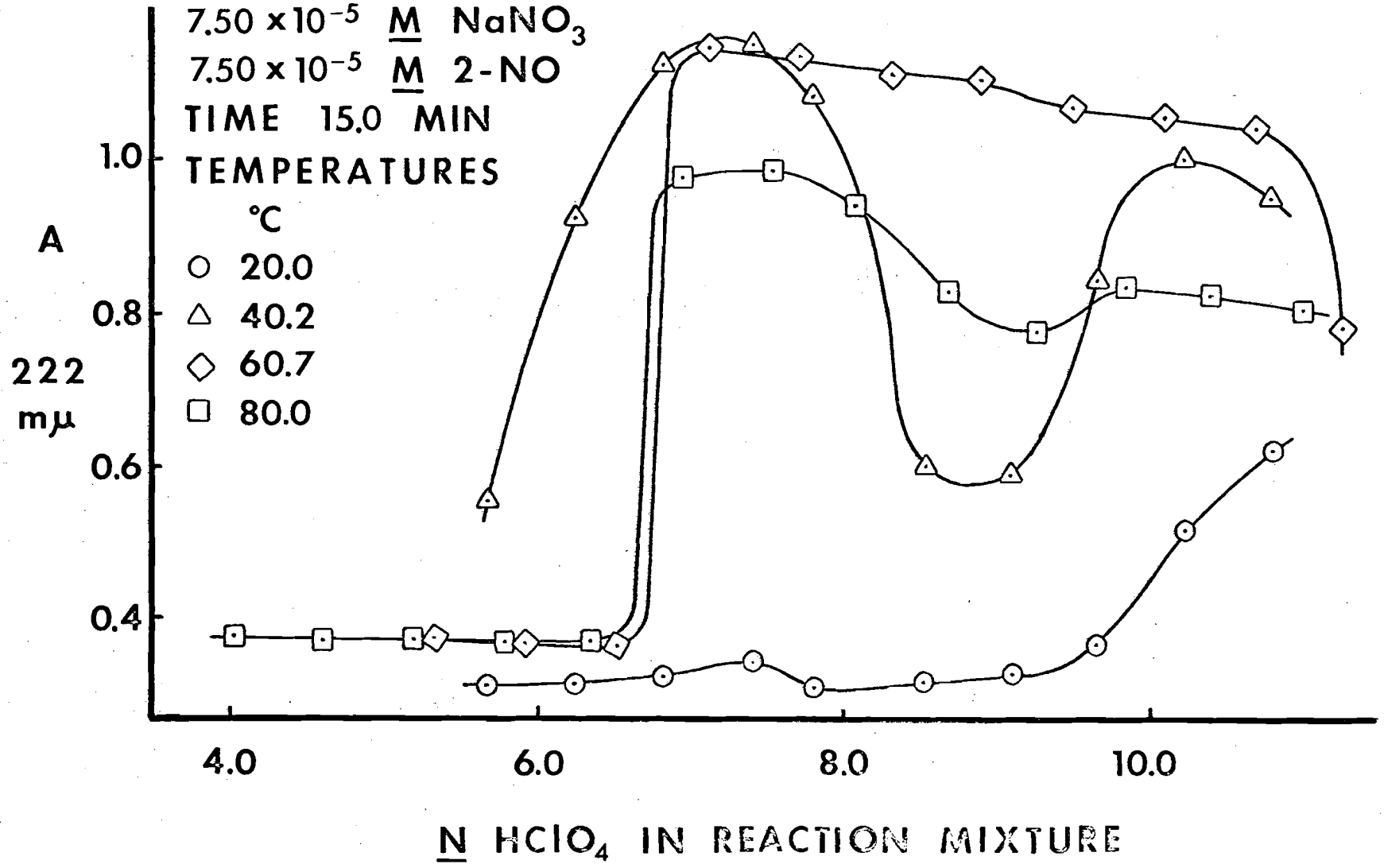


Figure 2. The effect of varied perchloric acid concentration on equimolar concentrations of 2-nitroso-1-naphthol-4-sulfonic acid and sodium nitrate at 20.0, 40.2, 60.7, and 80.0 °C

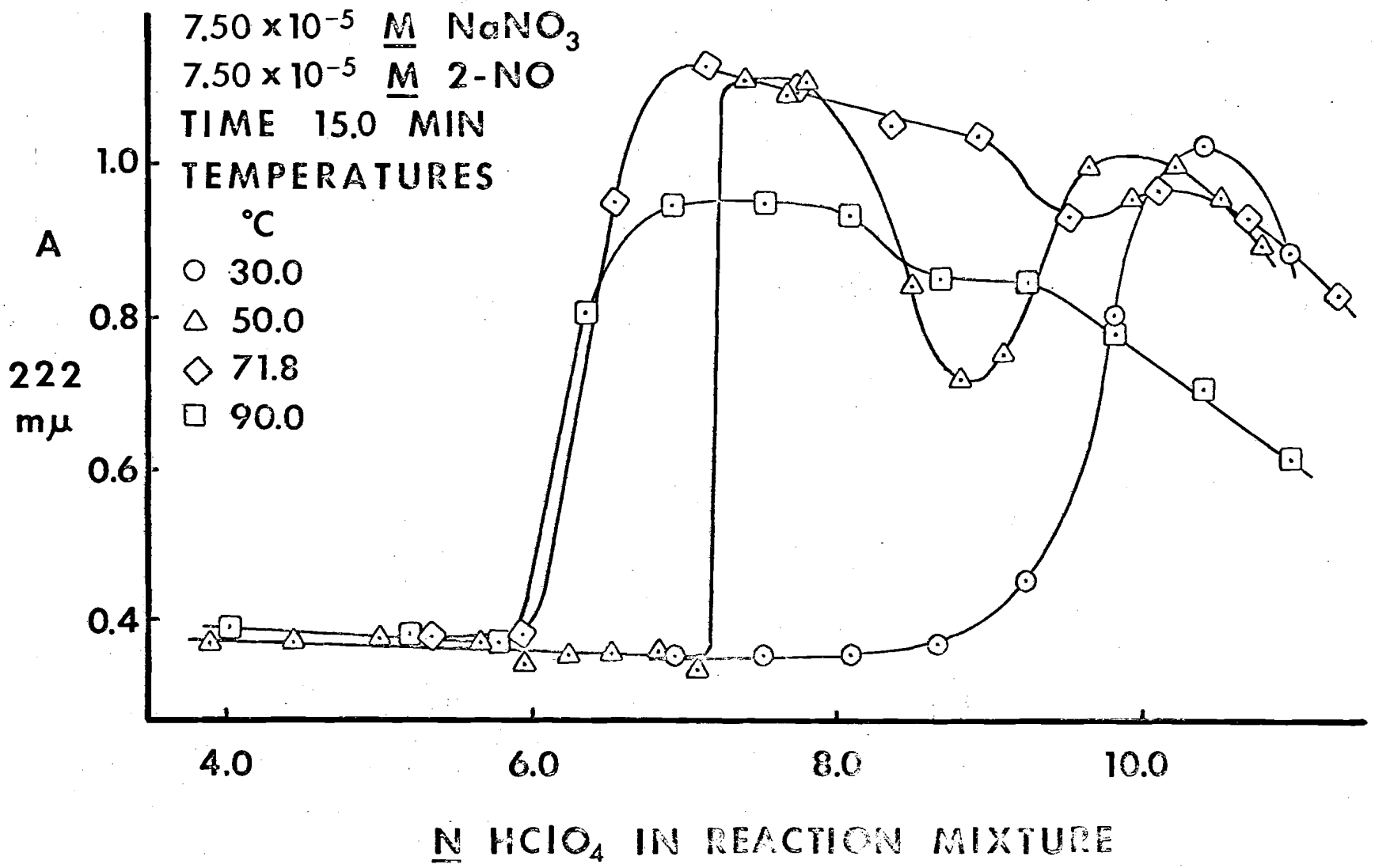


Figure 3. The effect of varied perchloric acid concentrations on equimolar concentrations of 2-nitroso-1-naphthol-4-sulfonic acid and sodium nitrate at 30.0, 50.0, 71.8, and 90.0 °c

The two regions of perchloric acid concentrations, 7-8 and 9.5-11 N, in which 2-nitro-1-naphthol-4-sulfonic acid was formed to a much greater extent than the region of 8.5-9 N perchloric acid was the first evidence in this study which indicated the possibility that 2-nitro-1-naphthol-4-sulfonic acid might have been formed by two different mechanisms from the reaction of nitrate with 2-nitroso-1-naphthol-4-sulfonic acid. Additional evidence to support this possibility was indicated by the dependence upon temperature of the formation of 2-nitro-1-naphthol-4-sulfonic acid in the region of 7-8 N perchloric acid. Relatively no 2-nitro-1-naphthol-4-sulfonic acid was formed at 20.0 and 30.0 ^{o}C in 7-8 N perchloric acid, but the formation of 2-nitro-1-naphthol-4-sulfonic acid at 40.2-90.0 ^{o}C was extensive. In 9.5-11 N perchloric acid, the relative amount of 2-nitro-1-naphthol-4-sulfonic acid formed was not as dependent upon temperature as in the 7-8 N perchloric acid systems. Also, 2-nitro-1-naphthol-4-sulfonic acid was formed from sodium nitrate and 2-nitroso-1-naphthol-4-sulfonic acid in the 9.5-11 N perchloric acid at 20.0 and 30.0 ^{o}C in an amount only slightly lower than that formed at the higher temperatures at the same perchloric acid concentrations.

Also, if it is correct to consider the existence of two mechanisms, then the high acid concentration mechanism occurs at lower and lower acid concentrations with increasing temperature. This is evident from the "tailing" effect noticed in the vicinity of 9.0 N perchloric acid. The increased absorbance values at 222 mμ in the 8.5-9 N perchloric acid region with increasing temperature, accompanied by the general curvature at the higher acid concentrations, suggests that the high acid concentration mechanism is occurring to a greater extent at lower acidities as the temperature increases.

The effect of perchloric acid concentration on the formation of 2-nitro-1-naphthol-4-sulfonic acid from 1.68×10^{-5} M sodium nitrate and 5.47×10^{-5} M 2-nitroso-1-naphthol-4-sulfonic acid at a mole ratio of 0.31 was studied over a temperature range of 40.0-57.5 °C, using a reaction interval of 45.0 minutes. A mole ratio of 0.31 was used because this was considered to be the ratio which would approximate the experimental conditions encountered in an analytical method for determination of nitrate more closely than would equal-molar concentrations. The effect of 5.3-10.3 N perchloric acid on the formation of 2-nitro-1-naphthol-4-sulfonic acid at 40.0, 50.0, and 55.0 °C has been presented graphically in Figure 4. The results of this study were similar to those obtained using equal molar concentrations of sodium nitrate and 2-nitroso-1-naphthol-4-sulfonic acid, with the exception that 2-nitro-1-naphthol-4-sulfonic acid was not formed to any great extent in perchloric acid of 8.0 N, or less, at 40.0 °C.

The effect of perchloric acid concentrations 5.4-7.4 N and seven temperatures in the range of 40.0-57.5 °C on the formation of 2-nitro-1-naphthol-4-sulfonic acid from 1.68×10^{-5} M sodium nitrate and 5.47×10^{-5} M 2-nitroso-1-naphthol-4-sulfonic acid was studied. The system was found to have only a slight dependence upon temperature. The results presented graphically in Figures 5 and 6 for 40.0 and 57.5 °C are representative examples of the results obtained, and define the range of absorbances obtained. The increase in absorbance at 222 mμ indicated that 2-nitro-1-naphthol-4-sulfonic acid was being formed in 6.20 N perchloric acid, but the greatest amount of 2-nitro-1-naphthol-4-sulfonic acid was formed in 6.61-7.44 N perchloric acid at all temperatures studied.

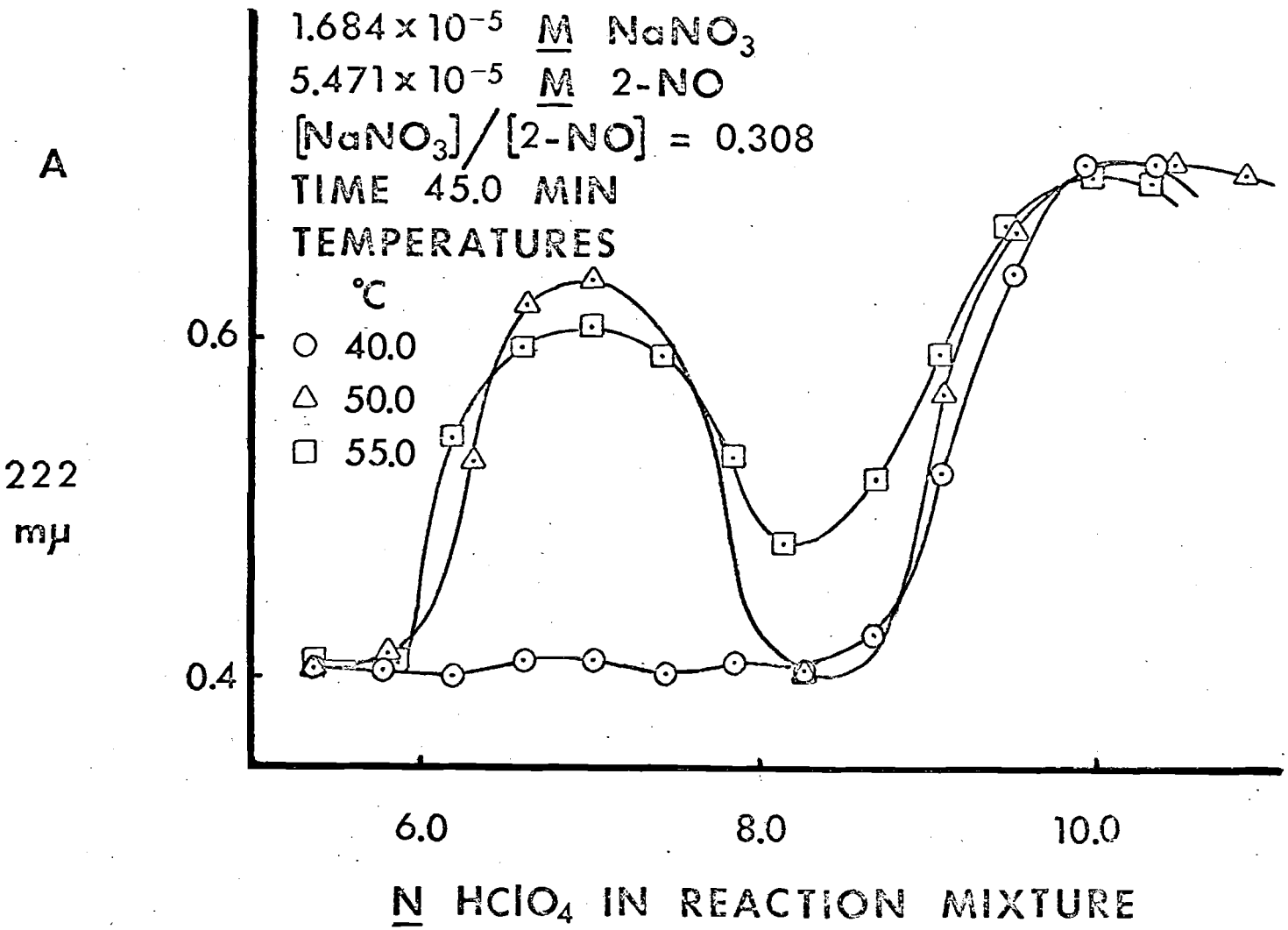


Figure 4. The effect of 5.3-10.3 N perchloric acid on a mole ratio, sodium nitrate:2-nitroso-1-naphthol-4-sulfonic acid, of 0.308 at 40.0, 50.0, and 55.0 °C

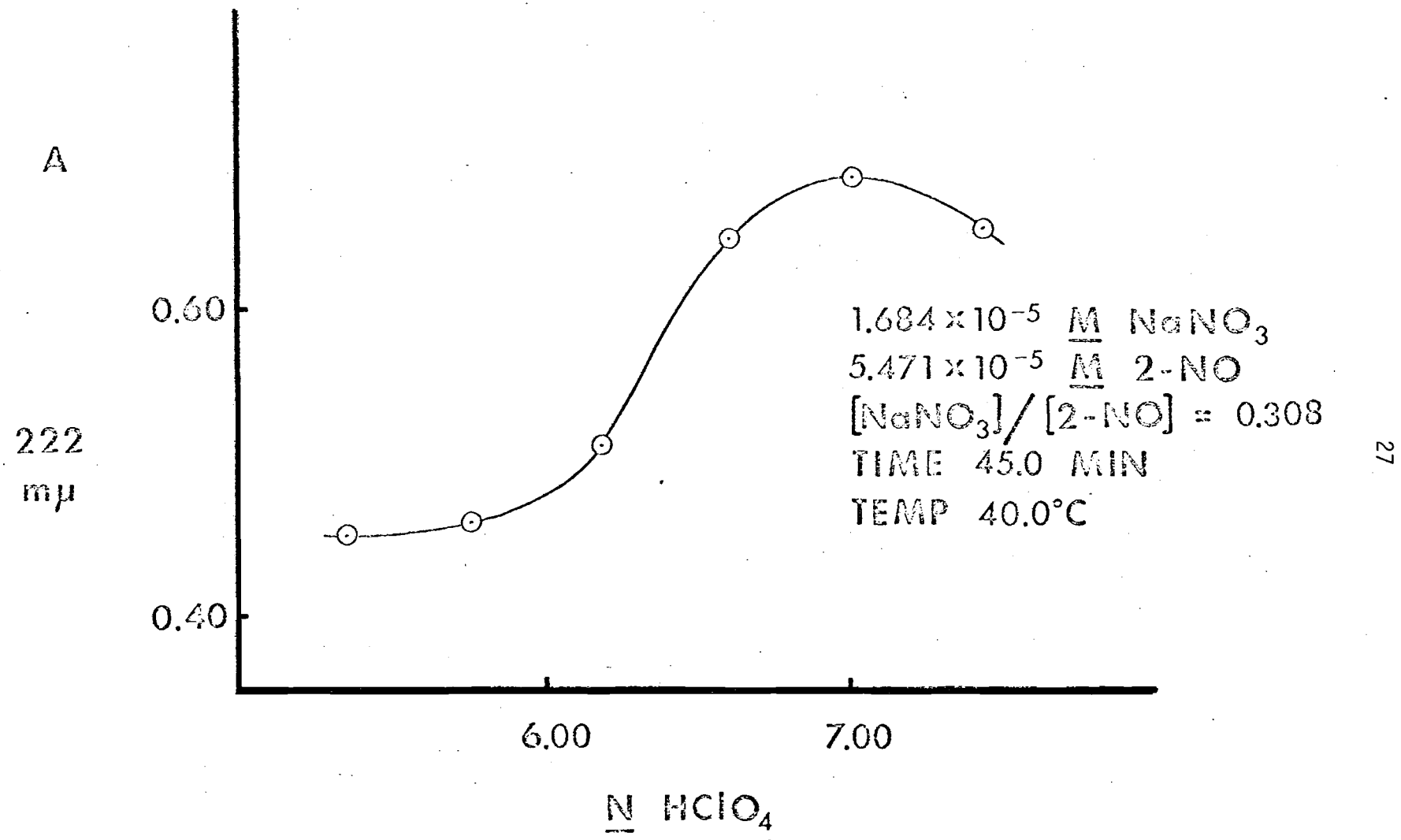


Figure 5. The effect of 5.4-7.4 N perchloric acid on a mole ratio, sodium nitrate:2-nitroso-1-naphthol-4-sulfonic acid, of 0.308 at 40.0 °C

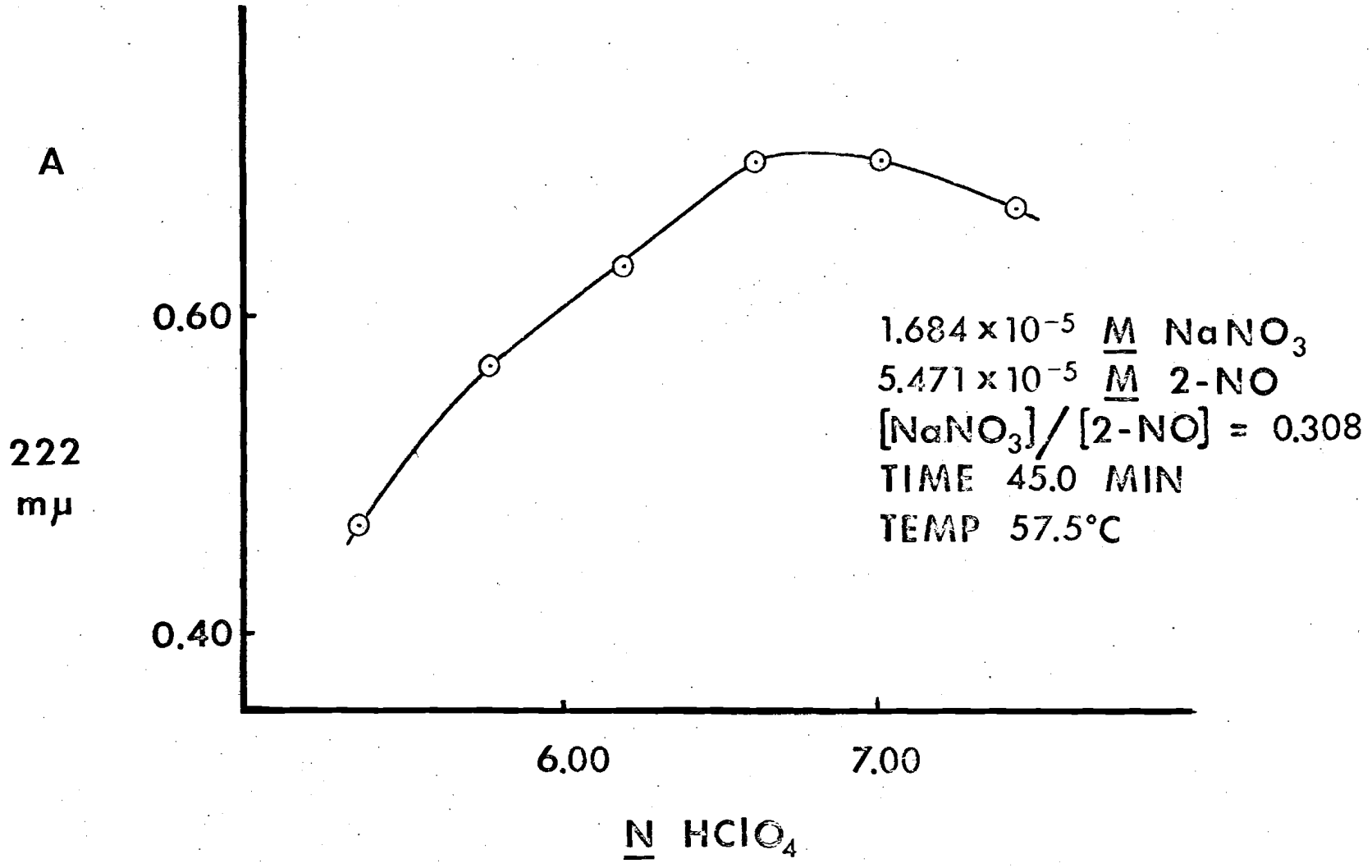


Figure 6. The effect of 5.4-7.4 N perchloric acid on a mole ratio, sodium nitrate:2-nitroso-1-naphthol-4-sulfonic acid, of 0.308 at 57.5 °C

The relative amount of 2-nitro-1-naphthol-4-sulfonic acid was independent of temperature in 6.61-7.44 N perchloric acid. The relative amount of 2-nitro-1-naphthol-4-sulfonic acid formed in 5.37-6.20 N perchloric acid increased slightly with increasing temperature.

C. Qualitative Rate Studies to Compare the Reactions of 2-Nitroso-1-Naphthol-4-Sulfonic Acid

The relative rate at which 2-nitro-1-naphthol-4-sulfonic acid is formed from 1.09×10^{-4} M 2-nitroso-1-naphthol-4-sulfonic acid and 3.37×10^{-5} M sodium nitrate was studied at 50.0, 60.0, and 70.0 °C in 6.73 N perchloric acid. The relative rate of decomposition of 1.09×10^{-4} M 2-nitroso-1-naphthol-4-sulfonic acid in 6.73 N perchloric acid was also studied at 50.0, 60.0, and 70.0 °C to serve as a basis of comparison. The results of these two studies are presented jointly in Figures 7-9. The concentration of perchloric acid chosen for this study was considered to be the minimum concentration which would consistently cause a maximum amount of 2-nitro-1-naphthol-4-sulfonic acid to be formed. The selection of a minimum concentration was considered to be important because of the slow decomposition of 2-nitroso-1-naphthol-4-sulfonic acid, as reported by Abercrombie and Caskey (16). In comparing the results obtained in Figures 7-9, it was apparent by the increase in absorbance values at 222 mμ for solutions containing nitrate that increasing the temperature decreased the time necessary for complete formation of 2-nitro-1-naphthol-4-sulfonic acid. The reaction was essentially complete within 70.0, 30.0, and 20.0 minutes at 50.0, 60.0, and 70.0 °C, respectively. Similar conclusions were reached using 261 mμ absorbance values to follow the decrease in concentration of 2-nitroso-1-naphthol-4-sulfonic acid for

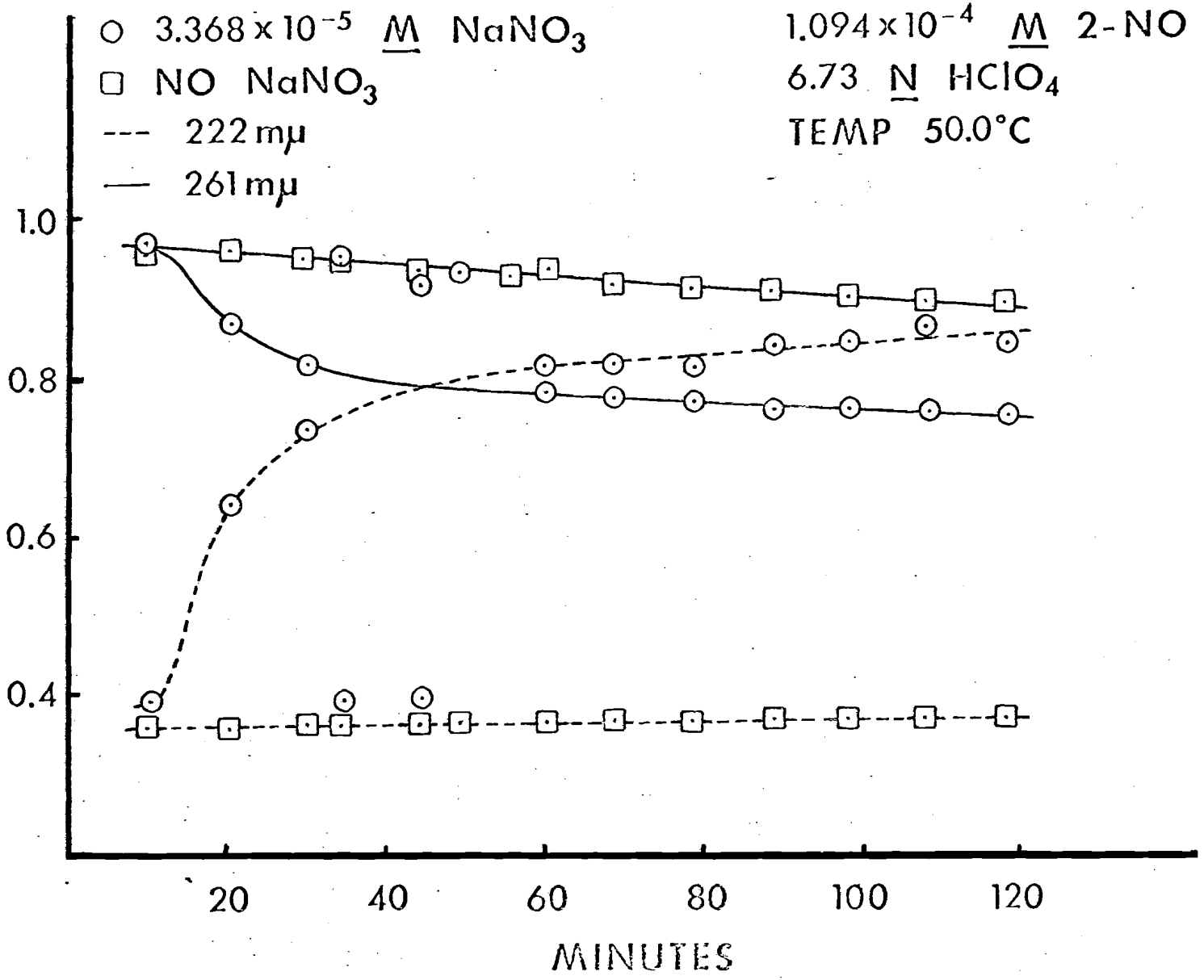


Figure 7. The effect of time at 50.0 °C on the formation of 2-nitro-1-naphthol-4-sulfonic acid and the decomposition of 2-nitroso-1-naphthol-4-sulfonic acid in 6.73 N perchloric acid

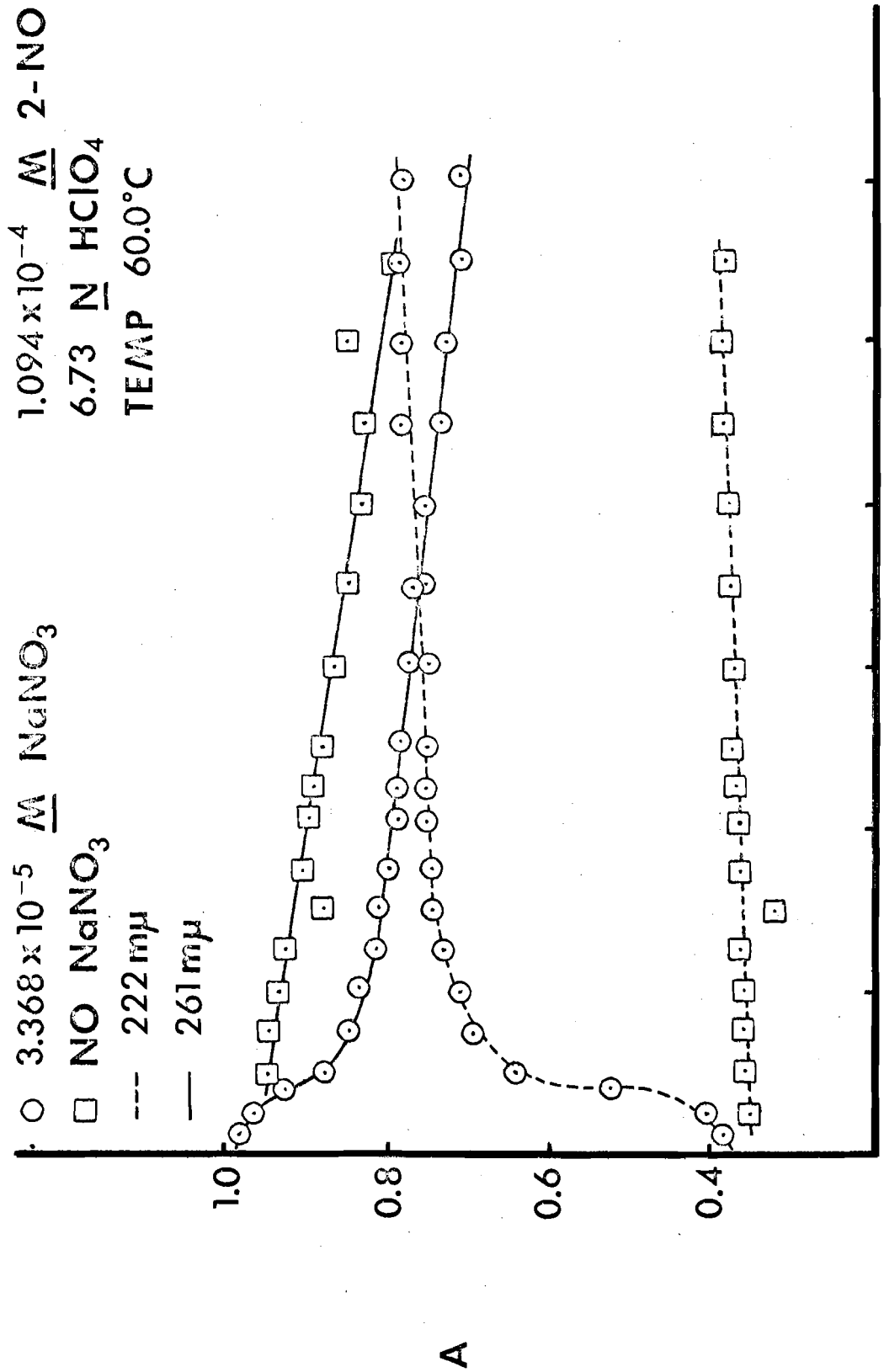


Figure 8. The effect of time at 60.0 °C on the formation of 2-nitro-1-naphthol-4-sulfonic acid and the decomposition of 2-nitroso-1-naphthol-4-sulfonic acid in 6.73 N perchloric acid

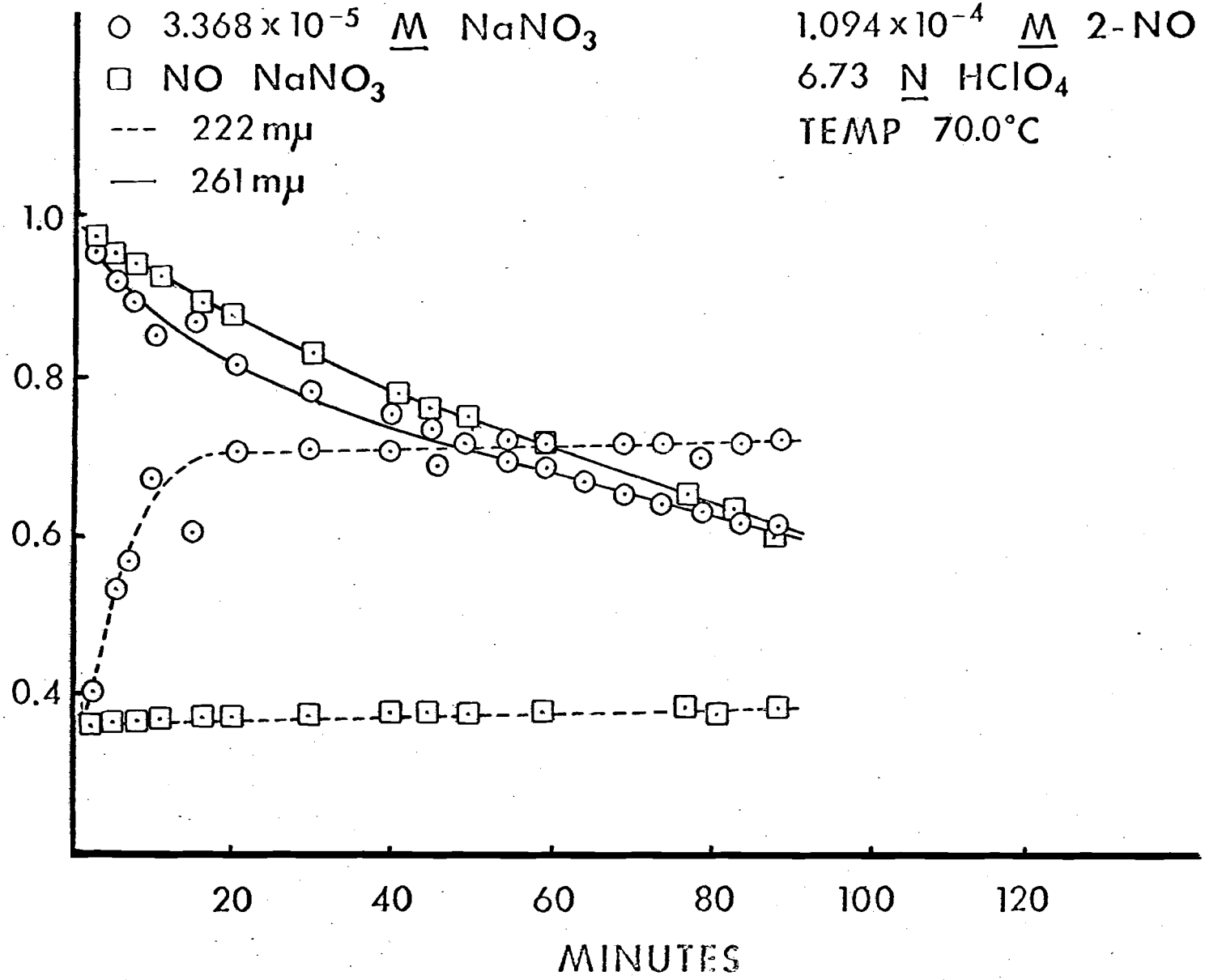


Figure 9. The effect of time at 70.0 °C on the formation of 2-nitro-1-naphthol-4-sulfonic acid and the decomposition of 2-nitroso-1-naphthol-5-sulfonic acid in 6.73 N perchloric acid

solutions containing nitrate. The relatively slight linear change in absorbance at 222 mμ, with increasing time and temperatures for solutions without nitrate, substantiated the use of the 222 mμ wavelength to study the chemical system of sodium nitrate and 2-nitroso-1-naphthol-4-sulfonic acid in perchloric acid. The decrease in absorbance values at 261 mμ for solutions with only 2-nitroso-1-naphthol-4-sulfonic acid indicated that the decomposition of 2-nitroso-1-naphthol-4-sulfonic acid increased with a temperature increase; a marked increase in the relative amount of decomposition occurred between 60.0 and 70.0 ^{o}C. The decomposition at 50.0 and 60.0 ^{o}C was essentially linear with time, but was nonlinear at 70.0 ^{o}C. The nature of the decrease in absorbance at 261 mμ (or the concentration of 2-nitroso-1-naphthol-4-sulfonic acid) at 70.0 ^{o}C, when comparing solutions with and without nitrate heated the same length of time, was such that there would be difficulty in accurately relating a decrease in absorbance at 261 mμ to the amount of nitrate present if a temperature of 70.0 ^{o}C were utilized in an analytical method; however, a temperature of 70.0 ^{o}C would require only 20 minutes of heating if nitrate concentrations were to be measured by an increase in absorbance at 222 mμ.

The differences between absorbance values at 261 mμ from solutions with and without sodium nitrate heated for identical time periods increased significantly from 60.0 to 50.0 ^{o}C. These results suggested that 50.0 ^{o}C and a maximum heating time of 70.0 minutes were probably the most reasonable conditions to utilize in an analytical method for nitrate, if nitrate concentrations were to be related to the decrease in the concentration of 2-nitroso-1-naphthol-4-sulfonic acid through absorbance measurements at

261 mμ or at 525 mμ after formation of the cobalt complex of 2-nitroso-1-naphthol-4-sulfonic acid. Also, even though nitrate concentrations could be determined very rapidly using 60.0 °C for 30 minutes and measuring absorbance values at 222 mμ, the disadvantage of being unable to measure nitrate concentrations at 222 mμ and 261 mμ simultaneously was considered to offset the advantage of the time decrease.

D. The Effect of Varied Sodium Nitrate Concentrations on the Formation of 2-Nitro-1-Naphthol-4-Sulfonic Acid in a Study of Stoichiometry

The results of Experiment B, a study (in systems in which the mole ratio of sodium nitrate to 2-nitroso-1-naphthol-4-sulfonic acid was 1.00 or 0.31) to determine the minimum perchloric acid concentration necessary to cause maximum product formation, suggested the possibility of two mechanisms for the formation of 2-nitro-1-naphthol-4-sulfonic acid from sodium nitrate and 2-nitroso-1-naphthol-4-sulfonic acid. In concentrated perchloric and sulfuric acid systems, the active nitrating specie has generally been considered to be the nitronium ion (20). Halberstadt, Hughes, and Ingold (21) have studied the kinetics of the nitration of 2-phenylethylsulfonic acid in aqueous perchloric acid which had the following typical molecular composition: H_2O, 72; HNO_3, 17; $HClO_4$, 11 mole %. While the concentration of nitric acid was much greater than that used in this work, the concentration of water and perchloric acid used was similar to the 7-8 N perchloric acid concentration range used in this work in which 2-nitro-1-naphthol-4-sulfonic acid was formed from 2-nitroso-1-naphthol-4-sulfonic acid. Halberstadt, *et. al.*, (21) were unable to find any evidence of the characteristc nitronium line at 1400 cm^{-1} in the Raman spectra of their aqueous perchloric acid systems previously mentioned. The assignment of the 1400 cm^{-1} line in the Raman spectra to the nitronium ion was made by Ingold, Millen and

Poole (22) in a study in which misunderstandings concerning the Raman spectra of nitric acid in strong acids was clarified. Ingold, *et al.*, (22) were able to show that a 1050 cm^{-1} line previously assigned to the nitronium ion was, in fact, due to the hydrogen sulfate ion formed by the ionization of the strong acid, sulfuric acid. Halberstadt, *et al.*, (21), with the aid of Raman spectra, were able to determine that the perchloric acid was completely ionized to the perchlorate ion because "the characteristic spectrum of the perchloric acid molecule is entirely absent" (21) in their perchloric acid-nitric acid-water system. By comparison of intensity relationships for the Raman lines for nitric acid and nitrate ion, Halberstadt, *et al.*, (21) were able to estimate that only 4 % of the nitric acid was ionized to nitrate ion. Because of the lack of a detectable amount of nitronium ion in their system, Halberstadt, *et al.*, (21) suggested that the active nitrating agent might perhaps be protonated nitric acid, $H_2NO_3^+$, which was referred to as the nitric acidium ion.

Abercrombie and Caskey (16) have described the preparation of 2-nitro-1-naphthol-4-sulfonic acid from 2-nitroso-1-naphthol-4-sulfonic acid in trifuloroacetic acid and hydrogen peroxide. This preparation of 2-nitro-1-naphthol-4-sulfonic acid from 2-nitroso-1-naphthol-4-sulfonic acid unequivocally proved that 2-nitroso-1-naphthol-4-sulfonic acid is capable of being oxidized to form 2-nitro-1-naphthol-4-sulfonic acid. Information presented later in this report proves that nitrite reacts with 2-nitroso-1-naphthol-4-sulfonic acid to form 2-nitro-1-naphthol-4-sulfonic acid in 6.0-7.0 N perchloric acid in much the same way that nitrate does.

By correlating this evidence in the literature with the fact that 2-nitro-1-naphthol-4-sulfonic acid was formed from 2-nitroso-1-naphthol-

4-sulfonic acid and sodium nitrate in two ranges of perchloric acid concentrations separated by a region of perchloric acid concentration in which the reaction was not as extensive, it seemed reasonable to postulate the following mechanisms for the formation of 2-nitro-1-naphthol-4-sulfonic acid. In the 7-8 N perchloric acid region, the 2-nitro-1-naphthol-4-sulfonic acid was possibly formed by a redox reaction which could have a stoichiometric relationship of

$$3(2\text{-NO}) + 2\ HNO_3 \rightleftharpoons 3(2\text{-NO}_2) + 2NO_{(g)} + H_2O$$

while the product in 9.5-11 N perchloric acid was possibly formed by a nitration reaction having a stoichiometric relationship of

$$2\text{-NO} + NO_2^+ \rightleftharpoons 2\text{-NO}_2 + NO^+ .$$

In the oxidation reaction presented, the ratio, nitrate:2-nitroso-1-naphthol-4-sulfonic acid in the formation of 2-nitro-1-naphthol-4-sulfonic acid would be 2:3. The ratio, nitrate:2-nitroso-1-naphthol-4-sulfonic acid in the formation of 2-nitro-1-naphthol-4-sulfonic acid would be 1:1 for a nitration reaction via a nitronium ion.

Experimentally obtained mole-ratio values have been presented in Table 3. Graphical representations of trials 4, 9, and 10 have been presented in Figures 10-12, respectively. The data for Figure 10 was obtained from duplicate studies on consecutive days.

The mole-ratio value of 0.922, obtained in trial 1 from a mole-ratio study in 8.06 N perchloric acid, was a value which could not be explained in terms of only one of the mechanisms suggested. The 8.06 N perchloric acid is very near the upper limit of the lower range of acid concentrations (see Figures 2, 3, and 4) which caused a reaction between sodium nitrate and 2-nitroso-1-naphthol-4-sulfonic acid. A possible explanation for the value of 0.922 is that it is the result of competing parallel reactions yielding a value intermediate between 0.667 and 1.00.

Table 3. Mole-Ratio Values

Figure Number	Trial Number	Perchloric Acid Normality	Temp. °C	Mole Ratio From 222 mμ	Mole Ratio From 261 mμ
	1	8.06	50.8	0.922	
	2	7.71	50.1	0.76	
	3	8.29	40.0	0.60	
10	4	8.29	60.1	1.01	
	5	6.73	70.0	0.68	0.61
	6	6.73	60.0	0.68	0.62
	7	6.73	50.0	0.95	0.93
	8	6.71	50.0	0.69	0.57
11	9	9.87	50.0	1.00	1.00
12	10	6.77	50.0	0.68	0.80

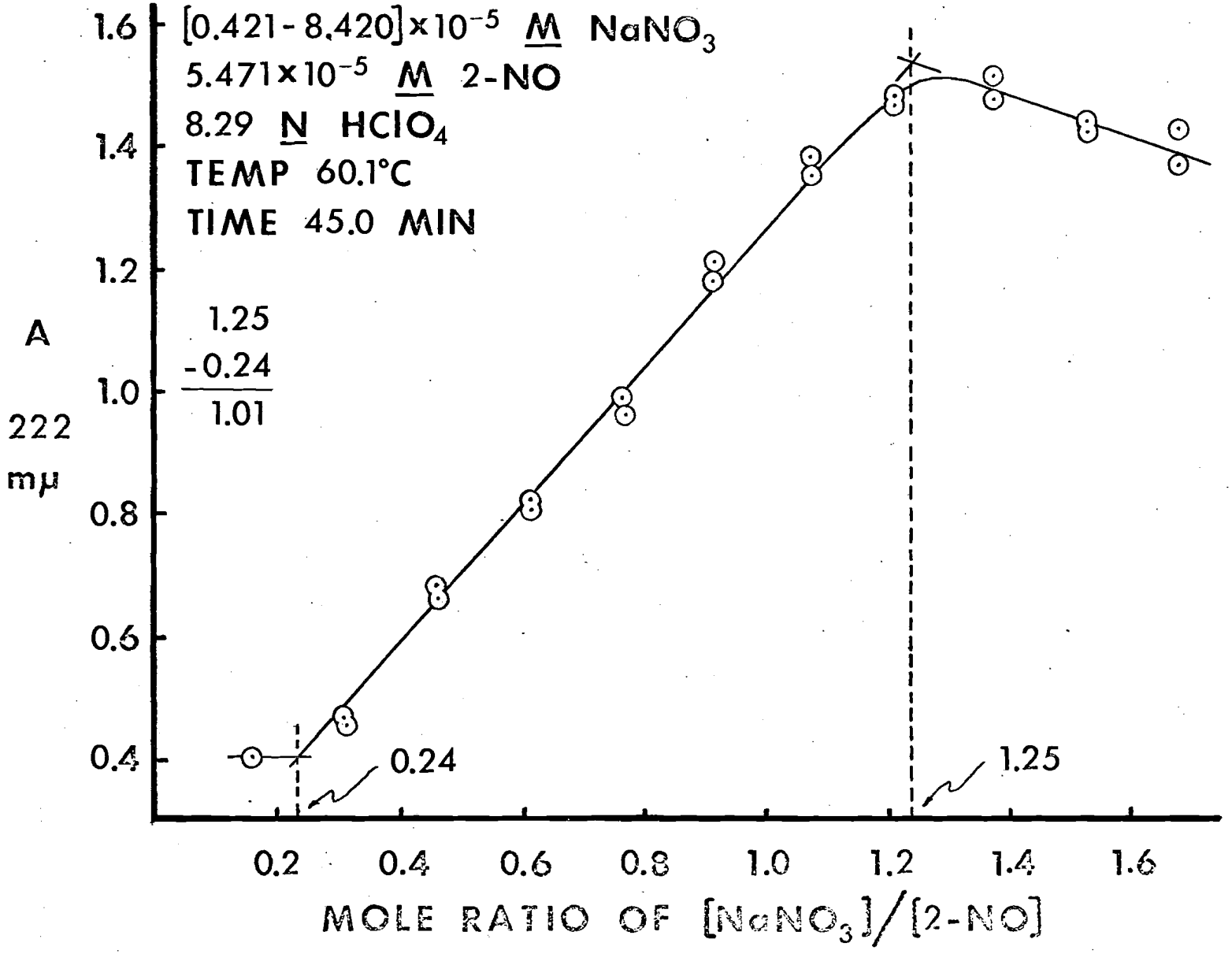


Figure 10. A mole-ratio study of the reaction between sodium nitrate and 2-nitroso-1-naphthol-4-sulfonic acid in 8.29 N perchloric acid at 60.1 °C for 45.0 minutes.

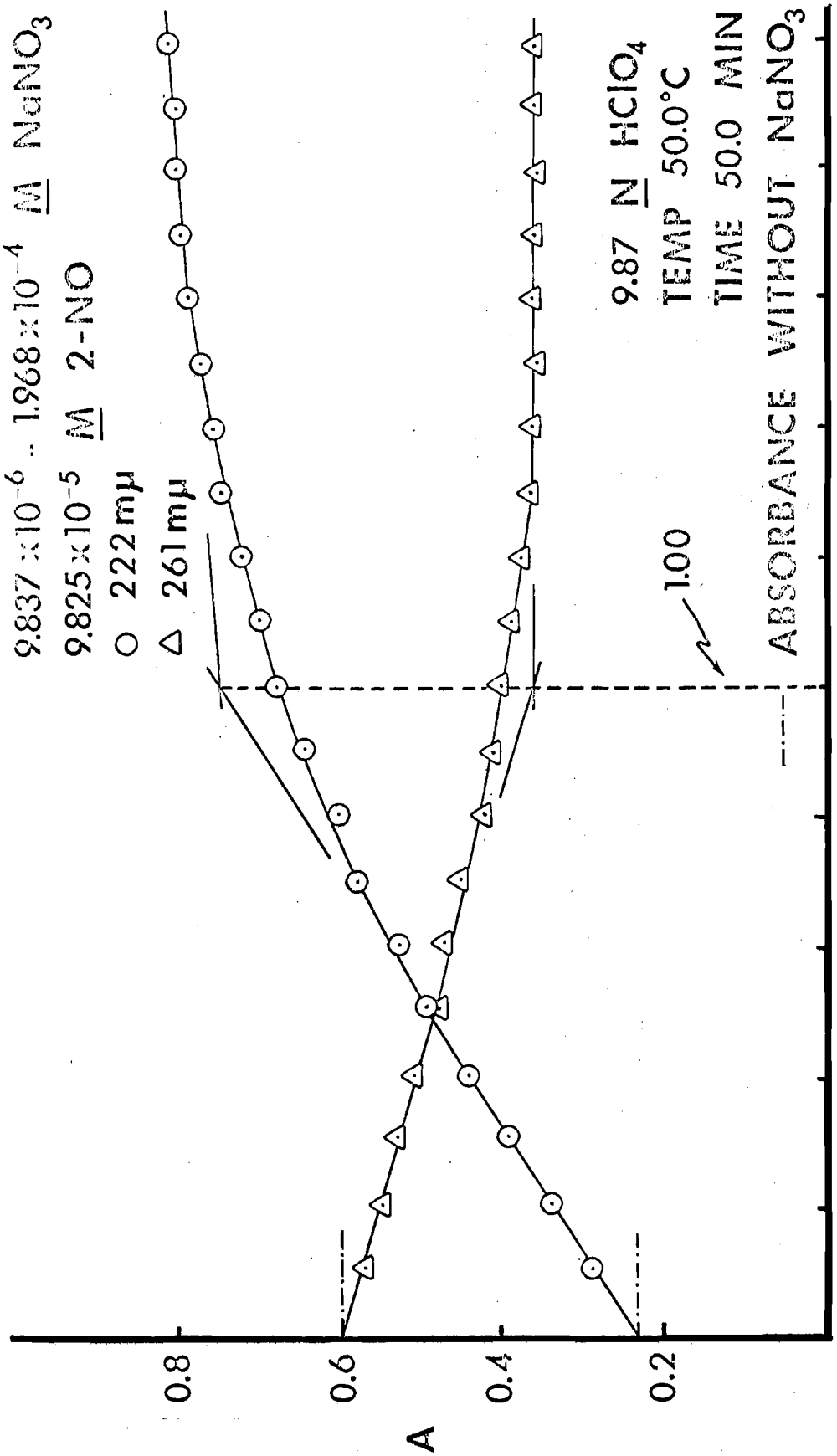


Figure 11. A mole-ratio study of the reaction between sodium nitrate and 2-nitroso-1-naphthol-4-sulfonic acid in 9.87 N perchloric acid at 50.0 °C for 50.0 minutes

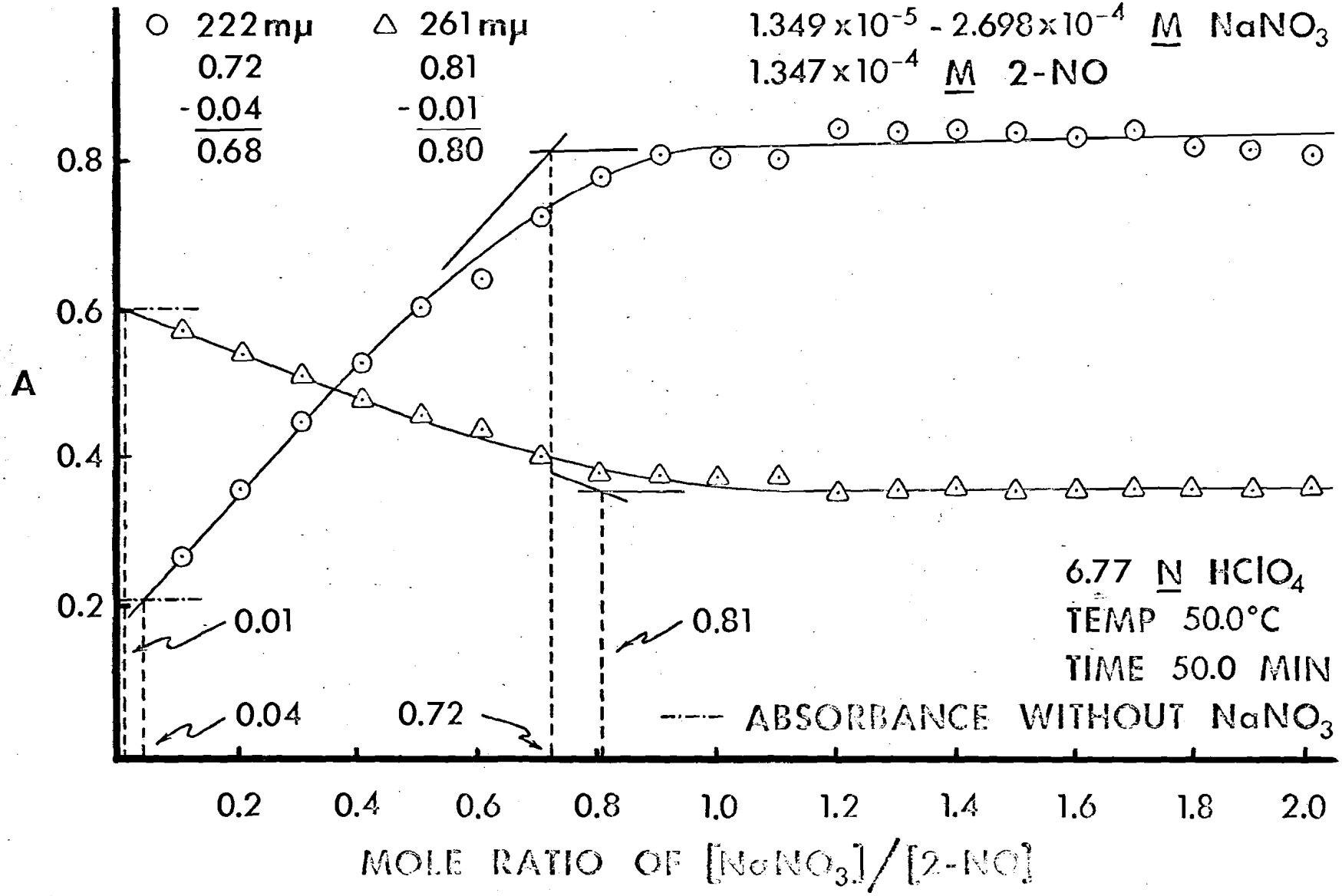


Figure 12. A mole-ratio study of the reaction between sodium nitrate and 2-nitroso-1-naphthol-4-sulfonic acid in 6.77 N perchloric acid at 50.0 °C for 50.0 minutes

The mole ratio of 0.76, obtained in trial 2 from a mole-ratio study in 6.71 N perchloric acid, also could not be explained in terms of one mechanism. Work presented later in this report supports the validity of using a reagent blank correction obtained from the absorbance of solutions not containing sodium nitrate. No such solutions were available to enable application of a reagent blank correction, but it is evident that the value of 0.76 is similar to the values of 0.77-0.82 obtained for trials 5, 6, 8, and 10 which, after a reagent-blank correction, yielded mole-ratio values consistent with a ratio of 2:3.

The conditions used in the work represented by trial 3 were at the region of acid concentrations where the extent of reaction was slight. It has been suggested earlier in this report that the predominent reaction pathway, occurring at this concentration, was probably the same as the pathway in the 9.5-11 N region of extensive reaction. This possibility was suggested in Figures 2 and 3 by the progressive increase in absorbance at 222 mμ with the increasing temperature for the 8.5-9.0 N perchloric acid concentrations. The mole-ratio values of 0.60 or 0.83, obtained in trial 3 from a mole-ratio study in 8.29 N perchloric acid, are not consistent with this explanation. (The value of 0.60 was obtained after applying a reagent blank correction.) A possible explanation for the inconsistent values obtained in trial 3 is the 40.0 ^{o}C temperature which may not have been sufficiently great enough to ensure a complete reaction or equilibrium necessary for accurate mole-ratio studies.

In trial 4, Figure 10, a mole-ratio value of 1.01 was obtained from a mole-ratio study in 8.29 N perchloric acid after correcting for a reagent blank. A value of 1.01 from 8.29 N perchloric acid supports the concept suggested in the preceding paragraph. In Figure 10, a horizontal

line was drawn through the absorbance value obtained for a mole ratio of 0.154 and was used for a reagent blank correction. Nitration did not occur in this solution, and the absorbance value represented the absorbance of a solution containing no 2-nitro-1-naphthol-4-sulfonic acid. This absorbance value is the value at which the absorbance axis should have been intercepted by the linear portion of the curve on the low mole ratio side of the intersection, if a reducing agent was not present in the system.

The mole-ratio values obtained from trials 5-10 were obtained from more carefully designed and conducted experiments, with the exception of trial 7. The information obtained in the qualitative kinetic studies (Experiment C, "Qualitative Rate Studies to Compare the Reactions of 2-Nitroso-1-Naphthol-4-Sulfonic Acid") was used in selecting the reaction intervals for trials 5-10.

In Figures 11 and 12, the "dashed-dotted" lines represent the absorbance values of solutions without nitrate. If more than one solution without nitrate was used, they represent the average absorbance values.

The results presented in Figures 11 and 12, trials 9 and 10, provide additional information concerning the fact that the reactions in 6.8 and 9.9 N perchloric acid are different. The solutions used in these two studies were obtained from the same reagent solutions, with the studies being conducted on consecutive days. The slopes of the linear region of the mole ratio curve on the low mole ratio side of the intersection are definitely different. Also, a reagent blank correction was not necessary for the 9.9 N perchloric acid, while it was necessary for the 6.8 N perchloric acid.

The mole-ratio values of 0.95 and 0.93 in trial 7 are not consistent with either a mole ratio of 2:3 or 1:1. The solutions used in the study for trial 7 were prepared to the extent that water, sodium nitrate, and perchloric acid has been added. The solutions were then allowed to remain

unused for about 16 hours, i.e., overnight. The possible loss of nitric acid through volatilization can not be eliminated under such conditions.

The mole-ratio values obtained in trials 5, 6, 8, 9, and 10 at both wavelengths (after correction for a reagent blank where necessary) are consistent, within experimental error, with an oxidation mechanism occurring in the 6.7 N perchloric acid and a nitration via the nitronium ion occurring in the 9.9 N perchloric acid. In trials 5, 6, and 8, lower mole ratios were obtained at 261 mμ than at 222 mμ. The lower values are probably due to the known decomposition of 2-nitroso-1-naphthol-4-sulfonic acid.

In order to unequivocally prove the existence of two reaction mechanisms and to assign a mechanism to each system, a study using ^{15}N labeled nitrate was conducted. The study was conducted experimentally by treating ^{15}N sodium nitrate and 2-nitroso-1-naphthol-4-sulfonic acid at a mole ratio of 0.15 with either 6.7 or 10 N perchloric acid. After different time intervals, sufficient ^{14}N sodium nitrate was added to convert the 2-nitroso-1-naphthol-4-sulfonic acid and 2-nitro-1-naphthol-4-sulfonic acid to 2,4-dinitro-1-naphthol.

The 2,4-dinitro-1-naphthol was separated by extracting with benzene and evaporating the benzene. Mass spectra were obtained for the 2,4-dinitro-1-naphthol. For 2,4-dinitro-1-naphthol, part of which was formed by nitration with ^{15}N, a parent ion peak at 235 mass units was expected, in addition to the normal parent peak at 234. For 2,4-dinitro-1-naphthol, which was formed by oxidation of the nitroso group of 2-nitroso-1-naphthol-4-sulfonic acid, a parent ion peak at 234 mass units was expected. It was not possible to interpret the mass spectra, because peaks at 240 mass units, and higher, indicated that the samples were contaminated with at least one

other compound. This contamination was still present after sublimation of the samples. Because of the presence of impurities, it was not possible to accurately compare the ratios of the 235 and 234 peaks obtained from the samples prepared at different concentrations of perchloric acid.

In the work described by Abercrombie (15), no study was conducted which proved that the concentration of nitrate could be related to the decrease in absorbance of the cobalt complex of 2-nitroso-1-naphthol-4-sulfonic acid. The results of such a study have been presented graphically in Figure 13. A linear relationship of the absorbance of the cobalt complex to nitrate concentration was obtained using excess cobalt. The concentration of cobalt complex is inversely proportional to the nitrate concentration, and the concentration of nitrate can be measured spectrophotometrically at 525 mμ.

E. Test of the Perchloric Acid for Redox Properties of Impurities

The results of some studies not presented in this report indicated that a greater yield of 2-nitro-1-naphthol-4-sulfonic acid was being obtained than could be accounted for in terms of the amount of sodium nitrate present in the system. The results of other studies indicated that 2-nitro-1-naphthol-4-sulfonic acid was not being formed in systems in which such formation was expected. The possibility of the presence of redox impurities was considered; the effect of various samples of perchloric acid on 2-nitroso-1-naphthol-4-sulfonic acid (with and without nitrate present) was studied, and the results have been presented in Table 4.

Only the perchloric acid in bottles 7, 8, and 10 contained oxidant which was indicated by the absorbance values greater than 0.425 at 222 mμ.

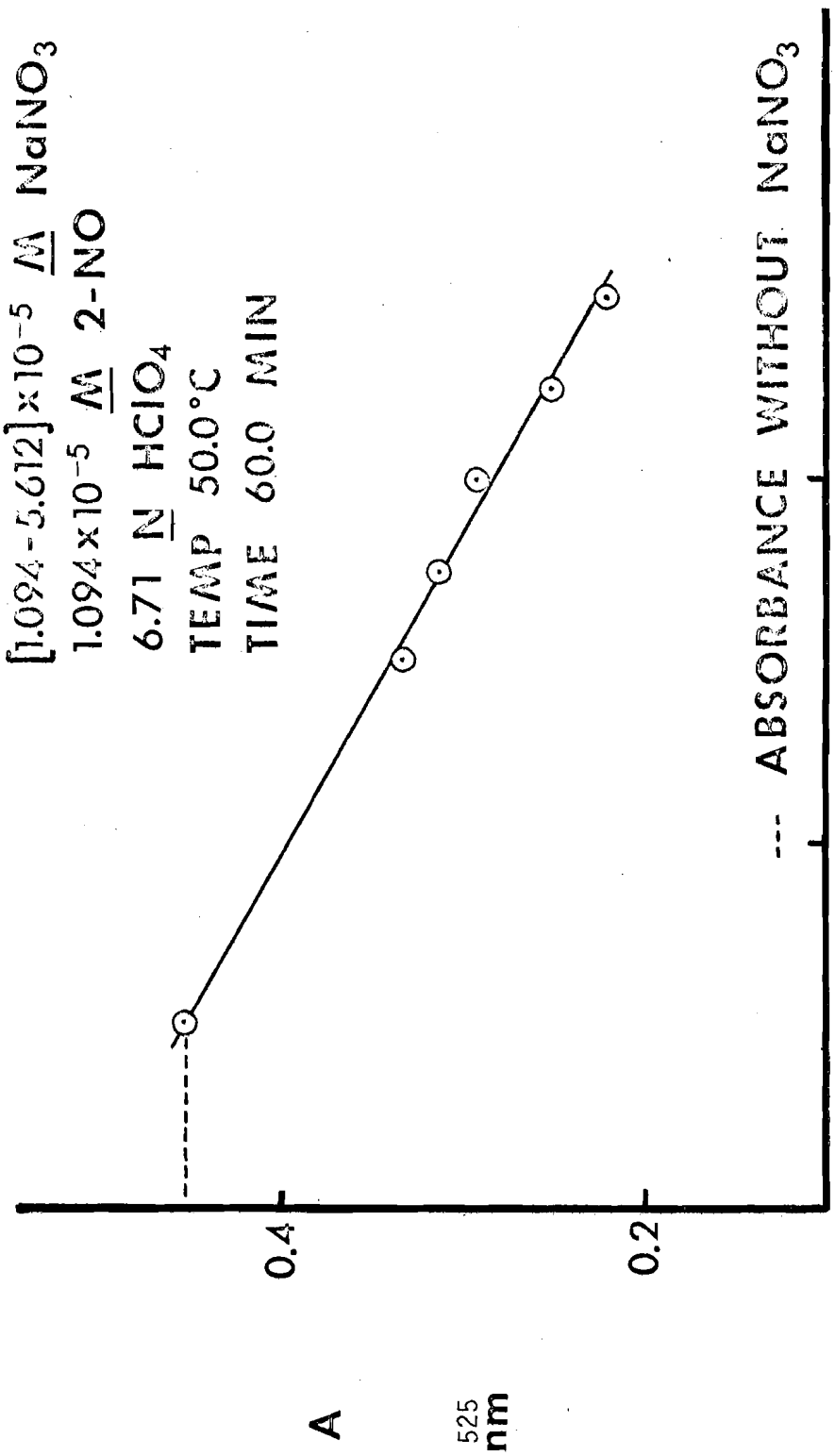


Figure 13. The absorbance of solutions of the cobalt complex of 2-nitroso-1-naphthol-4-sulfonic acid as a function of nitrate concentration

Table 4. Test of the Perchloric Acid for Redox Impurities*

Soln. No.	2-NO Soln. No.[a]	$NaNO_3$ Soln. No.[a]	Flask Size	H_2O ml	$HClO_4$ ml	$HClO_4$ Bottle No.	A @ 222 mμ
929	1	---	100	20.00	50.00	7	0.512
932	1	---	100	20.00	50.00	8	0.470
934	1	---	100	20.00	50.00	9	0.362
933	1	---	100	20.00	50.00	10	1.437
950	1	---	100	20.00	50.00	11	0.376
951	1	---	100	20.00	50.00	12	0.373
952	1	---	100	20.00	50.00	13	0.377
953	1	---	100	20.00	50.00	14	0.376
954	1	---	100	20.00	50.00	15	0.387
985	1	---	100	20.00	50.00	16	0.392
b						b	
1189	1	---	100	20.00	50.00	21	0.365
1190	1	---	100	20.00	50.00	22	0.361
1191	1	---	100	20.00	50.00	23	0.350
1192	1	---	100	20.00	50.00	24	0.355
1193	1	---	100	20.00	50.00	25	0.356
1194	1	---	100	20.00	50.00	26	0.355
1223	1	2	100	25.00	40.00	21	0.774
1225	1	2	100	25.00	40.00	22	0.810
1213	1	2	100	25.00	40.00	23	0.806
1214	1	2	100	25.00	40.00	24	0.823
1215	1	2	100	25.00	40.00	25	0.825
1216	1	2	100	25.00	40.00	26	0.816
1566	3	---	50	6.50	10.00	27	0.384
1567	3	---	50	6.50	10.00	28	0.388
1568	3	---	50	6.50	10.00	29	0.383
1569	3	---	50	6.50	10.00	30	0.399

*Continued on next page.

Table 4. Test of the Perchloric Acid for Redox Impurities--(Continued)

Soln. No.	2-NO Soln. No.	$NaNO_3$ Soln. No.	Flask Size	H_2O ml	$HClO_4$ ml	$HClO_4$ Bottle No.	A @ 222 mμ
1570	3	4	50	4.50	10.00	27	0.407
1571	3	4	50	4.50	10.00	28	0.405
1572	3	4	50	4.50	10.00	29	0.409
1573	3	4	50	4.50	10.00	30	0.410
1574	3	---	50	6.50	10.00	31	0.377
1575	3	---	50	6.50	10.00	32	0.374
1576	3	---	50	6.50	10.00	33	0.375
1577	3	---	50	6.50	10.00	34	0.379
1578	3	---	50	6.50	10.00	35	0.379
1579	3	---	50	6.50	10.00	36	0.379
1598	3	4	50	4.50	10.00	31	0.754
1599	3	4	50	4.50	10.00	32	0.830
1600	3	4	50	4.50	10.00	33	0.777
1583	3	4	50	4.50	10.00	34	0.743
1601	3	4	50	4.50	10.00	34	0.736
1584	3	4	50	4.50	10.00	35	0.727
1485	3	4	50	4.50	10.00	36	0.696

[a]Solution Number 1 was 3.830×10^{-3} M 2-nitroso-1-naphthol-4-sulfonic acid. Solution Number 2 was 5.894×10^{-4} M sodium nitrate. Solution Number 3 was 1.915×10^{-3} M 2-nitroso-1-naphthol-4-sulfonic acid. Solution Number 4 was 2.997×10^{-4} M sodium nitrate.

[b]Bottles 17-20 were tested for the presence of oxidant, but the absorbance values at 222 mμ were not recorded. Oxidant was not present in the acid in these bottles.

The other bottles did not contain oxidant. The criterion for the presence or absence of oxidant in the perchloric acid samples was not based on the absorbance values at 222 mμ, however, but on the shape of the spectra in the 230-210 mμ region. A trace of 2-nitro-1-naphthol-4-sulfonic acid was readily detected because of the difference in molar absorptivities of these two compounds over this wavelength range.

Of the bottles of perchloric acid tested with nitrate, only 27-30 failed to cause formation of 2-nitro-1-naphthol-4-sulfonic acid. This absence of product is indicated by the absorbances of 0.4 at 222 mμ for solutions 1570-1573. Solutions 1598-1601, which were tested similarly but with different acid, gave absorbances of 0.7 at 222 mμ. The acid from bottles 27-30 was tested on two other occasions, spaced weeks apart, with similar results occurring. Because of the failure of the acid from bottles 27-30 to cause nitrate to form 2-nitro-1-naphthol-4-sulfonic acid, the proven presence of oxidant in acids 7, 8, and 10, and the need for reagent blank corrections in mole-ratio and Beer's law studies, it is not possible to say that the perchloric acid was always free from reducing impurities.

F. The Effect of Sodium Nitrite as a Function of Perchloric Acid Concentration of Systems in Which the Mole Ratio, Sodium Nitrate:2-Nitroso-1-Naphthol-4-sulfonic Acid, was 0.31

In the literature discussing nitration kinetics and mechanisms, a considerable amount of attention was focused on the effect of nitrous acid on the nitration systems. Benford and Ingold (22) reported that the rate of nitration of benzene and its homologues was decreased by the presence of nitrous acid with the latter exerting a negative catalytic influence. Hughes, Ingold, and Reed (23) observed a similar effect by

nitrous acid, and were able to show that the concentration of nitrous acid, within the limits of experimental error, remained constant throughout the nitration process. Schramm and Westheimer (24) have shown that nitrous acid exerts a positive catalytic influence in the nitration of anisole by formation of nitrosoanisoles which subsequently formed nitroanisoles.

Bunton, Hughes, Minkoff, and Reed (25) reported that in the nitration of phenols, nitrous acid exerted a catalytic influence of both a positive and negative effect which was dependent upon the nitrous acid concentration.

Because nitrous acid has been reported to exhibit catalytic influences in nitration reactions and because nitrite commonly accompanies nitrate in natural water, it was considered necessary to determine the effect that nitrite might have on the formation of 2-nitro-1-naphthol-4-sulfonic acid. The effect of nitrite on the formation of 2-nitroso-1-naphthol-4-sulfonic acid at 40.0 and 50.0 ^{o}C was studied as a function of perchloric acid concentration. The mole ratio, sodium nitrate:2-nitroso-1-naphthol-4-sulfonic acid, was 0.308 and the mole ratio, sodium nitrite: sodium nitrate, was 0.10. The results of these studies have been presented in Figures 14 and 15. The solutions without sodium nitrite were used as controls to emphasize any effect nitrite might have on the formation of 2-nitro-1-naphthol-4-sulfonic acid from sodium nitrate and 2-nitroso-1-naphthol-4-sulfonic acid.

The effect of perchloric acid was the usual effect discussed previously; as the concentration was increased, a perchloric acid concentration was reached at which the formation of 2-nitro-1-naphthol-4-sulfonic acid

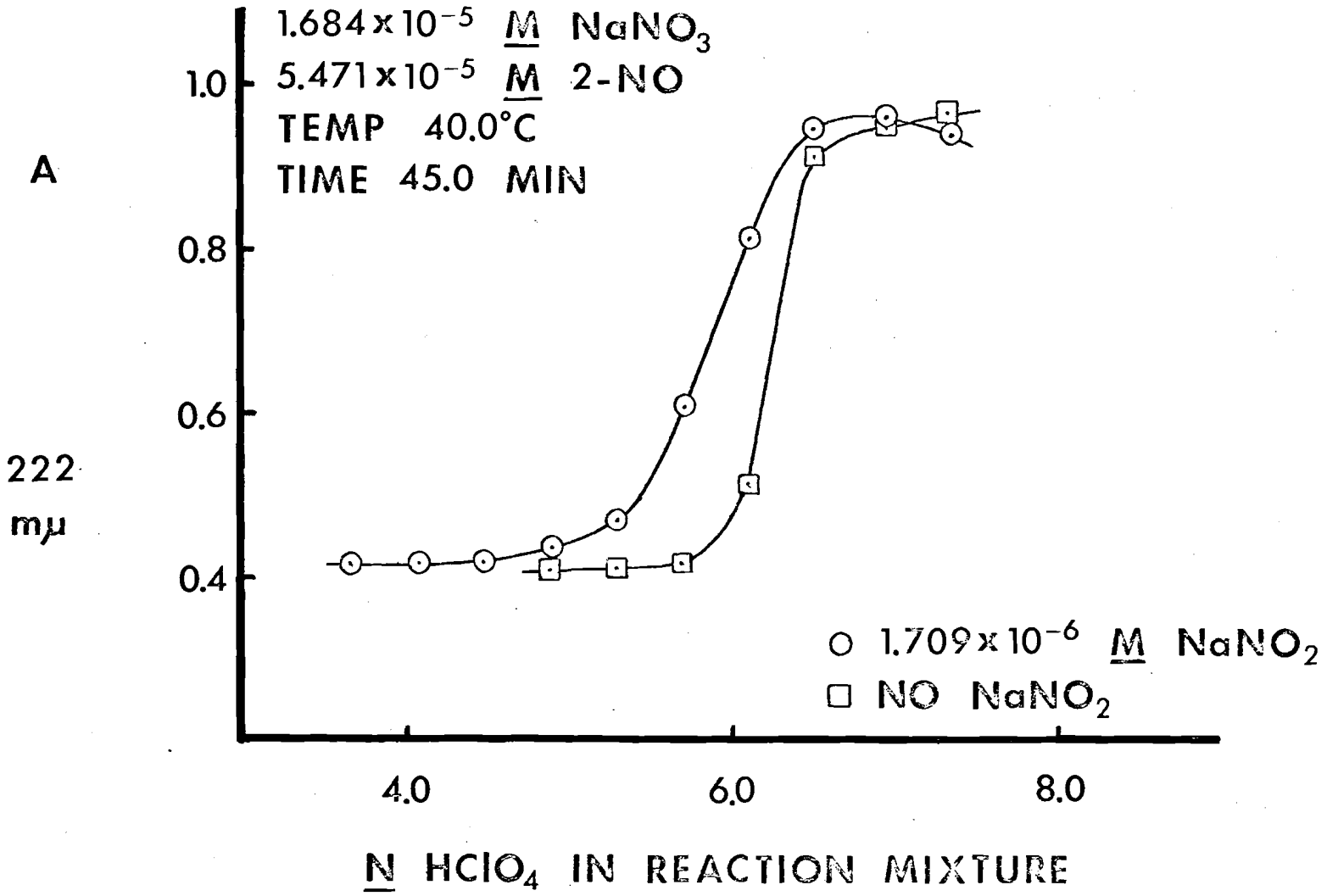


Figure 14. The effect of varied perchloric acid concentrations on the formation of 2-nitro-1-naphthol-4-sulfonic acid in the presence of a "catalytic" amount of nitrate at 40.0 °C

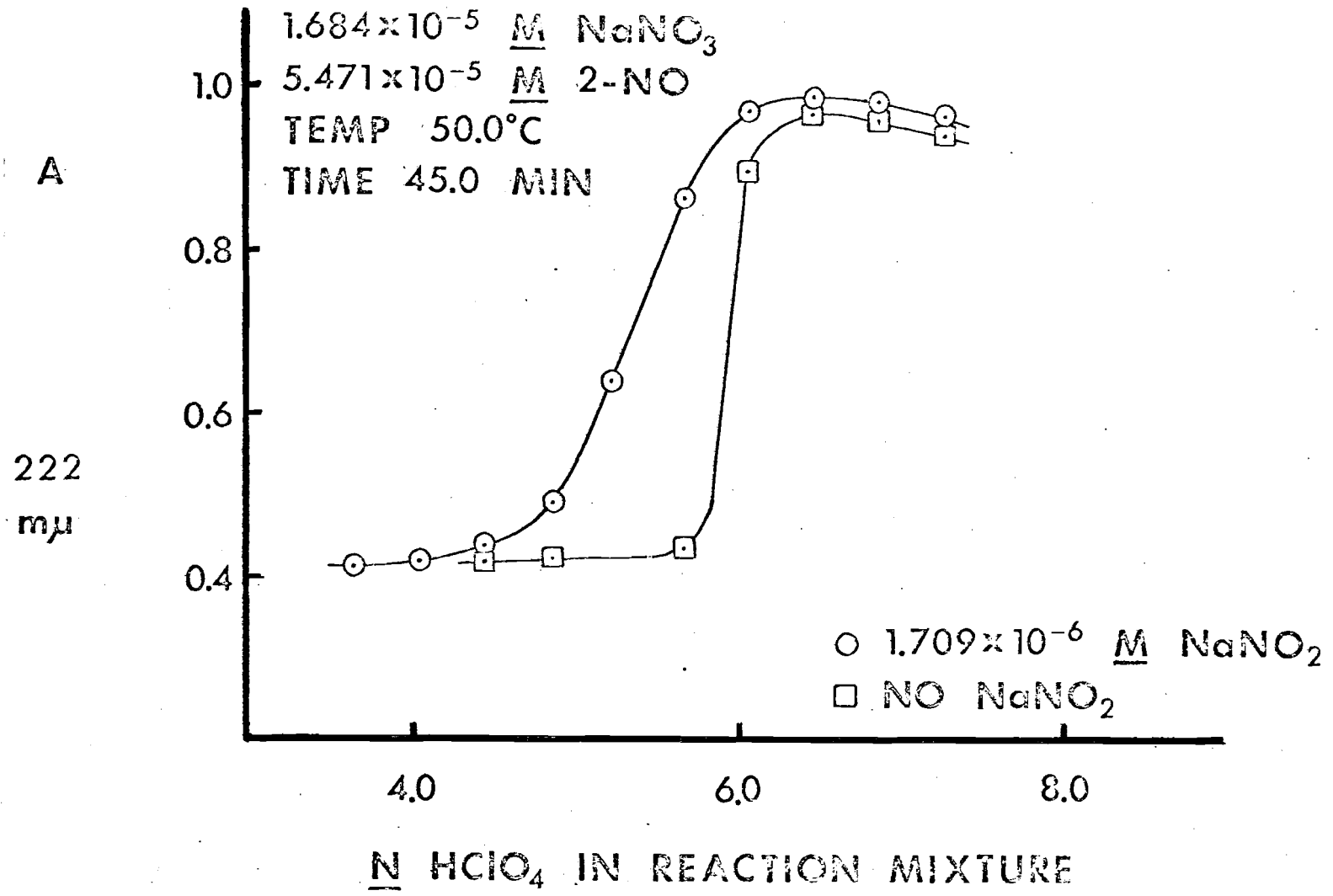


Figure 15. The effect of varied perchloric acid concentrations on the formation of 2-nitro-1-naphthol-4-sulfonic acid in the presence of a "catalytic" amount of nitrite at 50.0 °C

increased to a maximum, and decreased with a further increase in the perchloric acid concentration. The major difference between the systems with sodium nitrite and those without sodium nitrite was that the formation of 2-nitro-1-naphthol-4-sulfonic acid began at a significantly lower perchloric acid concentration when sodium nitrite was present. The perchloric acid concentration, in which the maximum formation of 2-nitro-1-naphthol-4-sulfonic acid occurred, was not significantly changed in the presence of sodium nitrite. The formation of 2-nitro-1-naphthol-4-sulfonic acid from 2-nitroso-1-naphthol-4-sulfonic acid was only slightly enhanced by the presence of nitrite. Had the presence of nitrite shifted the perchloric acid formation to a lower acid concentration, the acid decomposition of 2-nitroso-1-naphthol-4-sulfonic acid possibly would have decreased, thus creating better conditions for the determination of sodium nitrate.

G. The Redox Reaction Between Sodium Nitrite and 2-Nitroso-1-Naphthol-4-Sulfonic Acid at a Mole Ratio of 0.31 as a Function of Perchloric Acid Concentration

The results of the preceding study suggested that nitrite possibly enhanced the formation of 2-nitro-1-naphthol-4-sulfonic acid from 2-nitroso-1-naphthol-4-sulfonic acid in the presence of perchloric acid and sodium nitrate. Because nitrite is an oxidizing agent, it was necessary to determine whether or not nitrite was oxidizing 2-nitroso-1-naphthol-4-sulfonic acid in order to be able to correctly assess the results of Experiment F.

The results of a study of the effect of perchloric acid on the formation of 2-nitro-1-naphthol-4-sulfonic acid from 1.709×10^{-5} M sodium nitrite and 5.471×10^{-5} M 2-nitroso-1-naphthol-4-sulfonic acid using a reaction interval of 45.0 minutes, has been presented graphically, Figure 16.

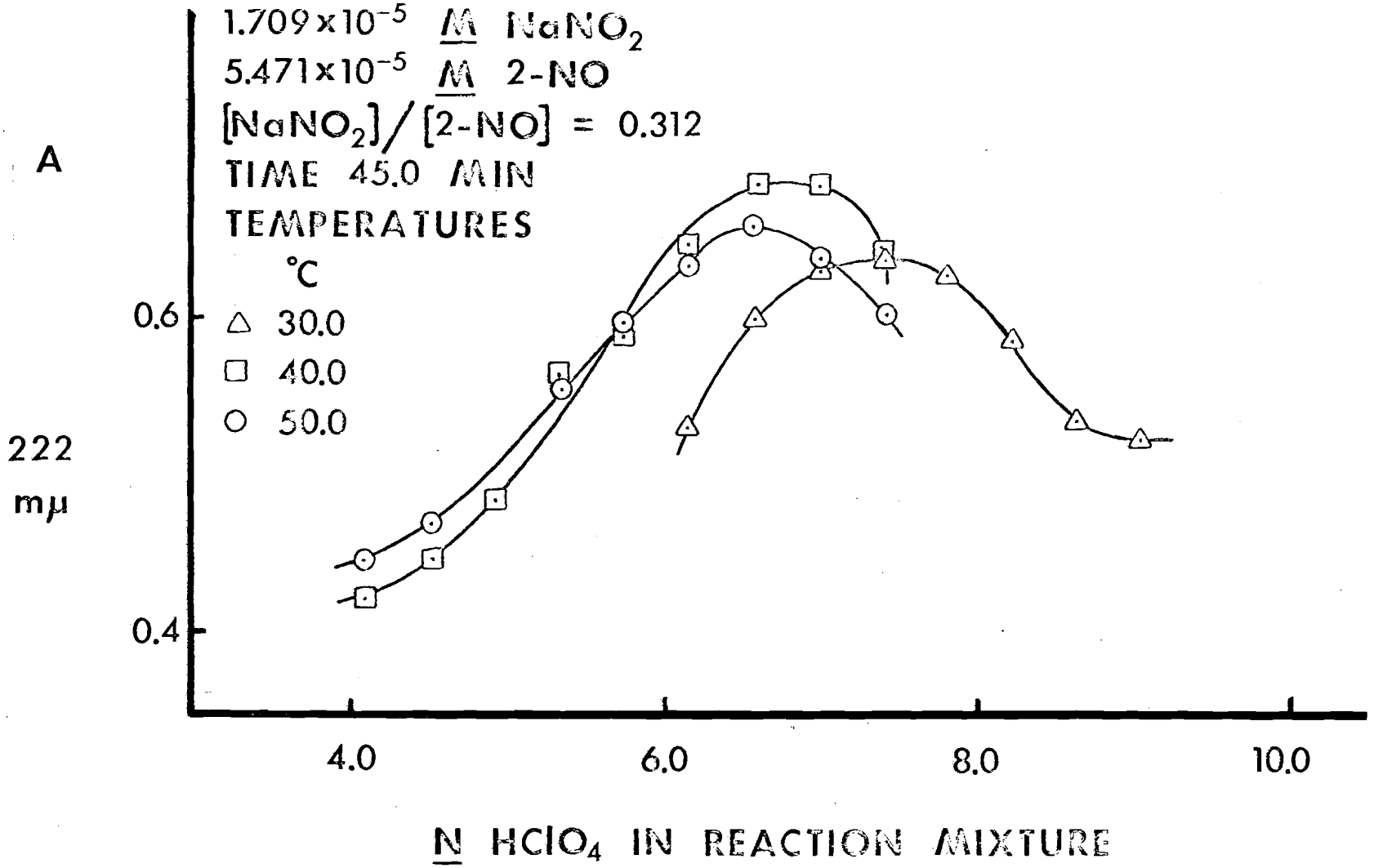


Figure 16. The oxidation of 2-nitroso-1-naphthol-4-sulfonic acid by sodium nitrite as a function of perchloric acid concentration at 30.0, 40.0, and 50.0 °C

The concentration of sodium nitrite in this study was comparable to the concentration of sodium nitrate used in the studies which yielded the results for Figures 14 and 15. In the presence of sodium nitrite, the perchloric acid concentrations at which maximum formation of 2-nitro-1-naphthol-4-sulfonic acid occurred were similar to the results obtained in the absence of sodium nitrite. The more gradual increase in the formation of 2-nitro-1-naphthol-4-sulfonic acid with increasing perchloric acid concentrations in the presence of sodium nitrite had been observed in Figures 14 and 15.

While there was extensive formation of 2-nitro-1-naphthol-4-sulfonic acid at 30-50 ^{o}C in 6-7.5 N perchloric acid, no reaction occurred at 0 ^{o}C. The results at 0 ^{o}C were not presented in Figure 16. The relatively constant absorbance values of 0.4 at 222 mμ for solutions treated in 6.15-9.03 N perchloric acid at 0 ^{o}C indicated that no reaction was occurring.

This experiment, and the earlier experiment in which sodium nitrite was present, definitely showed that sodium nitrite enhanced the formation of 2-nitro-1-naphthol-4-sulfonic acid from 2-nitroso-1-naphthol-4-sulfonic acid, and was oxidizing 2-nitroso-1-naphthol-4-sulfonic acid to 2-nitro-1-naphthol-4-sulfonic acid. With the information presented, it was difficult to assign the effect, observed in systems containing both nitrate and nitrite, to catalysis of the reaction by nitrite. In fact, the conditions under which 2-nitro-1-naphthol-4-sulfonic acid was formed, either by nitrate or nitrite, were so similar that in an analytical method for nitrate, the presence of nitrite in significant concentrations would interfere, thus giving high results for nitrate.

H. A Study of the Possible Catalytic Effect of Sodium Nitrite on the Reaction of 2-Nitroso-1-Naphthol-4-Sulfonic Acid with Sodium Nitrate as a Function of Time

Because the effect of nitrite on the reaction between nitrate and 2-nitroso-1-naphthol-4-sulfonic acid was not clearly defined in the earlier experiments (F and G), in terms of possible catalysis, the effect of the presence of 3.419×10^{-6} M sodium nitrite on the reaction between 5.471×10^{-5} M 2-nitroso-1-naphthol-4-sulfonic acid and 1.684×10^{-5} M sodium nitrate in 6.56 N perchloric acid was studied as a function of time at 50.0, 60.0, and 65.0 ^{o}C. The effect of 1.094×10^{-6} M sodium nitrite on the reaction between 5.471×10^{-5} M 2-nitroso-1-naphthol-4-sulfonic acid and 3.368×10^{-5} M sodium nitrate in 6.71 N perchloric acid was studied as a function of time at 40.0 ^{o}C. The results of these studies have been presented graphically in Figures 17-20. (The effect of perchloric acid upon 2-nitroso-1-naphthol-4-sulfonic acid as a function of time at 40.0 ^{o}C was also studied and presented to enable a more valid assessment of the other two systems at 40.0 ^{o}C; the 40.0 ^{o}C temperature was outside the range of temperatures studied in Experiment C.)

In the studies presented in Figures 18, 19, and 20, the molar ratio, nitrite:nitrate, was 0.20, while in the solutions used for Figure 17, this ratio was 0.03. In the solutions used for Figures 18, 19, and 20, the molar ratio, sodium nitrite:2-nitroso-1-naphthol-4-sulfonic acid, was 0.06, while this ratio was 0.01 in the solutions used for Figure 17.

The increase in rate of formation of 2-nitro-1-naphthol-4-sulfonic acid at 50.0, 60.0, and 65.0 ^{o}C for the systems containing nitrite, compared to systems without nitrite, was slight and while suggesting a catalytic effect, the difference in rate was not considered sufficiently definitive to be able to state that nitrite was acting as a positive catalyst. Because nitrite was able to react with 2-nitroso-1-naphthol-4-

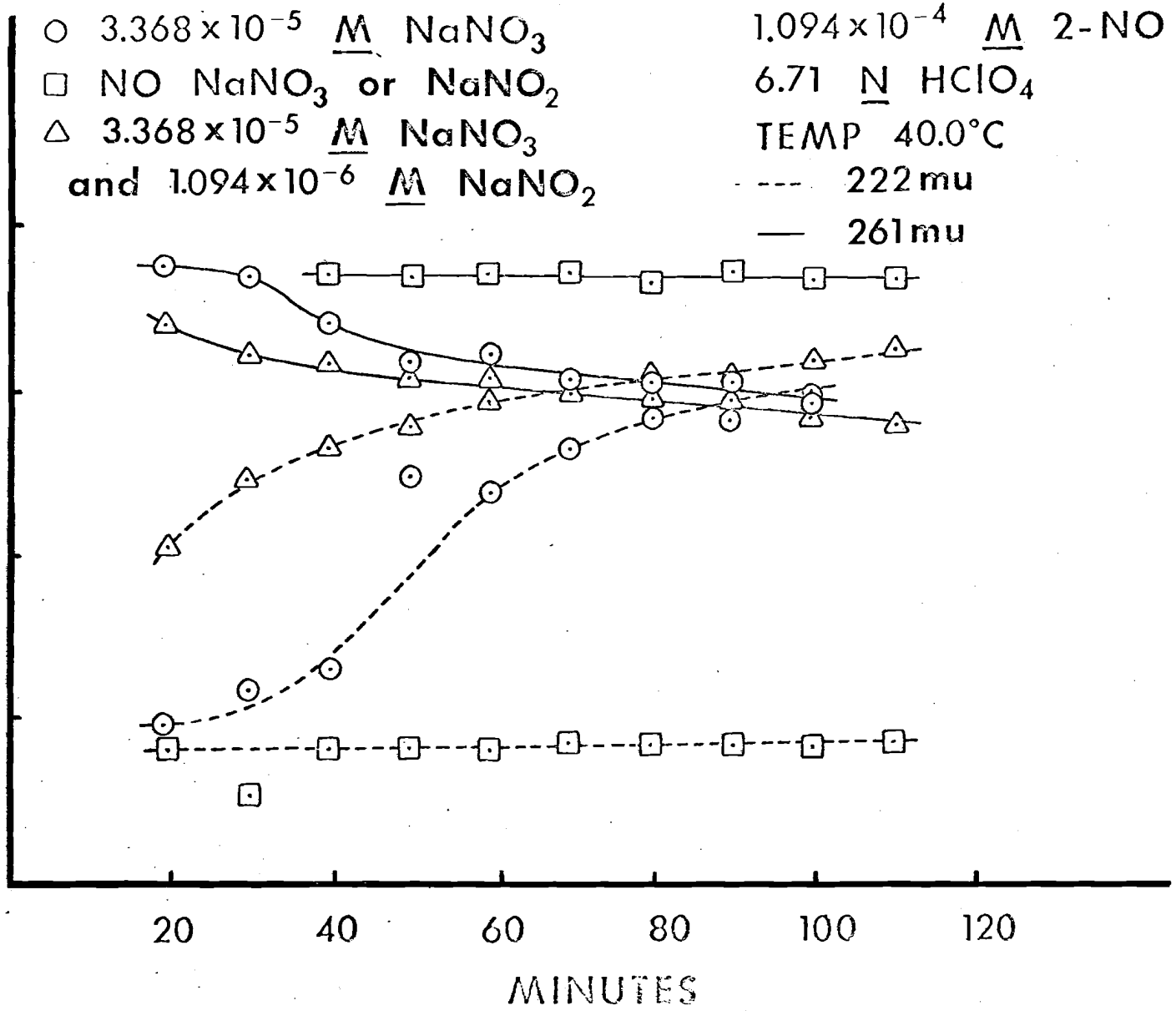


Figure 17. The formation of 2-nitro-1-naphthol-4-sulfonic acid (with and without a "catalytic" amount of sodium nitrite present) and the decomposition of 2-nitroso-1-naphthol-4-sulfonic acid as a function of time at 40.0 °C in 6.71 N perchloric acid

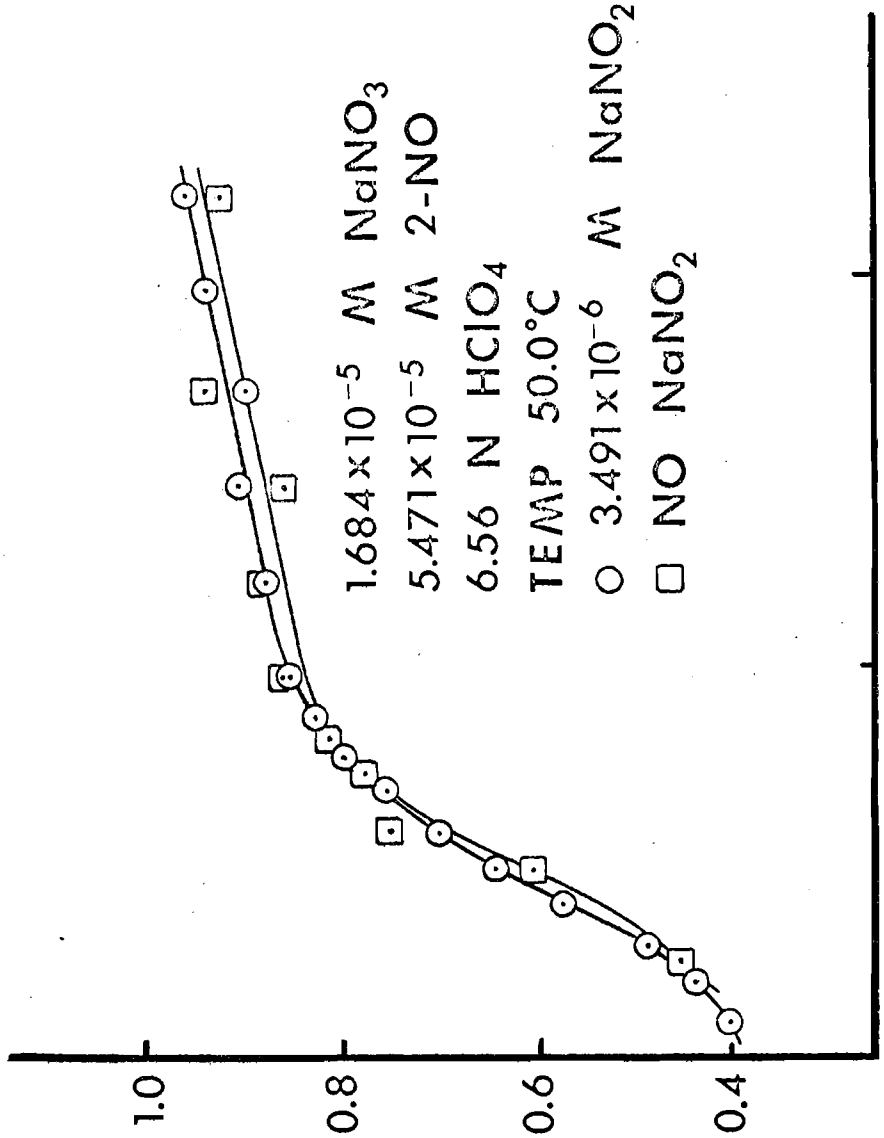


Figure 18. The formation of 2-nitro-1-naphthol-4-sulfonic acid (with and without a "catalytic" amount of sodium nitrite present) as a function of time at 50.0 °C in 6.56 N perchloric acid

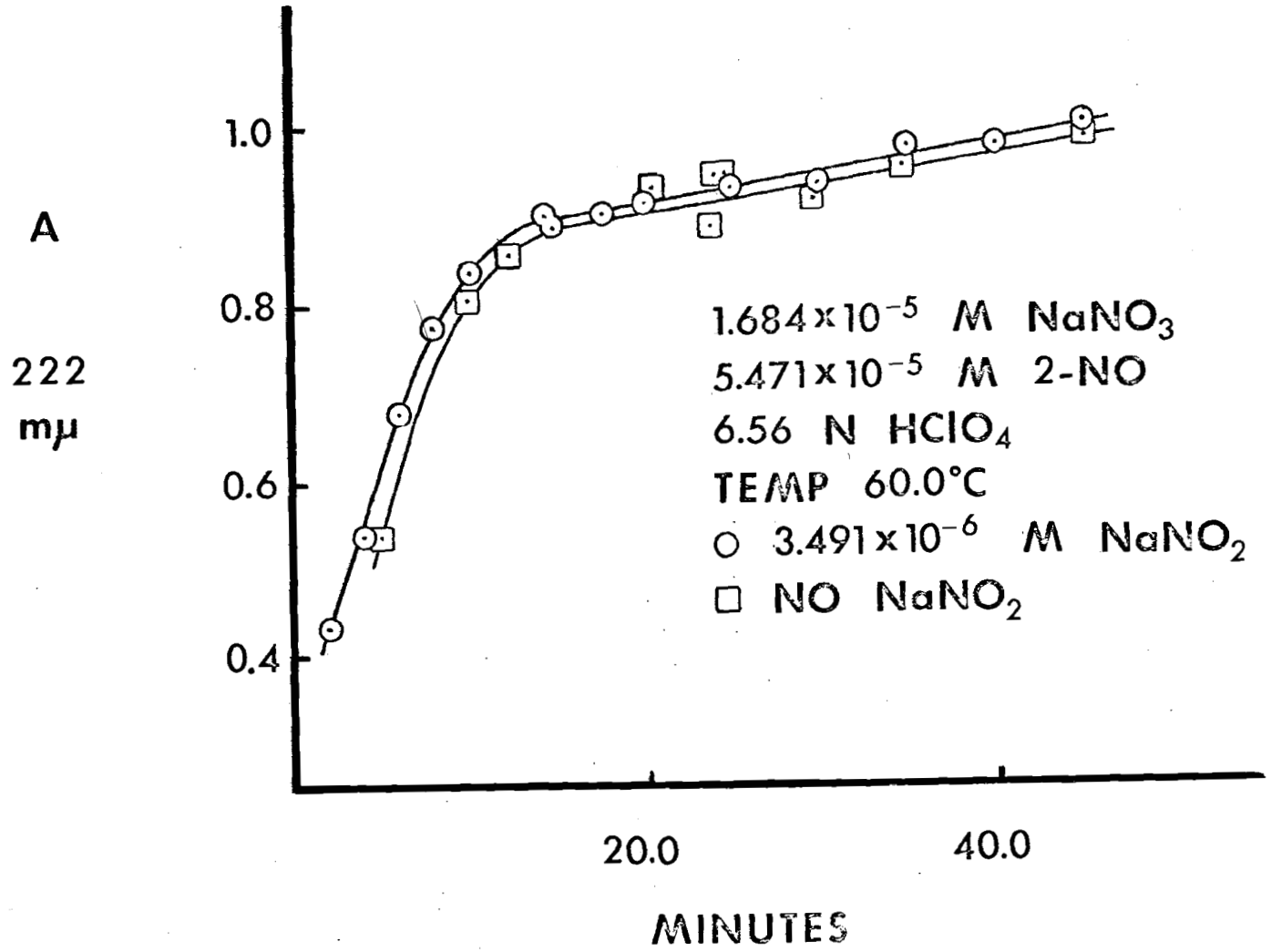


Figure 19. The formation of 2-nitro-1-naphthol-4-sulfonic acid (with and without a "catalytic" amount of sodium nitrite present) as a function of time at 60.0 °C in 6.56 N perchloric acid

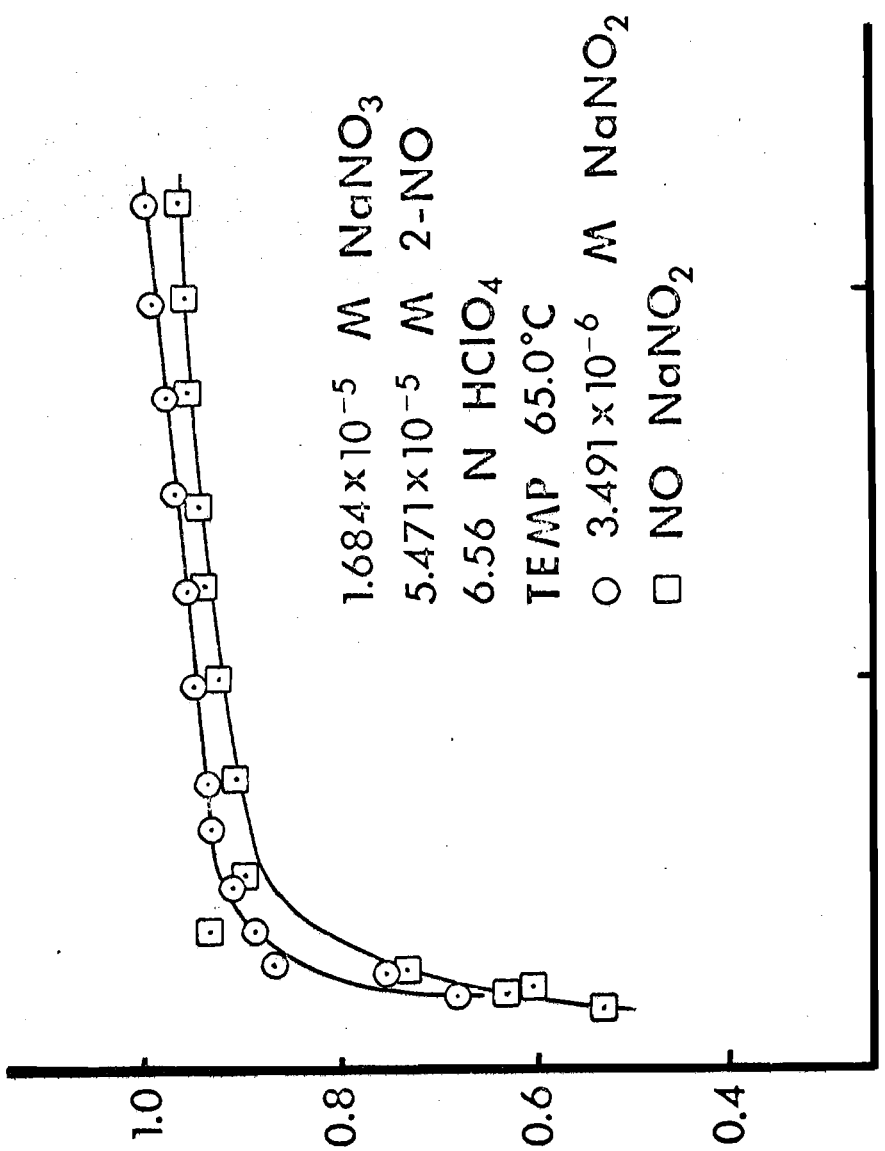


Figure 20. The formation of 2-nitro-1-naphthol-4-sulfonic acid (with and without a "catalytic" amount of sodium nitrite present) as a function of time at 65.0 °C in 6.56 N perchloric acid

sulfonic acid to form 2-nitro-1-naphthol-4-sulfonic acid, and considering the relative concentration of nitrite, the slight increase in the rate of formation of 2-nitro-1-naphthol-4-sulfonic acid might be accounted for in terms of an increase in the "mass action" principle.

A temperature of 40.0 ^{o}C, using lower concentrations of nitrite, was selected as a possible condition for the detection of a catalytic effect by nitrite. The results in Figure 17 indicated, by the relatively constant absorbance values at 222 mμ and 261 mμ, that relatively no decomposition of 2-nitroso-1-naphthol-4-sulfonic acid was occurring in the 6.71 N perchloric acid at 40.0 ^{o}C. The rapid increase in absorbance values at 222 mμ as a function of time for solutions containing nitrate and nitrite, when compared to the absorbance values of solutions which contained nitrate without nitrite, showed that nitrite enhanced formation of 2-nitro-1-naphthol-4-sulfonic acid. The nature of this increase was such that it seemed reasonable to believe that nitrite was possibly a positive catalyst in the formation of 2-nitro-1-naphthol-4-sulfonic acid from sodium nitrate and 2-nitroso-1-naphthol-4-sulfonic acid. A more extensive study, or at least a duplication of the study, at 40.0 ^{o}C with different nitrite concentrations, is necessary to unequivocally state that nitrite was acting as a positive catalyst in the system.

I. The Effect of Foreign Ions upon the Proposed Method for the Determination of Nitrate in Natural Waters

The effect of foreign ions upon the formation of 2-nitro-1-naphthol-4-sulfonic acid from 4.941 x 10^{-4} M sodium nitrate and 1.347 x 10^{-4} M 2-nitroso-1-naphthol-4-sulfonic acid was studied in 6.70 N perchloric acid at 50.0 ^{o}C for 70.0 minutes to determine which substance would interfere with the reactions, resulting in incorrect values for nitrate in an

analytical method. The results of these studies have been presented in Table 5. A substance was considered to interfere if its presence caused the absorbance of the solution to be outside of a range of $\pm$ 3 standard deviations of the average obtained from control solutions containing no foreign ions. The substances which interfered were Dreft, dichromate, chloride, iodide, iodate, iron(II), nitrite, hydroxylamine hydrochloride, sulfite, chlorate, thiosulfate, urea, metaarsenite, permanganate, and sulfamic acid. The effect of Dreft as an interference was studied at several concentrations. The results of this study indicated that Dreft did not interfere below the 10.0 to 12.5-ppm range. With the exceptions of Dreft and chloride, the interferences were oxidizing or reducing agents.

Attempts were made to determine if it was possible to remove some of the interfering ions encountered in natural waters. The results of this study have been presented in Table 6, and they indicated that the interferences of chloride and iodide could be removed by adding silver perchlorate and then filtering to remove the silver halide. After using this method, the absorbances of solutions, which originally contained halides, were within the 3σ range. The attempt (solutions 2157-2158) to remove dichromate by adding lead perchlorate and then filtering the solution to remove the precipitate was not clearly successful. The interference of iron(II) (solution 2160) was removed by adding sodium hydroxide, bubbling oxygen gas through the slurry, and filtering to remove the iron(II) hydroxide or hydrated iron(III) oxide.

J. Application of the Proposed Method for the Determination of Nitrate in Natural Waters

In order to assess the applicability of the proposed method for the determination of nitrate in natural waters, it was considered necessary to

Table 5. Foreign Ions

Substance Added	Conc.[a] ppm	Interference
$AgClO_4$	201	
NaCl	50	-
KI	5	-
$FeSO_4$	5	-
$Na_4P_2O_7$	4	
Na_2EDTA	45	
$Ni(ClO_4)_2$	5	
$Cu(ClO_4)_2$	5	
$Pb(ClO_4)_2$	5	
$Cr(ClO_4)_3$	5	
$Cd(ClO_4)_2$	5	
$Zn(ClO_4)_2$	5	
NH_4ClO_4	50	
Na_2SO_3	5	-
Na_2HPO_4	5	
$NaNO_2$	5	+
$Ca(ClO_4)_2$ (saturated with CO_2)	2000	
KH_2AsO_4	5	
$Na_2S_2O_3$	5	-
$CO(NH_2)_2$	5	-
DREFT	10-12	-
ALCONOX	20	
HEAMO-SOL	20	
monoethanolamine	5	
allylamine	5	
$K_2Cr_2O_7$	5	+
$Ce(SO_4)_2$	5	
$MgSO_4$	250	
Na_2SO_3	5	+
NH_2SO_3H	6	-
$KMnO_4$	5	+
$KClO_3$	5	+
NaC_2H_3O	5	
H_3BO_3	1	

[a]Concentration values are reported in terms of the underlined portion of the substance.

Table 6. The Effect of Foreign Ions, After Treatment for Removal, Upon the Proposed Method for the Determination of Nitrate in Natural Waters

Soln. No.	Substance Added	Conc. ppm[a]	Interference Removal Method	A @ 222 mμ	A @ 261 mμ
2108	KI	5.04	Ag^+ & filtration	0.613	0.509
2109	NaCl	5.00	Ag^+ & filtration	0.580	0.511
2110	NaCl	5.00		0.588	0.500
2111	$HgCl_2$	5.02	Ag^+ & filtration	0.600	0.506
2157	$K_2Cr_2O_7$	5.00	Pb^{++} & filtration	0.593	0.488
2158	$K_2Cr_2O_7$	5.00	Pb^{++} & filtration	0.593	0.487
2159	$FeSO_4$	5.00	EDTA	0.488	0.621
2160	$FeSO_4$	5.00	NaOH, O_2 & filtration	0.609	0.496

[a]This concentration refers to the concentration of the underlined portion of the foreign ion substance in a 5.00 -ml sample.

collect natural-water samples and to analyze these samples by an accepted method, and the proposed method. The phenoldisulfonic acid method was chosen as the comparison method for several reasons: 1) The phenoldisulfonic acid method has been the most extensively discussed method. 2) The product of the nitration reaction has been characterized in the phenoldisulfonic acid method. 3) The reagents in the phenoldisulfonic acid method were considered to be safer to use than the reagents involved in the brucine method. 4) The standard solutions needed for calibration curve could be prepared and stored, thus facilitating planning of work schedules around the application of two analytical methods to samples of questionable stability.

Both procedures required removal of chloride from the water samples. The results of the determination of the chloride content of the natural-water samples have been presented in Table 7. Table 7 also lists the volume of silver perchlorate added to each 200.0-ml sample subjected to pretreatment.

The results of the Beer's-law data for the phenoldisulfonic acid method have been presented in Figure 21. The nitrate-nitrogen content of the natural-water samples, as determined by the phenoldisulfonic acid method, have been presented in Table 8. The increase in nitrate-nitrogen in the spiked samples compared with the unspiked samples should have been 3.00-mg NO_3^--N/l.

The Beer's-law data obtained using 2-nitroso-1-naphthol-4-sulfonic acid have been presented graphically in Figure 22. The system conformed to Beer's law over a nitrate-nitrogen range of 3-13 µg, but the system was such that the working range of the Beer's law plot was 3-23 µg of NO_3^--N. (Using a chemical reagent blank correction of sodium nitrate in the

Table 7. The Chloride Content of the Natural Water Samples

Sample	KCNS ml[a]	Cl mg/l	mg $AgClO_4$ added to 200 ml
Ohio River	1.137	25.9	5.176
Crab Orchard Lake	1.292	2.2	0.429
Mississippi River	1.304	11.6	2.328
Little Grassy Lake	1.304	trace[b]	0.100
Big Muddy River	1.264	6.36	1.272
City Reservoir	1.303	trace[b]	0.100

[a]This is the volume of KCNS required to reach the end point in the Volhard titration of a 25.00-ml volume of sample to which 5.00 ml of the silver perchlorate (1.00 ml = 1.01 mg Cl) solution had been added. A 5.00-ml volume of silver perchlorate (1.00 ml = 1.01 mg Cl) required 1.306-ml KCNS.

[b]The presence of chloride was also detected by the turbidity in the sample after addition of the silver perchlorate solution.

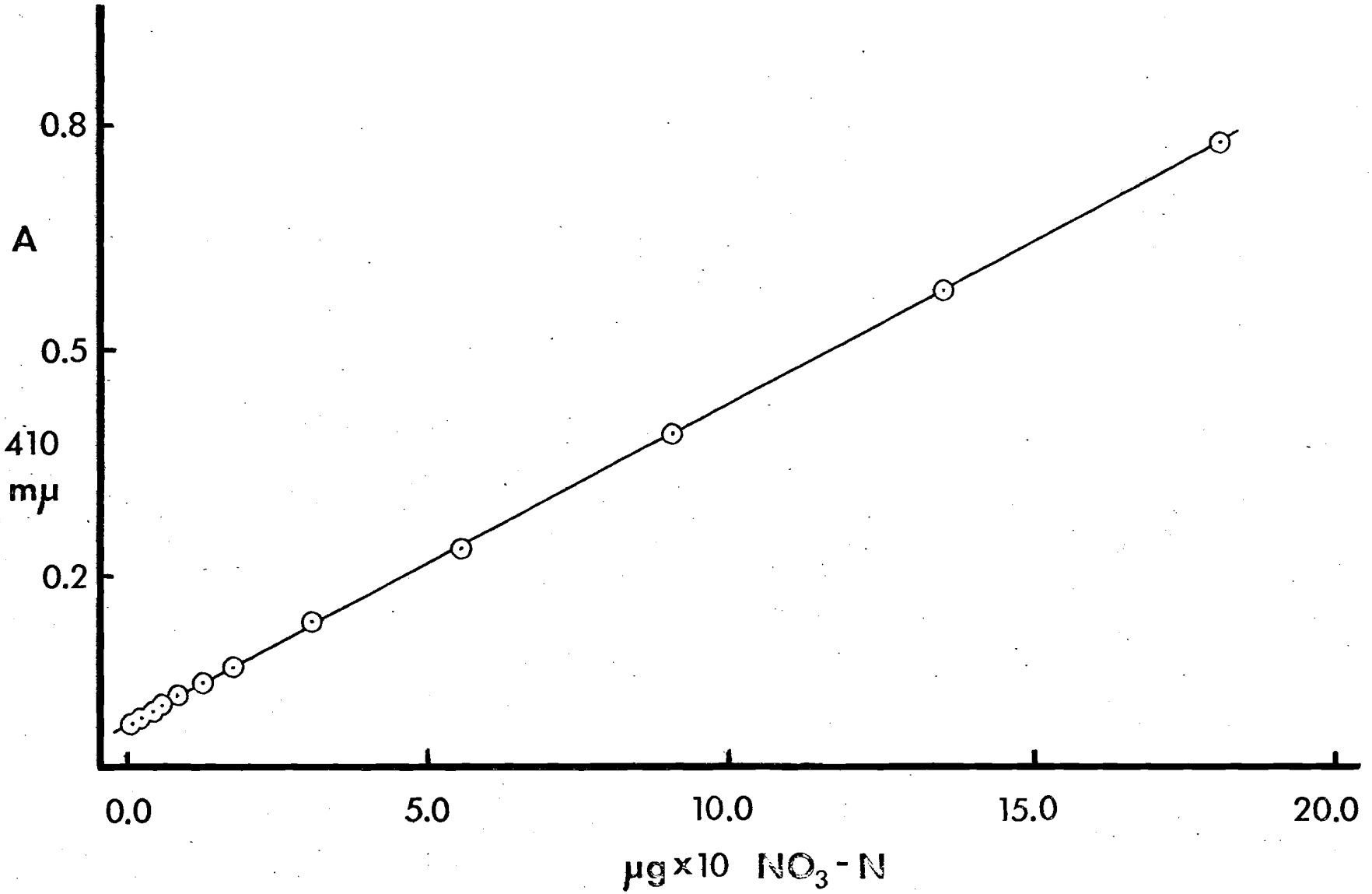


Figure 21. The Beer's-law plot of the nitrated phenoldisulfonic acid as a function of nitrate-nitrogen concentration

Table 8. The Nitrate-Nitrogen Content of Natural Waters

Sample	Cl^- ppm	Phenoldisulfonic Acid 410 mμ NO_3^--N ppm	% recov'd	2-Nitroso-1-Naphthol-4-Sulfonic Acid 222 mμ NO_3^--N ppm	% recov'd	261 mμ NO_3^--N ppm	% recov'd
City Reservoir	trace	0.018		b		b	
City Reservoir +[a]		2.01	66	2.95	98	2.94	98
Big Muddy	6.36	0.025		b		b	
Big Muddy +[a]		2.04	67	3.06	102	3.02	101
Little Grassy	trace	0.015		b		b	
Little Grassy +[a]		1.39	46	2.91	97	2.75	92
Mississippi	11.6	1.25		1.32		1.30	
				1.37		1.31	
Mississippi		4.54	115	4.34	101	4.29	99.7
				4.34	99.0	4.29	99.3
Ohio	25.9	1.75		2.12		2.04	
				2.14		2.04	
Ohio +[a]		5.21	110	5.11	99.7	5.00	98.7
				5.11	99.0	5.00	98.7
Crab Orchard	2.2	0.078		b		b	
Crab Orchard +[a]		1.70	54	2.93	98	2.74	91

[a]This solution was spiked with 3.00 ppm NO_3^--N.
[b]Nitrate was not detected in this solution.

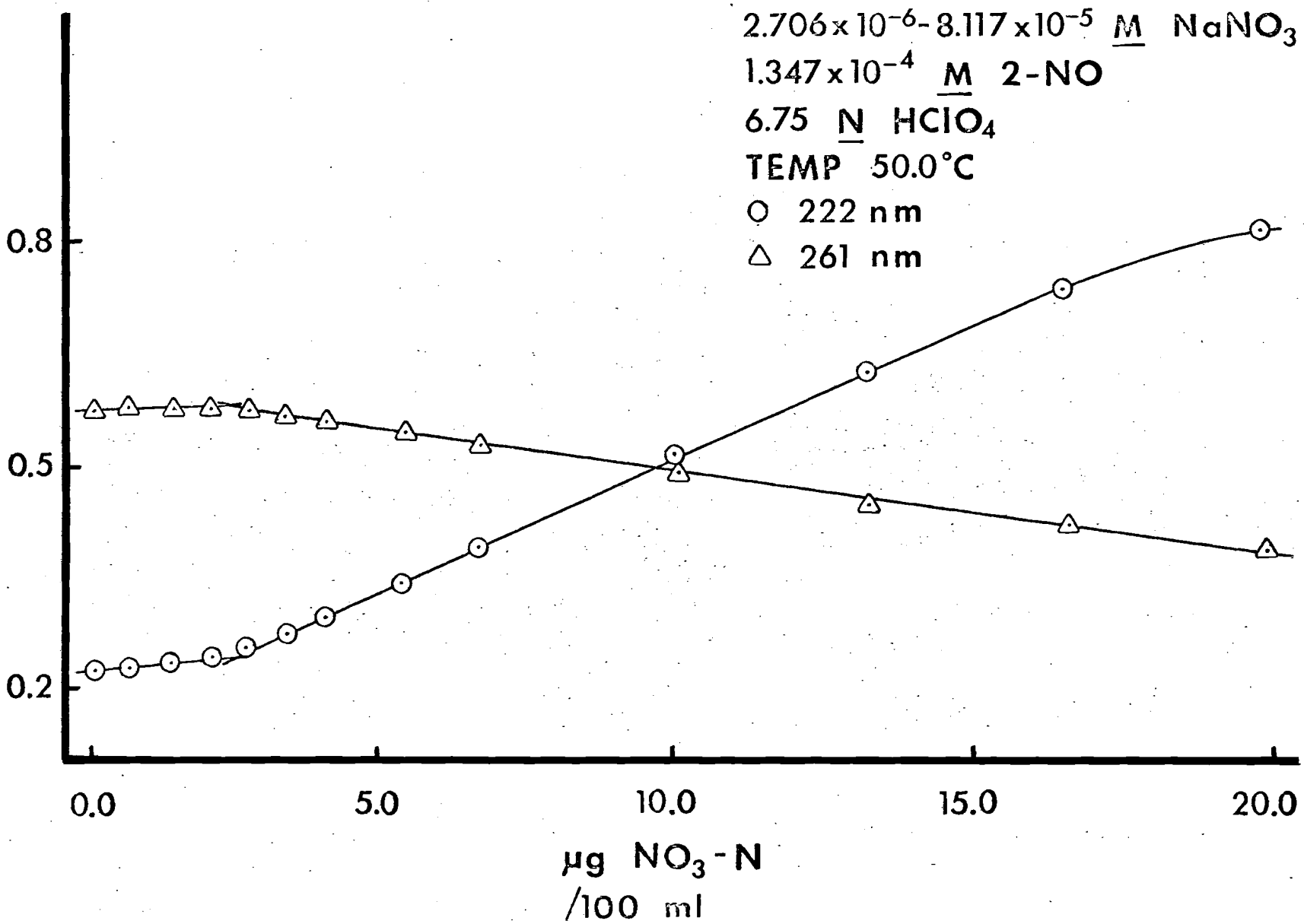


Figure 22. The Beer's-law plot of 2-nitroso-1-naphthol-4-sulfonic acid and 2-nitro-1-naphthol-4-sulfonic acid as a function of nitrate-nitrogen concentration

2-nitroso-1-naphthol-4-sulfonic acid reagent solution, the working curve was shifted to lower concentrations. The system then conformed to Beer's law over 0.25-10 μg of NO_3^--N with a working range of 0.25-20 μg of NO_3^--N.) The closeness of absorbance values obtained from the standard series solutions on separate days using the same reagent solutions suggested that the reproducibility of the method was within the limits of spectrophotometric error. It was not necessary to prepare Beer's law standards each day when the same reagents were used.

The relatively constant absorbance values obtained for solutions low in nitrate in Figure 22 suggested that a correction for a reagent blank was in order for Beer's-law and mole-ratio studies. The relationship of relatively constant absorbance values at low nitrate concentrations was reproducible.

The effect of using heating times of 70.0, 40.0, and 30.0 minutes have been presented graphically in Figure 23. The results of this study indicated only a slight decrease in the amount of 2-nitro-1-naphthol-4-sulfonic acid formed, occurred when the reaction time was reduced. The decrease in time did not seem to significantly affect the linearity of the Beer's-law curves.

The accuracy of the proposed method was determined by obtaining the percentage of nitrate recovered from a spiked sample. The nitrate-nitrogen concentrations of the natural-water samples, as determined by using 2-nitroso-1-naphthol-4-sulfonic acid, have been presented in Table 8. The proposed method gave analytical results which were very satisfactory in respect to the amount of nitrate recovered; the results also had reasonable quantitative agreement with the nitrate concentration as determined by using the phenoldisulfonic acid method. Most methods yield results

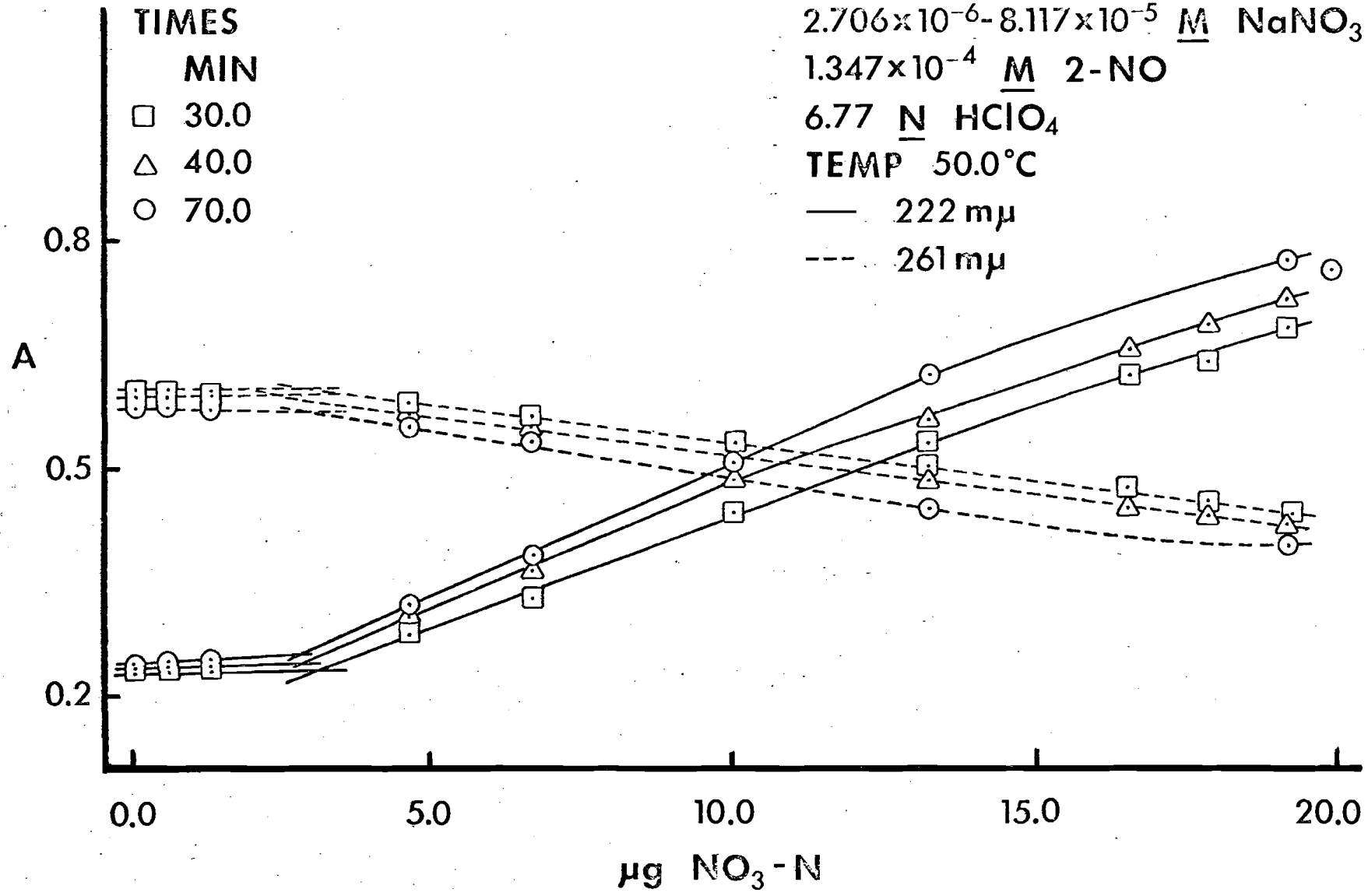


Figure 23. The effect of reaction intervals of 30.0, 40.0, and 70.0 minutes on the Beer's-law plots of 2-nitroso-1-naphthol-4-sulfonic acid and 2-nitro-1-naphthol-4-sulfonic acid as a function of nitrate-nitrogen concentration

higher than the results obtained using the phenoldisulfonic acid procedure. The recovery values obtained using the 2-nitroso-1-naphthol-4-sulfonic acid are within the ranges of recoveries obtained by Greenberg *et al.* (26) using the phenoldisulfonic acid and brucine methods. The range of average recoveries obtained by Greenberg *et al.* (26) using brucine were 96.9-102.2 %; the average recoveries obtained using phenoldisulfonic acid were 92.1-115.8 %.

Good recovery values were not obtained using 2-nitroso-1-naphthol-4-sulfonic acid with a different analytical procedure. All of the concentrations received were low, and in some water samples nitrate in the 1-2 ppm range was not detected. The procedure yielding low concentration values consisted of adding 10.00 ml of perchloric acid to 5.00 ml water samples. The water-acid mixture was heated for 15 minutes at 50 ^{o}C before adding the 2-nitroso-1-naphthol-4-sulfonic acid. A 70-minute reaction interval was used. Some of the water-acid mixtures were allowed to remain unused in excess of 16 hours before equilibrating 15 minutes at 50 ^{o}C. The concentration of perchloric acid in this system was sufficiently strong that essentially all nitrate was present as nitric acid. The low-nitrate values were probably the result of volatilization of nitric acid before or during equilibration. The proposed analytical procedure avoids conditions favorable to the volatilization of nitric acid until all reactants are present in the system. Heating each flask immediately after addition of the perchloric acid commences oxidation in such a manner that only a negligible amount of nitric acid is lost.

The reproducibility of the analytical values obtained for the nitrate content of natural water was studied and the results have been presented in Figure 24 and in Table 9 for 222 mμ and 261 mμ. The volumes

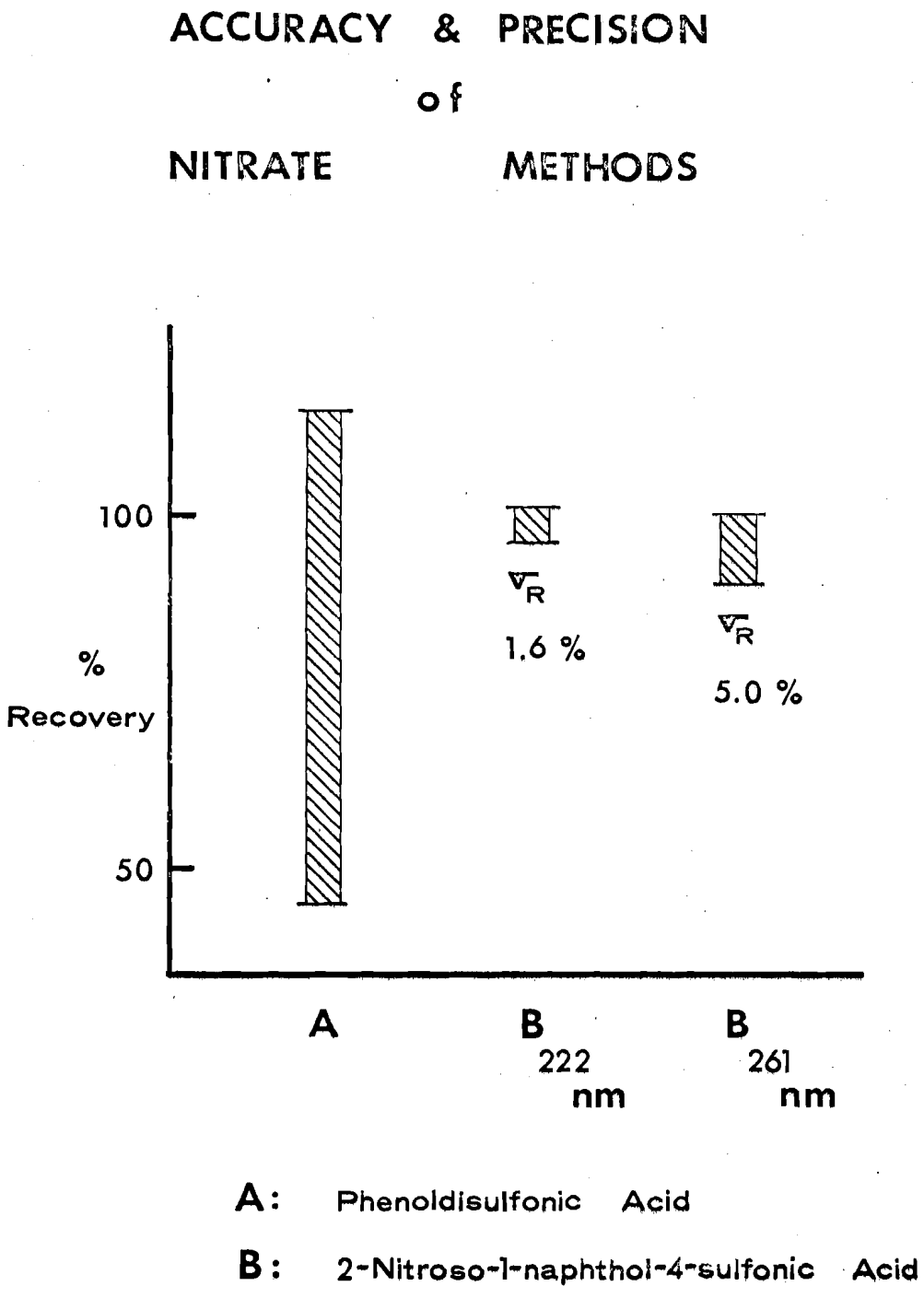


Figure 24. Accuracy and precision of methods of determining nitrate in water

Table 9. Precision Study Nitrate-Nitrogen Content of Natural Waters Using 2-Nitroso-1-Naphthol-4-Sulfonic Acid Method

	222 mμ				261 mμ	
Sample	A	NO_3^--N ppm	ave. NO_3^--N ppm	σ NO_3^--N ppm	ave. NO_3^--N ppm	σ NO_3^--N ppm
Ohio	0.264	1.64	1.76	0.069	1.67	0.096
	0.274	1.79				
	0.276	1.81				
	0.275	1.80				
	0.272	1.76				
Crab Orchard +[a]	0.480	2.89	2.90	0.011	2.81	0.072
	0.480	2.89				
	0.483	2.91				
	0.482	2.90				
	0.483	2.91				
Ohio +[a]	0.823	4.31	4.29	0.029	4.28	0.086
	0.817	4.25				
	0.820	4.28				
	0.819	4.27				
	0.829	4.32				
Mississippi	0.35		1.44 (ten trials)	0.026	1.30	0.125

[a]This solution was spiked with 3.00 ppm NO_3^--N.

of the water samples taken for the analysis were varied in such a manner that the reproducibility of the method was studied over the entire portion of the Beer's-law curve.

The analytical method for the determination of nitrate proposed in this discussion was found to have the following advantages over the phenol-disulfonic acid method:

1) A multipurpose, commercially-available, analytical reagent (2-nitroso-1-naphthol-4-sulfonic acid) was used for the color-developing compound.

2) Sample evaporation was unnecessary and absorbance values on a given sample could be obtained within a time period of 35 to 75 minutes after a sample pretreatment procedure common to both the phenoldisulfonic acid method and the 2-nitroso-1-naphthol-4-sulfonic acid method.

3) The use of a hazardous, strong-acid system (fuming sulfuric acid) has been avoided, thus helping to prevent serious burns. By personal experience, it was found that little tissue damage was encountered if spilled perchloric acid was rinsed from the skin within 5 to 10 seconds after contact. Cotton and wool materials were not damaged if areas spattered with perchloric acid were promptly neutralized with a sodium bicarbonate slurry.

4) The viscosity of the perchloric acid was such that pipet drainage times were very similar to those of aqueous solutions.

5) The use of ammonium hydroxide was not necessary, nor employed.

The proposed analytical method for nitrate determination was found to have the following advantages over the brucine method for nitrate:

1) The use of sulfuric acid was not necessary, thus avoiding the associated hazards.

2) The color-developing reagent was not a highly toxic alkaloid.

3) Special handling procedures or equipment (i.e., cardboard boxes to minimize light exposure) were not needed during color development.

4) It was not necessary to obtain Beer's-law data daily when the same reagent solutions were being used.

The proposed analytical method using 2-nitroso-1-naphthol-4-sulfonic acid was found to require the following equipment and procedure cautions:

1) An ultraviolet spectrophotometer was necessary if nitrate concentrations were to be determined using absorbance values from 222 mμ and 261 mμ. Filter photometers or Nessler tubes may be used if nitrate concentrations are to be measured by the decrease in the absorbance of the cobalt complex of the reagent.

2) A means of maintaining a temperature of 50 ± 2 °C was required.

3) The samples and Beer's-law standards should be heated for the same amount of time, that being within 60 seconds of one another.

4) The use of Dreft and probably other alkylbenzenesulfonate detergents in cleaning glassware should be avoided. The use of Alconox and Heamo-Sol cleaning powders was permissable.

5) It was necessary to survey each bottle of perchloric acid for oxidants and the ability to cause the formation of 2-nitro-1-naphthol-4-sulfonic acid. Perchloric acid from G. Frederick Smith Chemical Company was found to consistently pass these requirements.

V. CONCLUSIONS

The chemistry of the reaction of sodium nitrate with 2-nitroso-1-naphthol-4-sulfonic acid to form 2-nitro-1-naphthol-4-sulfonic acid in perchloric acid has been extensively studied and the results of these studies reported herein. The formation of 2-nitro-1-naphthol-4-sulfonic acid in 6.7 N perchloric acid has been shown to be essentially complete within 70, 30, and 20 minutes at 50.0, 60.0, and 70.0 ^{o}C, respectively. The relative amount of reaction has been shown to be a complex function of the perchloric acid concentration which could be explained by the fact that two possible mechanisms existed through which 2-nitro-1-naphthol-4-sulfonic acid could be formed from 2-nitroso-1-naphthol-4-sulfonic acid. Mole-ratio studies suggested that in 6.7 N perchloric acid, nitrate was oxidizing 2-nitroso-1-naphthol-4-sulfonic acid; while in 8.4 and 10 N perchloric acid, nitrate was nitrating 2-nitroso-1-naphthol-4-sulfonic acid to form 2-nitro-1-naphthol-4-sulfonic acid.

The effect of nitrite was studied and shown to possibly exert a positive catalytic effect on the reaction between sodium nitrate and 2-nitroso-1-naphthol-4-sulfonic acid in 6.5-7.3 N perchloric acid. Nitrite has also been shown to be able to react with 2-nitroso-1-naphthol-4-sulfonic acid to form 2-nitro-1-naphthol-4-sulfonic acid in 6.5-7.3 N perchloric acid.

Evidence has been presented which illustrated that the reaction between sodium nitrate and 2-nitroso-1-naphthol-4-sulfonic acid in 6.7 N perchloric acid could be used in an analytical method. Other than Dreft and chloride, the only interferences encountered were oxidizing or reducing

agents. The interference of chloride, iodide, and iron(II) were removed by filtration of precipitates formed by these ions. The interference of nitrite was to be removed by oxidation with permanganate, and subsequent corrections applied.

The system conformed to Beer's law from 0.25 to 10 μg of NO_3^--N, allowing for the detection of 0.04 mg NO_3^--N/l using a 6.00-ml sample of water. The nature of the Beer's-law curve was such that the working region was 0.25 to 20 μg of NO_3^--N, allowing for the determination of 0.04 to 3.3 mg NO_3^--N/l using a 6.00-ml sample, while the range for a 1.00-ml sample was 0.25 to 20.0 mg/l NO_3^--N.

The accuracy of the method, determined by the recovery of a known added amount of nitrate, was found to be better than the brucine method when the absorbance was measured at 222 mμ. The precision of the method was shown to be limited to the level of random spectrophotometric errors which was (1.1-1.9) x 10^{-2} mg NO_3^--N/l at 222 mμ and (7.2-12.6) x 10^{-2} mg NO_3^--N/l at 261 mμ. The measurement of absorbance, which was subsequently linearly related to nitrate concentration, was accomplished for 222 mμ, 261 mμ, and 525 mμ which correspond to absorption maxima for 2-nitro-1-naphthol-4-sulfonic acid, and the cobalt complex of the latter, respectively.

The natural-water samples were such that development of the cobalt complex was not necessary because the samples did not absorb strongly at 222 mμ or 261 mμ after being heated in perchloric acid.

The time suggested for color development of a pretreated sample was 70 minutes; however, a 30-minute period could be utilized with probably only a slight increase in the magnitude of precision values.

VI. LITERATURE CITED

(1) J. H. W. J. Burden, *Analyst, 86,* 429 (1961).

(2) T. E. Larsen and Laurel Henly, OWRR Final Report 65-05G, University of Illinois Water Resources Center, Urbana, Illinois, June 1966.

(3) A. M. G. Macdonald, *Ind. Chemist, 30,* 515 (1955).

(4) A. M. G. Macdonald, *Ind. Chemist, 30,* 568 (1955).

(5) M. W. Skougstad and M. J. Fishman, *Anal. Chem., 33,* 138R (1961).

(6) M. W. Skougstad and M. J. Fishman, *Anal. Chem., 35,* 179R (1963).

(7) M. W. Skougstad and M. J. Fishman, *Anal. Chem., 37,* 232R (1965)

(8) M. J. Fishman, B. P. Robinson, and M. R. Midgett, *Anal. Chem., 39,* 261R (1967).

(9) R. Szekely, *Israel J. Chem., 3,* 13 (1966); *Anal. Abstr., 14,* 2998 (1967).

(10) J. H. de Lange, *Chem. Tech. Rev., 21,* 636 (1966); *Chem. Abstr., 66,* 51827v (1967).

(11) Toni Klein, *Wasser, Luft Bertr., 11,* 462 (1967); *Chem. Abstr., 68,* 71996u (1968).

(12) Horst Thielemann, *Math.-Naturwiss. Reihe, 17,* 445 (1968); *Chem. Abstr., 70,* 117884c (1969).

(13) "Standard Methods for the Examination of Water and Wastewater," American Public Health Association, Inc., New York, 1962, pp. 175-180.

(14) A. L. Caskey and F. N. Abercrombie, Research Report No. 3, Water Resources Center, University of Illinois, Urbana, 1966.

(15) F. N. Abercrombie, M. A. Thesis, Southern Illinois University Carbondale, Illinois 1967.

(16) F. N. Abercrombie and A. L. Caskey, *Trans. Illinois State Acad. Sci.*, *62*, 161 (1969).

(17) F. N. Abercrombie, Ph.D. Dissertation, Southern Illinois University, Carbondale, Illinois 1969.

(18) F. N. Abercrombie and A. L. Caskey, Program, 61st Ann. Conf., Ill. Sect. Am. Water Works Assoc., Chicago, 17-19 March 1970.

(19) A. L. Caskey, *Dissertation Abstr.*, *22*, 61-6156 (1962).

(20) R. J. Gillespie and D. J. Millen, *Quant. Reviews* (London), *2*, 277 (1948).

(21) E. S. Halberstadt, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2441 (1950).

(22) G. A. Benford and C. K. Ingold, *J. Chem. Soc.*, 929 (1938).

(23) E. D. Hughes, C. K. Ingold, and R. I. Reed, *J. Chem. Soc.*, 2400 (1950).

(24) R. M. Schramm and F. H. Westheimer, *J. Am. Chem. Soc.*, *70*, 1782 (1948).

(25) C. A. Bunton, E. D. Hughes, G. J. Minkoff, and R. I. Reed, *Nature*, *158*, 514 (1946).

(26) A. E. Greenberg, J. R. Rossum, N. Moskowitz, and P. A. Villarruz, *J. Am. Water Works Assoc.*, *50*, 821 (1958).

Chapter 2

SOME ASPECTS OF THE DETERMINATION OF NITRATE IN WATER USING 1-NAPHTHOL-4-SULFONIC ACID

Richard J. Antepenko and Albert L. Caskey

I. INTRODUCTION

Natural waters and water supplies contain varying amounts of trace impurities. Methods for the determination of these impurities are significant for the welfare of man and animals. The nitrate ion, recognized as a significant contributor to pollution in natural waters, is the final product of the aerobic decomposition of organic matter containing nitrogen and its presence in water indicates the final stages of biological oxidation. Trace quantities of nitrate are generally present in most surface waters and ground waters. High concentrations indicate contamination by organic matter. Sources of nitrate pollution include the manufacture and use of fertilizers and various industrial operations. The toxic effects of high-nitrate levels in water consumed by man, animals, and fish as well as suitable limits for the presence of this constituent have been reported (1,2).

Among the numerous methods available for the determination of nitrate in trace quantities, the phenoldisulfonic acid method proposed by Springel (3) is perhaps the most widely used method today. The nitrate, on treatment with phenoldisulfonic acid, forms a yellow-colored compound, the color of which is intensified in basic media. The concentration of nitrate is estimated either by colorimetric comparisons against standard solutions, or by spectrophotometrically measuring the absorbance of the solutions and comparing with a similarly obtained calibration curve.

Osmo Makitie (4) reported a method for the determination of nitrate in water using sodium 1-naphthol-4-sulfonate in dilute sulfuric acid. The system was reported to follow a nitration procedure similar to that of the phenoldisulfonic acid method. The paste, containing nitrate, obtained after evaporation of the sample, was treated with the reagent in 2.5 M sulfuric acid at room conditions; the slurry was made basic and the concentration of nitrate was estimated by measuring the absorbance of the nitration product, said to be 2-nitro-1-naphthol-4-sulfonic acid.

Abercrombie (5) prepared 2-nitro-1-naphthol-4-sulfonic acid by two independent methods. First, 2-nitroso-1-naphthol-4-sulfonic acid was reacted with equal molar or less nitrate in dilute acid to form the product. In the second method of synthesis, 2-nitroso-1-naphthol-4-sulfonic acid was oxidized by hydrogen peroxide in a trifloracetic acid medium to form the desired species. A comparison of the spectral data for 2-nitro-1-naphthol-4-sulfonic acid reported by Makitie with spectral data obtained by Abercrombie revealed several discrepancies.

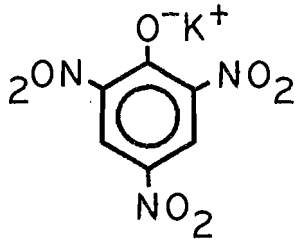
Makitie reported that nitration of 1-naphthol-4-sulfonic acid proceeded in 5 N [2.5 M] sulfuric acid to form 2-nitro-1-naphthol-4-sulfonic acid, but attempts in this laboratory to repeat the nitration reaction

following the reported procedure failed. The study reported here was undertaken in an attempt to identify the product or products formed in this system, as well as establish more optimum conditions for the nitration, and thereby evaluate the method proposed by Makitie.

II. HISTORICAL

The phenoldisulfonic acid method for the determination of nitrate was first proposed by Sprengel (3) in 1863. In 1885, Grandval and Lajoux (6) provided a procedure for this method on a practical basis which remains essentially the same today. The procedure consisted of moistening the residue, obtained by evaporating a water sample, with a solution of phenol in concentrated sulfuric acid. The resulting solution was diluted with water and made basic with ammonium, sodium or potassium hydroxide. The yellow color produced, thought to result from the formation of an alkali salt of picric acid (*I*), was then matched against the color of standard solutions prepared in a similar manner.

After much controversy concerning the identity of the species producing the yellow color in basic media, Chamot and Pratt (7,8) showed, through isolation and characterization, that the color was caused by the formation of the tripotassium salt of nitrophenoldisulfonic acid (*II*).



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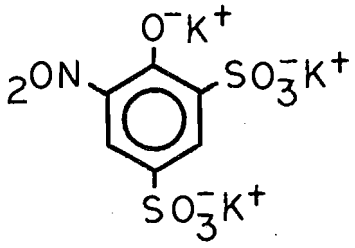

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The American Water Works Association (9) has tenatively accepted the phenoldisulfonic acid method for the determination of nitrate, a method which estimates nitrate-nitrogen levels down to 0.01 mg/l. The reagent, 1-phenol-2,4-disulfonic acid (*III*), is prepared by dissolving 25 g of white phenol (*IV*) in 150 ml of concentrated sulfuric acid, adding 75 ml of

of chloride without interference. Besides chloride, carbonate and nitrite interfered with the method but ammonia, magnesium salts and phosphate did not. Maximum precision and accuracy were obtained on sample sizes containing from 0.05 to 1 mg nitrate-nitrogen residue after evaporation. Results from samples containing more than 1.5 mg nitrate after evaporation were not reliable.

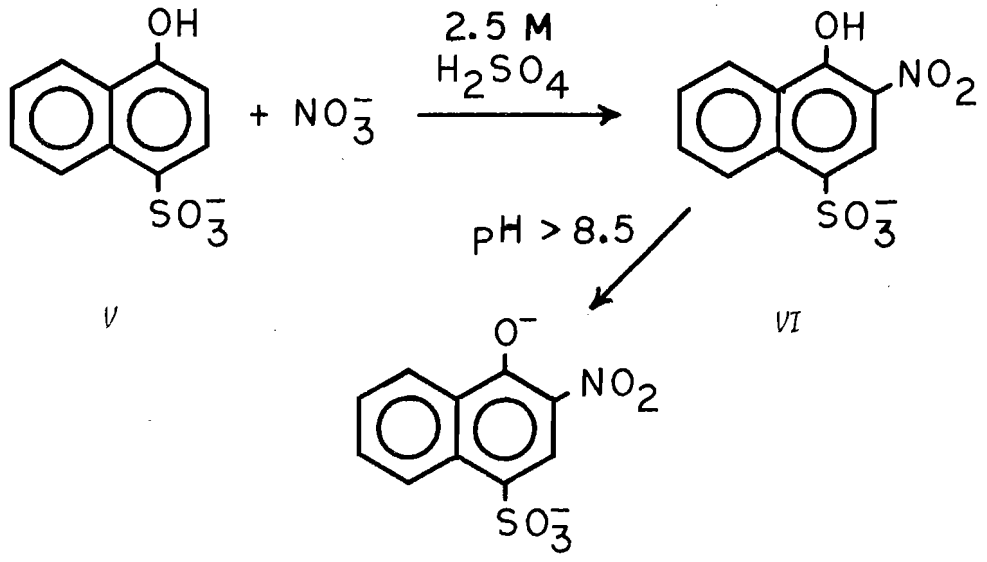
The reagent was prepared by dissolving 20 g of α-naphthol in 200 ml of hot, concentrated sulfuric acid. The mixture was heated on a steam bath for 1 to 1½ hours with stirring.

The proposed procecure for the determination of nitrate in water was similar to the one used by the phenoldisulfonic acid method. An aliquot of nitrate solution was evaporated to dryness on a steam bath and allowed to cool. Two ml of α-naphthol sulfonic acid solution was mixed thoroughly with the nitrate residue. After 15 minutes the reaction solution was diluted and neutralized with 8 ml of 10 N potassium or sodium hydroxide and finally diluted to 250 ml. The developed color was compared with those of similarly prepared standards using a Duboscq colorimeter.

Murty (11) later described a modification of the α-naphthol sulfonic acid method for the determination of nitrate in the presence of nitrite. The nitrate sample containing nitrite was treated with an excess of 1 % urea solution followed by four of five drops of 0.002 N sulfuric acid. The sample was then subjected to the usual procedure for the determination of nitrate (10).

Makitie (4) reported a spectrophotometric method for the determination of nitrate in water as a nitronaphtholsulfonate. 1-Naphthol-4-sulfonic acid (*V*), the reagent, which was also the major species in the reagent solution employed by Murty and Gopalarao (10), was said to react with

nitrate to form the "ortho"-nitronaphtholsulfonic acid. The nitration product was described to exist as the yellow-green anionic form, 2-nitro-1-naphthol-4-sulfonate (*VI*), when present in acidic medium, but as the dianion (*VII*) in a highly alkaline medium with the color being intensified through naphtholic dissociation.



V *VI*

VII

Makitie reported that "the nitration is easily carried out by the procedure normally used in the phenoldisulfonic acid method".

Procedure for determination of nitrates (4)

The sample solution has to be treated with silver sulphate to eliminate chlorides and with activated charcoal to decolourize it, if need be.

An aliquot of not less than 10 micrograms of nitrate-N is evaporated to dryness in a dish on a water bath, cooled and the residue dissolved in 2 ml of 0.1 M solution of 1-naphthol-4-sulfonic acid (sodium salt) in 5 N sulphuric acid.

The coloured solution is diluted with water, buffered to alkaline pH by means of borax/ammonium hydroxide buffer (at least pH 8.5), and made up to 100 ml.

The absorbance is measured, preferably spectrophotometrically at 435 mμ, against a blank and compared with a calibration curve obtained similarly.

Makitie listed two references, Jackson (12), and Theroux, *et.al.* (13), of which both provided procedures for a phenoldisulfonic acid method for nitrate determination similar to the one used by the American Water Works Association. Jackson applied the method for the determination of nitrate in soil. He described the nitration taking place at the 6 position of 2,4-phenoldisulfonic acid (*III*) forming nitrophenoldisulfonic acid (*II*). Theroux employed the method for the determination of nitrate in water and sewage. He reported the product was picric acid (*I*), a product reported incorrect by Chamot and Pratt (7,8).

The proposed nitration procedure using 1-naphthol-4-sulfonic acid as the reagent was reported to be similar to the one used in the phenoldisulfonic acid method. In the procedures presented by Jackson or Theroux, the nitration reaction occurred in concentrated sulfuric acid containing fuming sulfuric acid. The nitrate sample was evaporated to dryness previous to the determination since "the reaction must be effected in the virtual absence of water" (12). If Makitie's procedure was similar to the phenoldisulfonic acid method, why was the reagent used in 2.5 M sulfuric acid when a similar procedure would call for a nonaqueous, concentrated acid system? If the nitration of 1-naphthol-4-sulfonic acid proceeded in dilute sulfuric acid, what purpose was there in evaporating the nitrate

sample to dryness, since all this did was complicate the procedure as well as consume time.

Witt and Kaufman (14), in 1891, reported that 2-nitroso-1-naphthol-4-sulfonic acid reacted rapidly and quantitatively with excess nitrate in hot, acidic, aqueous media to form 2,4-dinitro-1-naphthol. Abercrombie and Caskey (15), as presented in detail by Abercrombie (5), studied the effects of temperature and nitrate concentration in varied, aqueous, perchloric acid media and found that when an excess of 2-nitroso-1-naphthol-4-sulfonic acid was treated with nitrate under similar conditions, the product formed was 2-nitro-1-naphthol-4-sulfonic acid. Utilizing the latter reaction, Abercrombie and Caskey (16), as presented in detail by Abercrombie (17), proposed a spectrophotometric method for the determination of nitrate in natural waters. The product, 2-nitro-1-naphthol-4-sulfonic acid, obtained by Abercrombie and Caskey (15), was the same product reported by Makitie to be formed from the reaction of nitrate with 1-naphthol-4-sulfonic acid in a 2.5 M sulfuric acid medium. For identification purposes, Abercrombie and Caskey attempted to use the spectral data reported by Makitie (4) for 2-nitro-1-naphthol-4-sulfonic acid, but found that the observed spectral values (15) were significantly different from the reported values (4).

The characteristics of the ultraviolet spectra for 2-nitroso-1-naphthol-4-sulfonic acid, 2,4-dinitro-1-naphthol and 2-nitro-1-naphthol-4-sulfonic acid, reported by Abercrombie and Caskey (15), and for 2-nitro-1-naphthol-4-sulfonic acid, reported by Makitie (4), are presented in Table 1. 2,4-Dinitro-1-naphthol was confirmed by Abercrombie and Caskey to be a product of the system when excess nitrate reacted with 2-nitroso-1-naphthol-4-sulfonic acid. 2-Nitro-1-naphthol-4-sulfonic acid was reported to be a product both by Makitie and by Abercrombie and Caskey. One can

Table 1. Ultraviolet Absorption Spectral Data

2-Nitroso-1-Naphthol-4-Sulfonic Acid		2,4-Dinitro-1-Naphthol		2-Nitro-1-Naphthol-4-Sulfonic Acid			
Lit.[a]		Lit.[a]		Lit.[a]		Lit.[b]	
λ_{max} (mμ)	ε	λ_{max} (mμ)	ε	λ_{max} (mμ)	ε	λ_{max} (mμ)	ε
		210	22,400	221	38,700		
261	27,000	249	16,800	270	21,300		
		299	12,300	295	9,610		
347	5,000	375	8,450	387	5,280	360	3,000

[a]Abercrombie and Caskey (15)

[b]Makitie (4), the wavelength maximum and molar absorbtivity were estimated from a graph of $\varepsilon \times 10^{-3}$ vs. λ

easily see that the molar absorptivity value for 2-nitro-1-naphthol-4-sulfonic acid obtained by Makitie was 50 % lower than the value reported by Abercrombie and Caskey. Also the position of the absorbance maximum, reported by both parties for the same species, differed by almost 25 mμ. With respect to the position of wavelength maximum and molar absorptivity, the product Makitie reported to be 2-nitro-1-naphthol-4-sulfonic acid, appeared to compare closer with the 2-nitroso species.

The ultraviolet spectra of the reagents and reaction products as reported by Makitie (4) and by Abercrombie and Caskey (15), the latter being graphically presented as shown earlier by Abercrombie (5), have been simultaneously presented in Figure 1. 1-Naphthol-4-sulfonic acid, 2-nitroso-1-naphthol-4-sulfonic acid, 2-nitro-1-naphthol-4-sulfonic acid and 2,4-dinitro-1-naphthol have been symbolized by 1-OH, 2-NO, 2-NO_2 and 2,4-NO_2, respectively. Inasmuch as the spectra were plotted as a function of molar absorptivity, concentration effects should not be present.

The notable differences in spectral characteristics, which were reported for the same organic compound, formed the basis for an examination of the nitration system reported by Makitie. The objective of the following study was to identify the species involved in the reaction of 1-naphthol-4-sulfonic acid with nitrate as well as establish the laboratory conditions that best facilitated the reaction. Before making an extensive, detailed study of the system, a "preliminary study," covering the main points of concern, was completed and has been presented in this report.

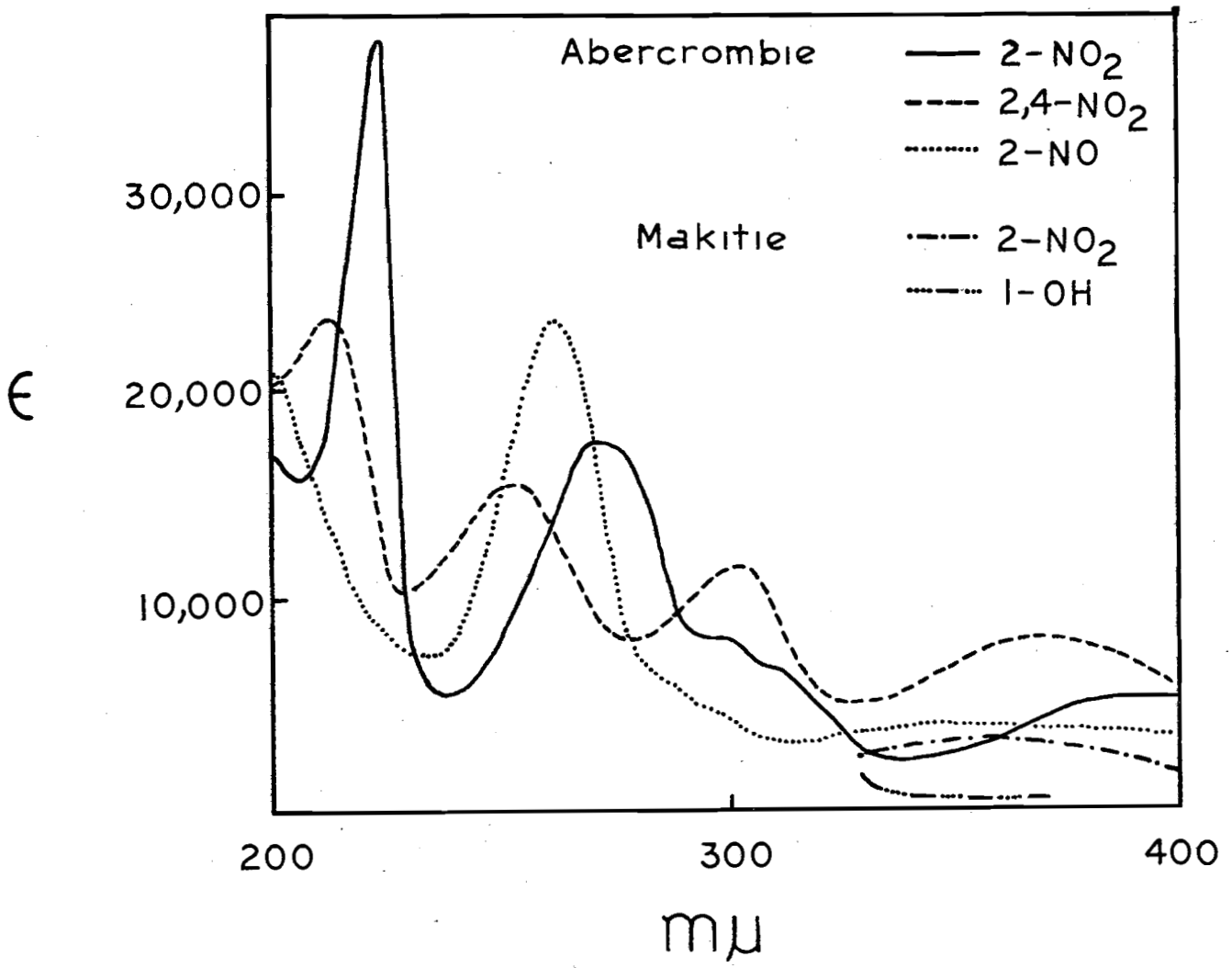


Figure 1. Ultraviolet absorption spectra, in acidic media, of 1-naphthol-4-sulfonic acid (1-OH), 2-nitroso-1-naphthol-4-sulfonic acid (2-NO), 2-nitro-1-naphthol-4-sulfonic acid (2-NO_2), and 2,4-dinitro-1-naphthol (2,4-NO_2)

III. EXPERIMENTAL

A. Reagents

Reagent grade chemicals meeting American Chemical Society specifications were used whenever they were commercially available. A list of the pertinent chemicals used has been presented in Table 2.

All water used was deionized water prepared by passing distilled water through a column of monobed, self-indicating, ion-exchange resin, Rohm and Haas Amberlite MB3 (Mallinckrodt 332G). The deionized water was stored free from carbon dioxide.

B. Equipment

A Beckman Model DB (1401) recording spectrophotometer, equipped with 1.0-cm, matched, silica, absorption cells, was used for absorbance measurements.

A Perkin Elmer Model 137B Infracord was used to obtain infrared spectra.

A Thomas Hoover Unimelt Capillary Melting-Point Apparatus (Thomas 6406M) was used to obtain melting points.

A Buchler Portable Flash Evaporator (Buchler PTFF-1C) was used to remove solvents.

A Blue M Magni Whirl Utility Water Bath and a constant-temperature bath equipped with a Precision Scientific Co. Portatemp regulator (Sargent 84875) were used.

A National Appliance Company, full-view, vacuum oven (Model No. 5830) was used for drying at reduced atmospheres.

A water bath was constructed from a large, stainless-steel pan placed on a Corning PC-351 hot-plate-magnetic-stirrer and was connected to

Table 2. Chemicals Used and Chemical Suppliers

Compound	Formula	Vendor*	Vendor's Catalog Number
Sodium-1-Naphthol-4-Sulfonate	$HOC_{10}H_6SO_3Na$	1	P232
2,4-Dinitro-1-Naphthol	$(NO_2)_2C_{10}H_5OH$	1	P5168
Sodium Nitrate	$NaNO_3$	2	SX655
p-Toluidine	$CH_3C_6H_4NH_2$	1	254
Darco G-60 Activated Carbon		2	CX645
Amberlite CG-120 Ion-Exchange Resin	$R_zSO_3^-Na^+$	3	3337
Rexyn 102(H) Ion-Exchange Resin	$R_zCO_2^-Na^+$	4	R184
Sulfuric Acid	H_2SO_4	5	1180

* 1. Eastman
2. Matheson Coleman & Bell
3. Mallinckrodt
4. Fisher
5. Baker and Adamson

a ring-stand. Microclamps were used to hold a maximum number of six, 100-ml flasks in the bath at one time.

Borosilicate glassware was used exclusively. All volumetric ware was NBS Class "A" quality. An Ace 6684 standard-taper unit was used for vacuum sublimations. Whatman GF/A glass filter paper was used extensively.

C. Purification of Sodium 1-Naphthol-4-Sulfonate

Sodium 1-naphthol-4-sulfonate was purified as the p-toluidinium salt. Equal-molar quantities of sodium 1-naphthol-4-sulfonate and p-toluidine were dissolved in a minimum amount of hot (1:5 v/v) hydrochloric acid. The dark-brown solution was decolorized with activated carbon and cooled to 5 °C to facilitate crystallization. After several recrystallizations from dilute hydrochloric acid, the p-toluidinium 1-naphthol-4-sulfonate was suspended in water and sodium hydroxide added to increase the pH of the suspension to 9. The suspension was extracted with ether to remove the p-toluidine, and the remaining aqueous solution was then passed through a column containing a strong-acid, cation-exchange resin in the hydrogen-ion form. The highly-acidic, effluent solution was adjusted to pH 6.8 with sodium hydroxide and the solvent removed by flash evaporation at 50 °C. The sodium 1-naphthol-4-sulfonate was dried in a vacuum oven at 40 °C for 24 hours.

D. Preparation of Potassium 1-Naphthol-4-Sulfonate

Potassium 1-naphthol-4-sulfonate was prepared in a manner analogous to the purification of sodium 1-naphthol-4-sulfonate, except that the highly-acidic, effluent solution collected from the column, which consisted of an aqueous solution of 1-naphthol-4-sulfonic acid, was passed

through a second column containing a weak acid, cation-exchange resin in the potassium-ion form. The effluent solution was evaporated to dryness with a flash evaporator at 50 °C and the resulting solid, potassium 1-naphthol-4-sulfonate, was dried in a vacuum oven at 40 °C for 24 hours.

E. Elemental Analysis

Quantitative elemental analyses were made by Galbraith Laboratories, Inc., P. O. Box 4187, Knoxville, Tennessee.

F. Procedures

1. Solution Preparation

All solutions and carbon used for recrystallization were degassed by a short period of boiling.

Solution preparation consisted of dissolving a precisely weighed amount of material in water followed by dilution to volume in a volumetric flask.

2. The Reaction of 1-Naphthol-4-Sulfonic Acid with Nitrate in 2.5 M Sulfuric Acid

Nitrate samples were prepared by placing 2.00-ml aliquots of 0.1000 M sodium nitrate solution in small beakers followed by heating on either steam cones or hot plates to dryness. After the beakers and contents cooled to room temperature, 2.00-ml aliquots of 0.1000 M potassium 1-naphthol-4-sulfonate in 2.5 M sulfuric acid were mixed thoroughly with the nitrate residues for a short period. Some reaction mixtures were heated by either steam cones or hot plates for varied periods of time. Sometimes

when a brown precipitate formed, it was isolated. The reactions were stopped by dilution with cold water, followed by equilibration to room temperature and dilution to 100.0 ml with water. Aliquots, 5.00 ml, were placed in 100-ml volumetric flasks and made either acidic or basic by addition of either perchloric acid or sodium hydroxide, and after dilution to volume with water, their ultraviolet spectra were recorded.

A solution of the brown residue was prepared by dissolving 2.7 mg in water; the ultraviolet and visible spectra of aliquots in acidic and basic solutions were recorded.

A small portion of the brown residue was sublimed under vacuum at 100 °C.

3. A Study on the Reactant Combinations Which Promote a Color Change in the Nitration System

Four varied arrangements of reactants were placed in four, medium-sized beakers fitted with beaker covers. Sodium nitrate and reagent (sodium 1-naphthol-4-sulfonate) were employed in concentrations of 0.1000 M. The first beaker contained nitrate and reagent in 2.5 M sulfuric acid, the second beaker contained nitrate and reagent, the third beaker contained nitrate in 2.5 M sulfuric acid and the fourth beaker contained reagent in 2.5 M sulfuric acid. The beakers were heated by steam cones either to dryness or until a color change occurred.

4. The Effect of Acid Concentration on the Reaction of 1-Naphthol-4-Sulfonic Acid with Nitrate

Fourteen solutions, each containing a total volume of 20.00 ml, were prepared in 100-ml volumetric flasks. In each flask was placed 1.00-ml 0.1000 M sodium nitrate solution, 1.00-ml 0.1000 M sodium 1-naphthol-4-

sulfonate solution and 18.00 ml of varied amounts of concentrated sulfuric acid and water providing a sulfuric acid concentration range of 2.5 M to 9.1 M. The solutions were stoppered, shaken, and allowed to react for 60 minutes at 91 °C in a water bath. The reactions were quenched with cold water, the solutions allowed to equilibrate to room conditions, and after dilution to volume, their visible and ultraviolet spectra were recorded.

5. The Reaction of 1-Naphthol-4-Sulfonic Acid with Nitrate under Varying Conditions of Acid Concentration, Temperature, and Time

The procedure employed in the studies consisted of adding precisly measured volumes of sodium nitrate solution and sulfuric acid solution to 100-ml volumetric flasks. Water was next added in studies where a constant volume was desired. Just prior to immersion of the flask in the bath, a precise volume of sodium 1-naphthol-4-sulfonate solution was added. The flask was immediately stoppered, shaken, and placed in the bath at the desired temperature. After the allotted time had passed, the reactions were stopped with the addition of ice water. The solutions were warmed to room temperature and after dilution to volume, aliquots were taken. The aliquots were treated until they contained 0.01 M sodium hydroxide, and then their visible and ultraviolet spectra were recorded.

a. The system was studied in 2.5 M sulfuric acid at 81 °C for 10 to 35 minutes. Stock solutions of 0.2000 M sodium nitrate in 2.5 M sulfuric acid and 0.2000 M sodium 1-naphthol-4-sulfonate in 2.5 M sulfuric acid were used.

b. The system was studied in 7.3 M and 8.2 M sulfuric acid at 60 °C for 3 to 5 hours. Stock solutions of 0.1000 M sodium nitrate, 0.1000 M sodium 1-naphthol-4-sulfonate and either 7.4 or 8.3 M sulfuric acid were used.

c. The system was studied in 9.9 M sulfuric acid at 72 °C for 20 to 90 minutes. Stock solutions of 0.1000 M sodium nitrate, 0.1000 M sodium 1-naphthol-4-sulfonate and 10 M sulfuric acid were used.

d. The system was studied in 9.9 M sulfuric acid at 79 °C for 30 to 94 minutes. Stock solutions of 0.0294 M sodium nitrate, 0.0324 M sodium 1-naphthol-4-sulfonate and 10 M sulfuric acid were used.

e. The system was studied in 9.9 M sulfuric acid at 95 °C for 5 to 60 minutes. The stock solutions described above for study d were used.

f. The system was studied in 17.6 M sulfuric acid at room conditions for 5 and 15 minutes. Stock solutions of 0.1000 M sodium nitrate, 0.1000 M sodium 1-naphthol-4-sulfonate and concentrated sulfuric acid were used.

6. The Effect of Nitrate Concentration on the Reaction of 1-Naphthol-4-Sulfonic Acid

Nitrate solutions were prepared by delivering 10.0 ml of 10.6 M sulfuric acid and 0.10 ml of either 0.00100 M, 0.0100 M, 0.0200 M or 0.0300 M sodium nitrate solution into 100-ml volumetric flasks. Then, 0.10-ml 0.04328 M sodium 1-naphthol-4-sulfonate was added just before the flasks were placed in the bath at 79 °C. After 15 minutes the reactions were stopped by the addition of ice water, and after equilibration to room conditions and dilution to volume, the visible and ultraviolet spectra of the solutions were recorded.

IV. RESULTS AND DISCUSSION

Purified sodium 1-naphthol-4-sulfonate was characterized as the monohydrate by obtaining a neutralization equivalent, a loss of water and an elemental analysis. A potentiometric titration with aqueous sodium hydroxide (0.1249 N with rel. std. dev. 0.098 %, 3 trials) gave an equivalent weight of 274.6, theoretical 264.2 for the monohydrate. The loss of water, determined by loss in weight on drying, was experimentally found to be 6.64 % in comparison to a theoretical loss of 6.82 % for the monohydrate. Anal. Calcd. for $C_{10}H_7O_4NaS$: C, 45.42; H, 3.43; O, 30.31; Na, 8.70; S, 12.13. Found: C, 45.45; H, 3.26; O, 30.38 (by difference); Na, 8.80; S, 12.11.

Infrared spectra of the potassium and sodium 1-naphthol-4-sulfonates were recorded and are presented in Figures 2 and 3. Both spectra contained the strong sulfonic acid absorption bands between 1260 - 1150 cm^{-1} for asymmetric-stretching vibrations and between 1080 - 1100 cm^{-1} for symmetric-stretching vibrations of the $-SO_2-$ functional group, which according to Nakanishi are the same for the salts of sulfonic acids (18).

The ultraviolet spectrum of sodium 1-naphthol-4-sulfonate dissolved in 95 % ethanol was obtained. The results were compared to the spectral data reported by Daglish (19). The experimentally obtained values for $\log_{10}\varepsilon$ of 4.64, 3.95 and 3.69, at wavelength maxima of 230.7, 295 and 320 mμ, respectively, were greater than the reported values for $\log_{10}\varepsilon$ of 4.50, 3.85 and 3.64, at wavelength maxima of 234, 300 and 320 mμ, respectively. A complete tabulation of the experimental and literature values is presented in Table 3.

The reaction of 1-naphthol-4-sulfonic acid with nitrate was studied under the conditions reported by Makitie (experiment 2). Dry nitrate

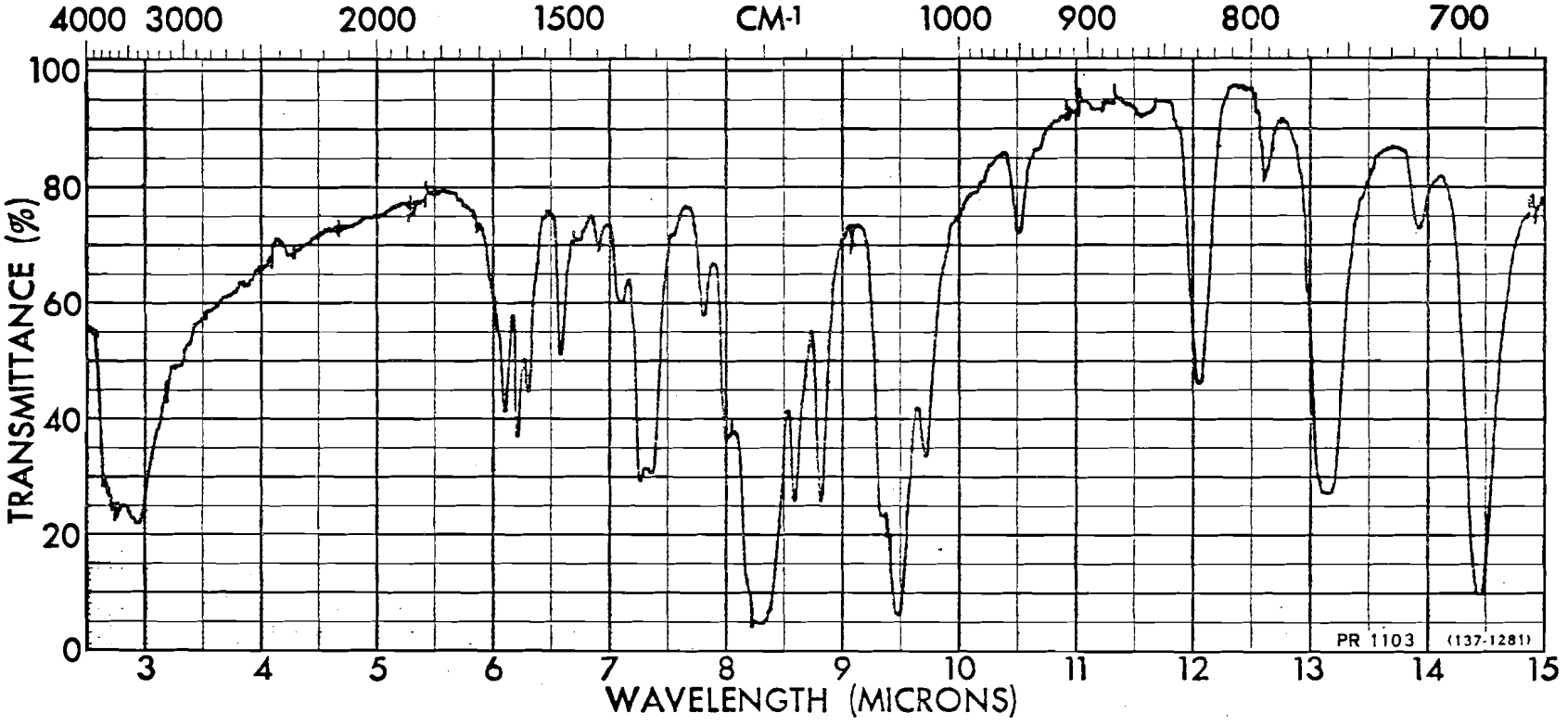


Figure 2. Infrared spectrum of potassium 1-naphthol-4-sulfonate, potassium bromide pellet

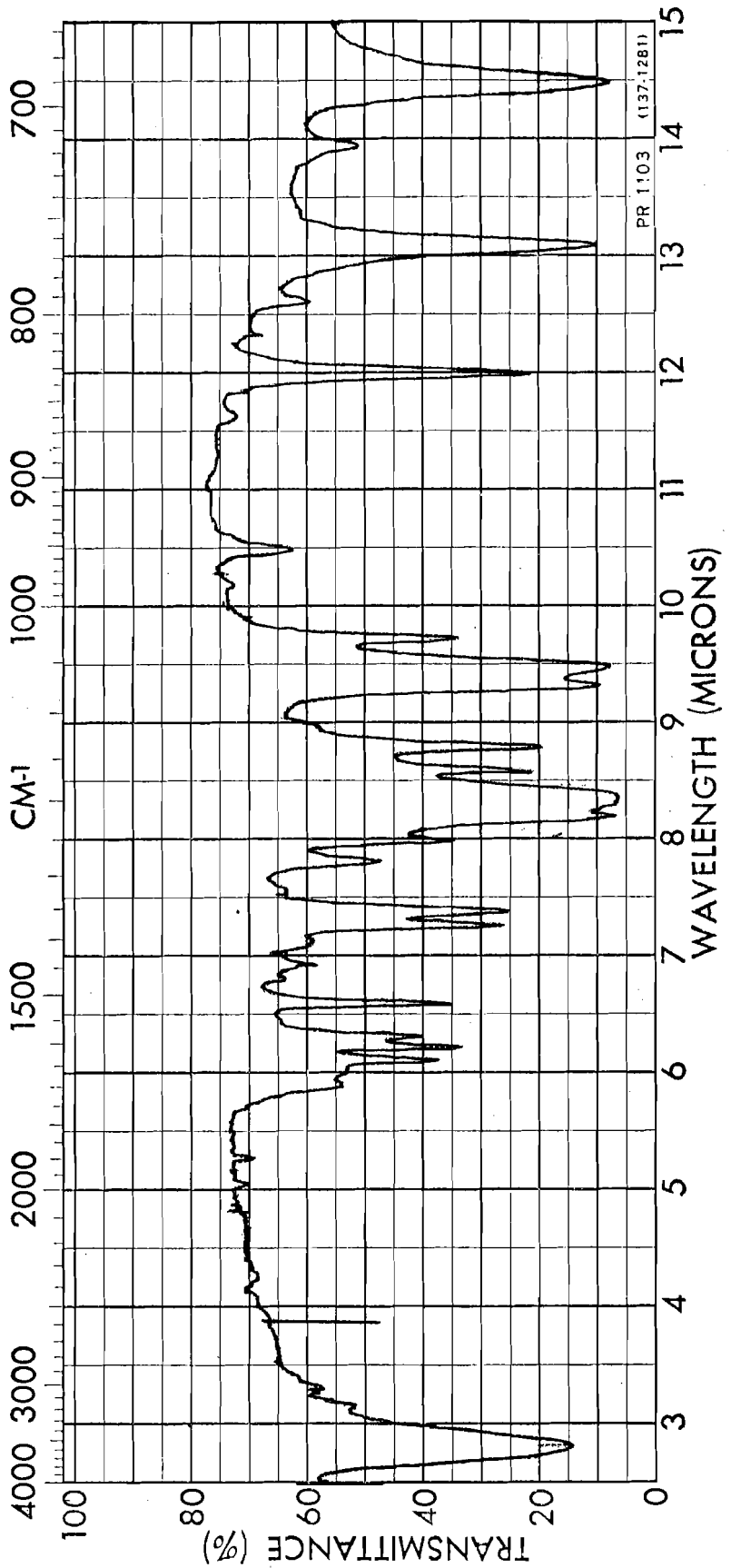


Figure 3. Infrared spectrum of sodium 1-naphthol-4-sulfonate, potassium bromide pellet

Table 3. Spectral Data of Sodium 1-Naphthol-4-sulfonate in Acidic 95 % Ethanol

Experimental		Literature[a]	
λ_{max} (mμ)	$\log_{10} \varepsilon$	λ_{max} (mμ)	$\log_{10} \varepsilon$
223	4.64		
231	4.64	234	4.50
250	3.86		
295	3.95	300	3.85
320	3.69	320	3.64

[a]Reference 19.

samples were reacted with potassium 1-naphthol-4-sulfonate in 2.5 M sulfuric acid at room conditions. The ultraviolet spectra of the diluted reaction mixtures, in either acidic or basic solution, were identical in appearance to the spectra of the reagent, potassium 1-naphthol-4-sulfonate. Molar absorptivity values for the reaction mixtures were approximately the same as those for the reagent and therefore indicated little nitration, if any occurred. Since no reaction was detected under the subjected conditions, the small differences between the molar absorbtivity values for the reaction spectra and those for the reagent were presumably due to reagent decomposition. The characteristics of the ultraviolet spectra for potassium 1-naphthol-4-sulfonate and the reaction solutions have been presented in Table 4.

Several reaction mixtures were heated with either steam cones or hot plates in an effort to facilitate the reaction. At specific acid concentrations depending upon the rate of evaporation and temperature, the reaction mixtures changed from colorless to orange and finally to a deep red. Either continued heating or dilution with water, reverted the red colored nitration solution to orange. During the time that the red color was present in the reaction mixture, a brown precipitate was formed.

The reaction in one solution was stopped at the first appearance of red color by dilution with ice-cold water. The visible and ultraviolet spectra of aliquots diluted in acidic or basic solution were recorded and their spectral characteristics have been presented in Table 5, as the "diluted red nitration reaction mixture." The spectra were similar in appearance and in the position of the wavelength maximum with the spectra of 2-nitro-1-naphthol-4-sulfonic acid, for which the spectral characteristics have also been presented in Table 5. A major difference between the two

Table 4. Ultraviolet Absorption Spectra

Reaction Product		Potassium 1-Naphthol-4-Sulfonate	
λ_{max} (mμ)	ε	λ_{max} (mμ)	ε
296[a]	5,200	296[a]	5,000
329[b]	6,200	329[b]	7,000

[a]This solution contained 0.01 M perchloric acid

[b]This solution contained 0.01 M sodium hydroxide

Table 5. Ultraviolet and Visible Absorption Spectral Data

	Diluted red nitration reaction mixture		2-Nitro-1-naphthol-4-sulfonic acid[1]		Brown precipitate		2,4-Dinitro-1-naphthol[1]	
Acid[2]	λ_{max} (mμ)	ε	λ_{max} (mμ)	ε	λ_{max} (mμ)	ε	λ_{max} (mμ)	ε
	220		221	44,000	209	22,100	212	27,000
	255	10,400			250	16,300	252	18,000
	265[4]		270	20,000	299	10.900	300	14,000
	295	3,940	297	9,000	367	7,300	375	9,000
	382	2,500	384	6,000				
Base[3]								
	226	13,300	226	27,000	259	11,500	259	15,600
	266	7,500					278	11,000
	284[4]		282	14,200	391	9,200	391	14,700
	320[4]		320[4]		434	9,760	434	15,600
	428	3,550	427	10,600				

[1]Values from reference 5.
[2]Solutions in 0.01 M perchloric acid.
[3]Solutions in 0.01 M sodium hydroxide.
[4]Estimated shoulder peak on spectrum.

was a λ_{max} at 255 mμ in the spectrum of the nitration reaction in acidic media, but absent in the spectrum of 2-nitro-1-naphthol-4-sulfonate anion. Also, a λ_{max} at 270 mμ in spectrum of 2-nitro-1-naphthol-4-sulfonate anion was present as a small shoulder peak in the reaction mixture spectrum. The spectrum of the nitration solution in basic solution contained a λ_{max} at 266 mμ that was absent in the spectrum of 2-nitro-1-naphtholate-4-sulfonate dianion.

The resemblance in the spectra of the reaction solution with the spectra of 2-nitro-1-naphthol-4-sulfonic acid indicated that this species was a product in the reported nitration system, but was not formed under the proposed conditions of 2.5 M sulfuric acid at room temperature. Also, the spectral characteristics of the reaction mixture indicated 2-nitro-1-naphthol-4-sulfonic acid was not the only product formed, but that several species were formed under the nitration conditions used.

The brown precipitate, which formed during the nitration reaction, was collected and air dried at room temperature. The material, which melted at 126-128 °C, was identified as 2,4-dinitro-1-naphthol. Sublimation of the brown material yielded long, bright-yellow needles, which melted sharply at 135-136 °C. Davis (20) in 1922, reported a melting point of 138 °C for 2,4-dinitro-1-naphthol. Mixed melting points with commercially available 2,4-dinitro-1-naphthol, mp 133-134 °C, occurred at 134-135 °C.

The ultraviolet and visible spectra of the brown material dissolved in acidic or basic solution were analogous to the spectra of 2,4-dinitro-1-naphthol found by Abercrombie (5), The spectral characteristics of the solutions containing the brown precipitate and the literature values for 2,4-dinitro-1-naphthol have been presented in Table 5 for comparison. The spectrum of the precipitate dissolved in acidic solution contained λ_{max}

at 209, 250, 299 and 367 mμ that were similar to λ_{max} at 212, 252, 300 and 375 mμ values reported for 2,4-dinitro-1-naphthol. The spectrum of 2,4-dinitro-1-naphtholate anion contained a λ_{max} at 278 mμ that was absent in the spectrum of the precipitate dissolved in basic solution. Both spectra contained identical λ_{max} values at 259, 391 and 434 mμ.

An infrared spectrum of the sublimate was identical to the spectrum of sublimed commercially available 2,4-dinitro-1-naphthol, as well as to the spectrum of 2,4-dinitro-1-naphthol reported by Abercrombie (5). The two strongest absorption bands were at 1590 cm^{-1} and 1365 cm^{-1}, which according to Nakanishi (18), are characteristic for the nitro group and are the result of asymmetric-stretching vibrations of $-NO_2$ for absorptions between 1650-1500 cm^{-1} and symmetric-stretching vibrations of $-NO_2$ for absorptions between 1370-1250 cm^{-1}.

The intense red color, which developed within the reaction mixture, was produced by a species formed in the nitration of 1-naphthol-4-sulfonic acid in sulfuric acid (experiment 3). The only combination of reactants, that produced a red color similar to the one observed in the nitration system, consisted of nitrate, reagent and sulfuric acid. Nitration did not occur in the absence of sulfuric acid at elevated temperatures.

The effect of sulfuric acid concentration on the formation and stability of 2-nitro-1-naphthol-4-sulfonic acid was studied at 91 °C, for a 1 hour reaction time (experiment 4). The pertinent results are graphically presented in Figure 4. The curves represent the absorbance of the diluted reaction mixture vs. the molar concentration of sulfuric acid in the reacting system. The formation of 2-nitro-1-naphthol-4-sulfonic acid was followed by an increase in absorbance at 264 mμ or 270 mμ, which are absorbance maxima for solutions of this species in basic or acidic media, respectively,

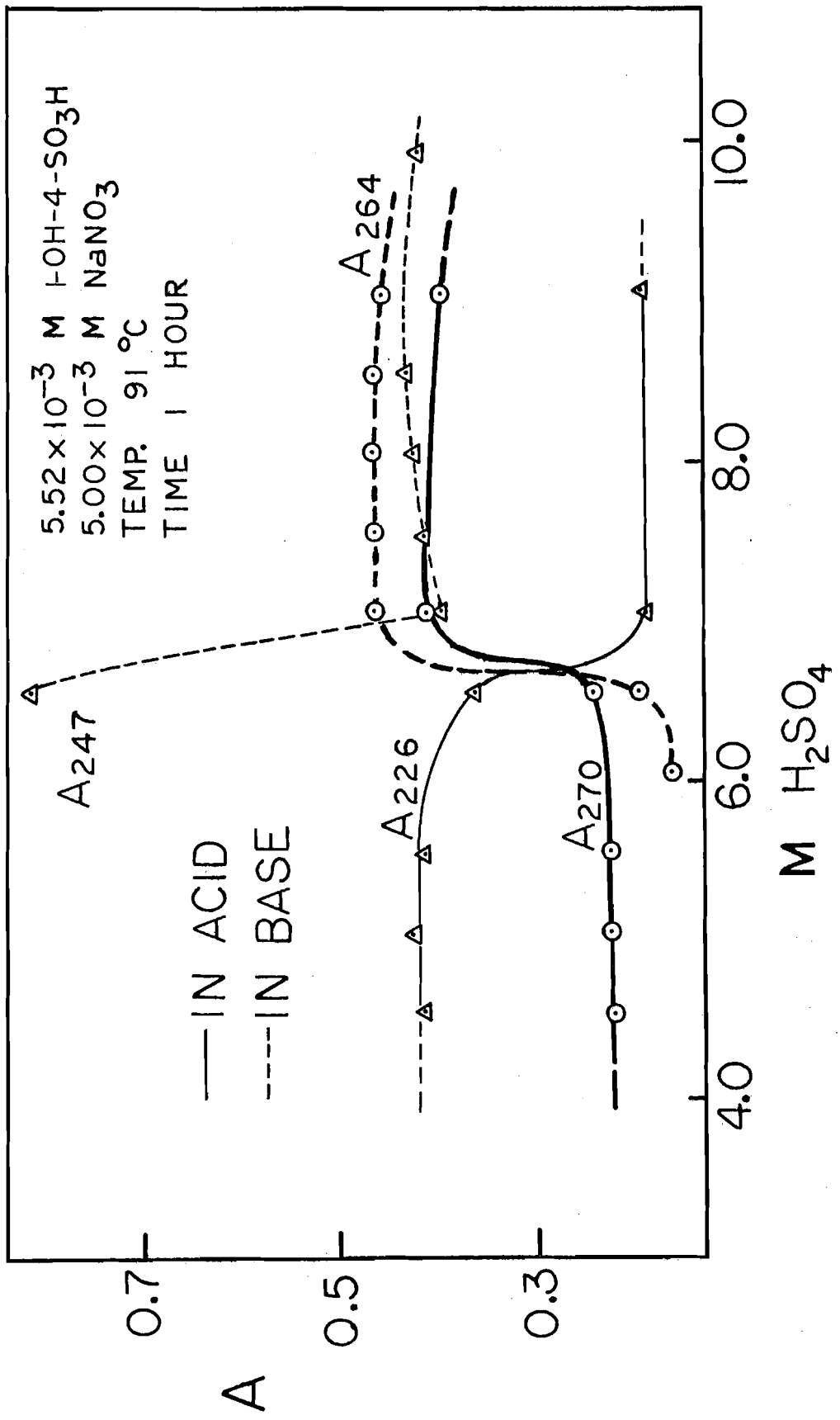


Figure 4. The formation and stability of 2-nitro-1-naphthol-4-sulfonic acid as a function of sulfuric acid concentration

or by a decrease in absorbance at 226 mμ or 247 mμ, which are absorbance maxima for the reagent in acidic or basic solution, respectively. As the acid concentration of the reaction mixture increased, the increase in absorbance at 270 and 264 mμ for solutions in acidic and basic media, respectively, and the decrease in absorbance at 226 and 247 mμ for solutions in acidic and basic media, respectively, indicated nitration proceeded in 7 M sulfuric acid or greater. The spectral shape and position of wavelength maximum, for the solutions reacted in 7 M sulfuric acid or greater, indicated that no single species was present, but a mixture of products were formed. Below 7 M sulfuric acid, the amount of nitration which occurred was negligible. The visible and ultraviolet spectra of these solutions were similar to the spectrum of the reagent in an acid blank run without nitrate.

The effect of time on the nitration of 1-naphthol-4-sulfonic acid was studied in various sulfuric acid concentrations and reaction temperatures (experiment 5). The nitration of 1-naphthol-4-sulfonic acid was carried out in 2.5 M sulfuric acid at 81 °C over a time range of 10 to 35 minutes. Visible inspection of the reaction mixtures detected no color changes. The visible and ultraviolet spectra of the diluted reaction mixtures were identical to one another and similar to the spectra of 1-naphthol-4-sulfonic acid. The absence of absorbance in the spectra of the reaction solutions, other than those by the reagent, indicated nitration did not occur.

The nitration of 1-naphthol-4-sulfonic acid was carried out in 7.4 M and 8.3 M sulfuric acid at 60 °C over a time range of 3 to 5 hours. As in the preceeding study, no color changes were observed in the reaction mixtures. The visible and ultraviolet spectra of the diluted reaction mixtures in acidic media were identical to one another and similar to the

reagent spectrum. The results, as in the preceeding study, indicated nitration failed to proceed under the attempted conditions.

The nitration of 1-naphthol-4-sulfonic acid was carried out in 9.9 M sulfuric acid at 72 °C for a time range of 20 to 90 minutes. Color changes were observed in the systems and indicated nitration occurred. The visible and ultraviolet spectra of the diluted reaction mixtures in acidic media indicated several species were present. No one species could be identified as the major product. Therefore, under the conditions employed, several products were formed.

The nitration of 1-naphthol-4-sulfonic acid was carried out in 9.9 M sulfuric acid at 79 °C for a reaction time ranging from 30 to 94 minutes. Color changes were observed in every solution and indicated that nitration occurred. The ultraviolet and visible spectra of the diluted reaction mixtures were recorded and the pertinent data is presented in Figure 5, a graph of the absorbance of the diluted reaction mixture as a function of reaction time. The increasing curve at 270 mμ, a wavelength maximum for 2-nitro-1-naphthol-4-sulfonic acid, indicated the product or products formed with increasing time have larger absorbances. The decreasing curve at 220 mμ, also a maximum for 2-nitro-1-naphthol-4-sulfonic acid, indicated the formation of other products. The results showed that 2-nitro-1-naphthol-4-sulfonic acid was a major product formed first. As the time increased, a mixture of products was formed which produced the decreasing curve at 220 mμ and increasing curve at 270 mμ.

The nitration of 1-naphthol-4-sulfonic acid was carried out in 9.9 M sulfuric acid at 95 °C for a reaction time ranging from 5 to 60 minutes. The results were similar to the ones obtained in the preceeding study at 79 °C. The pertinent data is presented in Figure 6, a graph of the absorbance of the diluted reaction mixtures versus reaction time. As in the

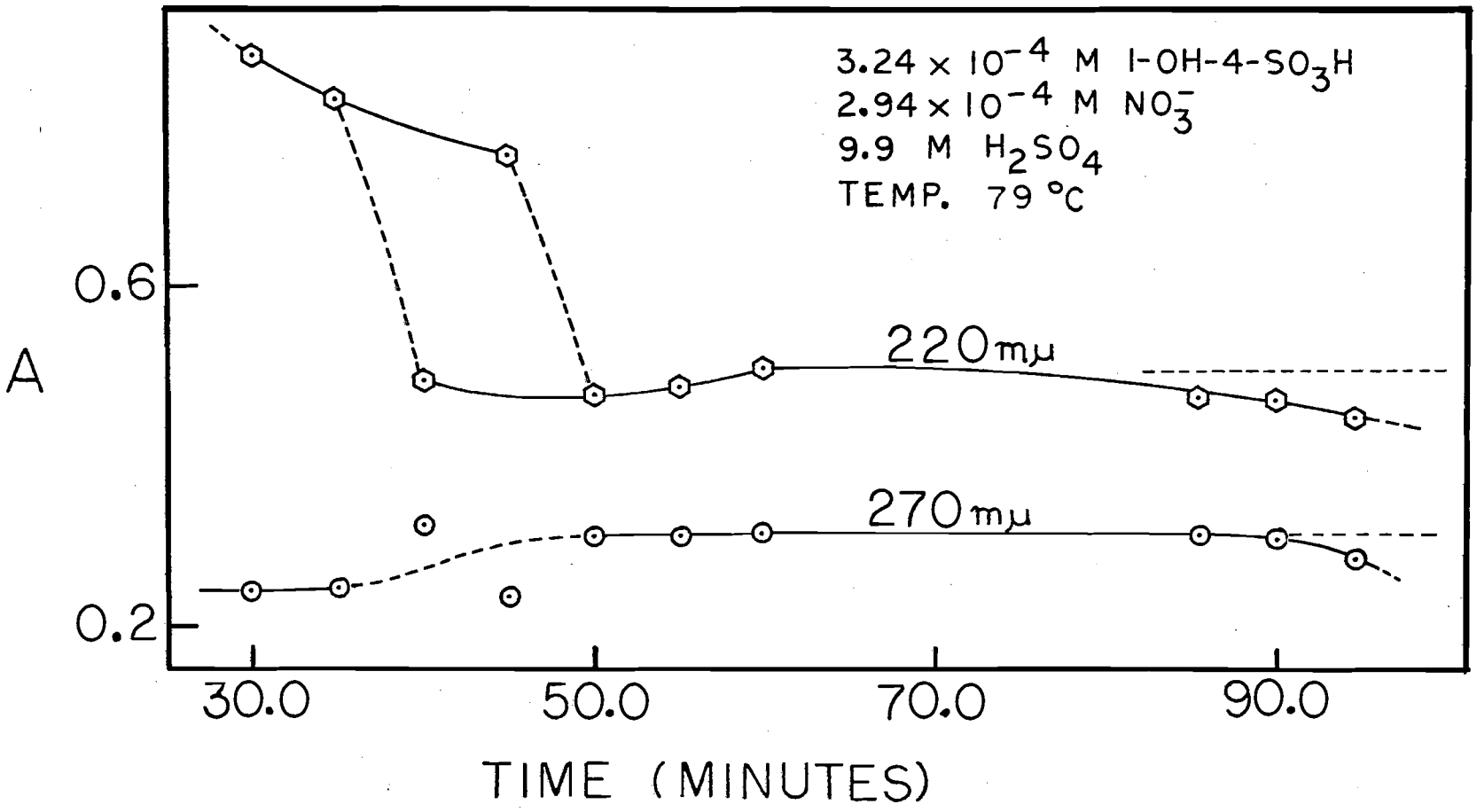


Figure 5. The formation and stability of 2-nitro-1-naphthol-4-sulfonic acid as a function of time at 79 °C

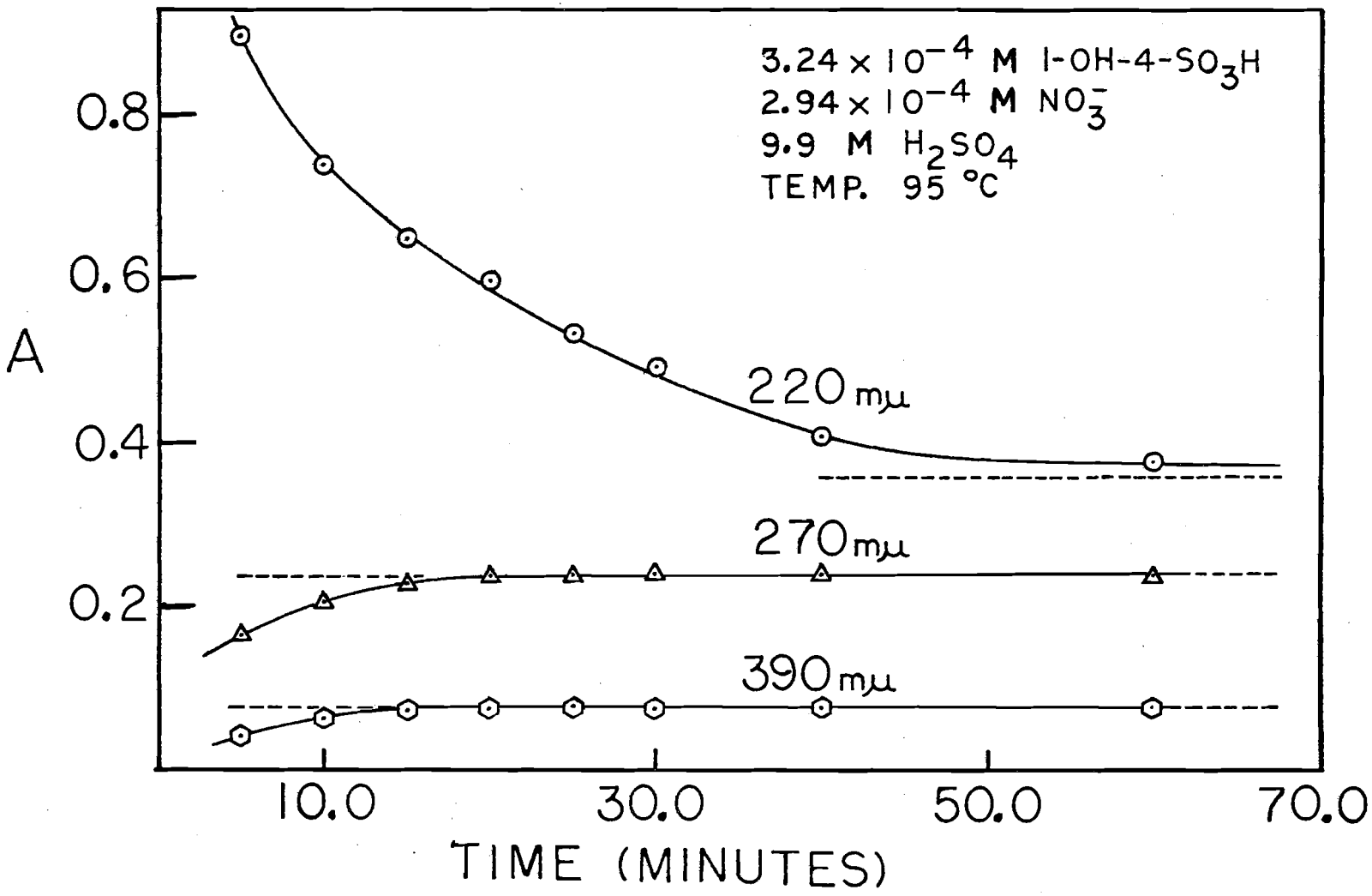


Figure 6. The formation and stability of 2-nitro-1-naphthol-4-sulfonic acid as a function of time at 95 °C

study at 79 °C, the progress of the nitration reaction was followed by an increase in absorbance at 270 mμ, a maximum for 2-nitro-1-naphthol-4-sulfonic acid and a minimum for 1-naphthol-4-sulfonic acid. Maximum product was formed within 20 minutes. The decreasing curve for absorbance at 220 mμ indicated there was more than 2-nitro-1-naphthol-4-sulfonic acid forming. Both 2-nitro-1-naphthol-4-sulfonic acid and 1-naphthol-4-sulfonic acid have molar absorbtivity values approximately the same in magnitude. If 2-nitro-1-naphthol-4-sulfonic acid was the only product formed, there would not be a decrease in absorbance but the curve would be almost parallel to the abscissa.

The increasing curve for absorbance at 390 mμ was a point picked at random to illustrate a familiar phenomenon. This was not a maximum for any of the considered products. A similar curve would be obtained from points chosen within 50 mμ either side. This curve was presented to show that with increasing time the spectra lost all peak characteristics and formed a continuous line which may indicate decomposition.

The nitration of 1-naphthol-4-sulfonic acid was carried out in concentrated sulfuric acid at room temperature for 5 and 15 minutes. The visible and ultraviolet spectra of the diluted reaction mixtures indicated nitration occurred in both solutions. Both spectra contained absorbance maxima at 221, 295, and 325 mμ. The increase in reaction time from 5 to 15 minutes shifted λ_{max} from, 269 mμ to 274 mμ and from 374 mμ to 372 mμ. This observed shift of the absorbance maxima with increased reaction time indicated the product first formed was mainly 2-nitro-1-naphthol-4-sulfonic acid and as time increased 2,4-dinitro-1-naphthol, along with other products, was formed.

A summary of the studies on the reaction of 1-naphthol-4-sulfonic acid with nitrate under varied sulfuric acid concentrations, temperatures and

reaction times is presented in Table 6. The studies are listed in order of increasing sulfuric acid concentration, since this seemed to be the predominant factor in the nitration system, over-riding the effects of temperature and reaction time. Also listed in Table 6 are the predominant reaction species found in the system.

The effect of nitrate concentration on the nitration of 1-naphthol-4-sulfonic acid was studied in 10.6 M sulfuric acid (experiment 6). The pertinent data is presented in Figure 7, a plot of the absorbance versus the nitrate concentration in the reaction mixture. The decreasing curve at 225 mμ, a maximum for 1-naphthol-4-sulfonic acid, and the increasing curve at 270 mμ, a maximum for 2-nitro-1-naphthol-4-sulfonic acid, show the absorbance of the treated solutions can be related to the concentration of nitrate present.

In 1967, the preliminary results of this study and its implications were reported by Antepenko, Abercrombie and Caskey (21).

Table 6. The Effects of Acid Concentration, Temperature, and Reaction Time on the Nitration of 1-Naphthol-4-Sulfonic Acid

# Study	Molar Conc. H_2SO_4	Temp. (°C)	Maximum Reaction Time (min)	Products(s)
5a	2.5 M	81	35	No reaction
5b	7.4 M	60	300	No reaction
5b	8.3 M	60	300	No reaction
5c	9.9 M	72	90	Unidentified products
5d	9.9 M	79	94	Major product is 2-nitro-1-naphthol-4-sulfonic acid plus others.
5e	9.9 M	95	60	Major product is 2-nitro-1-naphthol-4-sulfonic acid plus others.
5f	17.6 M	R.T.[1]	15	Major product is 2-nitro-1-naphthol-4-sulfonic acid plus others.

[1]Room Temperature

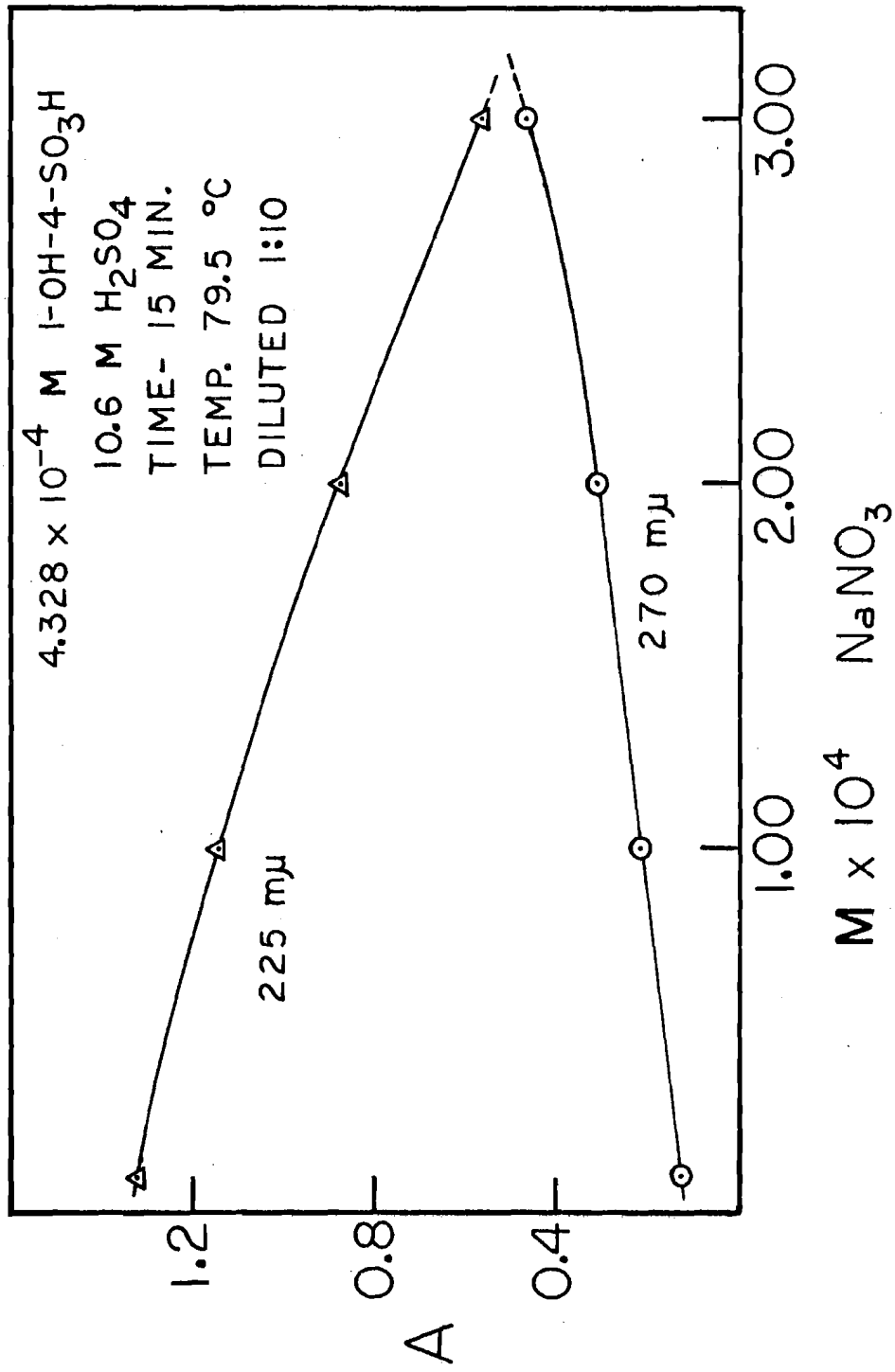


Figure 7. The Beer's-law plot of 1-naphthol-4-sulfonic acid and 2-nitro-1-naphthol-4-sulfonic acid as a function of nitrate concentration

V. CONCLUSION

1-Naphthol-4-sulfonic acid reacted with nitrate to form one or more products depending upon the conditions employed. When an excess of 1-naphthol-4-sulfonic acid over nitrate was used, the major product formed was 2-nitro-1-naphthol-4-sulfonic acid. When nitrate was in excess, 2,4-dinitro-1-naphthol as well as 2-nitro-1-naphthol-4-sulfonic acid was the product.

Even though 1-naphthol-4-sulfonic acid was in slight excess, both 2-nitro-1-naphthol-4-sulfonic acid and 2,4-dinitro-1-naphthol were formed as products, the former forming first and being transformed into the latter. Other products, probably resulting from decomposition of the reagent, were observed when long reaction times were used.

The nitration of 1-naphthol-4-sulfonic acid could not be duplicated under the conditions reported by Makitie, 5 N sulfuric acid at room temperature, or even at temperatures close to that of boiling water. The nitration required a 7 M or more concentrated sulfuric acid medium as well as heating.

The preliminary study indicated the reaction of 1-naphthol-4-sulfonic acid with nitrate may be adaptable to a spectrophotometric method for the determination of nitrate. Before such a method could be reported, more optimum conditions of acid concentration, time for complete reaction, as well as reaction temperature must be found.

VI. LITERATURE CITED

(1) E. H. W. J. Burden, *Analyst, 86,* 429 (1961).

(2) D. W. Fassett, *Nat. Acad. Sci. - Nat. Res. Counc., Pub. No. 1354,* 250 (1966); *Chem. Abstr., 67,* 31024y (1967).

(3) H. Sprengel, *Pogg. Ann., 121,* 188 (1863).

(4) O. Makitie, *Ann. Agr. Fenniae, 2,* 159 (1963).

(5) F. N. Abercrombie, *Masters Thesis,* Southern Illinois University, Carbondale, Illinois, 1967.

(6) A. Grandval and H. Lajous, *Compt, rend., 101,* 62 (1885).

(7) E. M. Chamot and D. S. Pratt, *J. Amer. Chem. Soc., 31,* 992 (1909).

(8) E. M. Chamot and D. S. Pratt, *J. Amer. Chem. Soc., 32,* 630 (1910).

(9) "Standard Methods for the Examination of Water and Wastewater," American Public Health Association Inc., 3rd Ed., New York, 1960, p. 175-8.

(10) G. L. V. N. Murty and G. Gopalarao, *Z. Anorg. Allgem. Chem., 231,* 298 (1937).

(11) G. L. V. N. Murty, *Proc. Indian Acad. Sci., 7A,* 108 (1938).

(12) M. L. Jackson, "Soil Chemical Analysis," Prentice-Hall, Inc., New Jersey, 1958, p. 197-201.

(13) F. R. Theroux, E. F. Eldridge and W. L. Mallmann, "Laboratory Manual for Chemical and Bacterial Analysis of Water and Sewage," McGraw-Hill Book Company, Inc., New York, 1957, p. 37, 66, 117, 172, 173.

(14) O. N. Witt and H. Kaufman, *Ber., 24,* 3157 (1891).

(15) F. N. Abercrombie and A. L. Caskey, *Trans. Illinois State Acad. Sci., 62,* 161 (1969).

(16) F. N. Abercrombie and A. L. Caskey, "Use of 2-Nitroso-1-Naphthol-4-Sulfonic Acid as a Spectrophotometric Reagent for Nitrate in Natural Waters," Annual Conference, Illinois Section American Water Works Association, Chicago, Illinois, 1970.

(17) F. N. Abercrombie, *Ph.D. Dissertation,* Southern Illinois University, Carbondale, Illinois, 1969.

(18) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, 1966.

(19) C. Daglish, *J. Amer. Chem. Soc.*, *72*, 4860 (1950).

(20) T. L. Davis, *J. Amer. Chem. Soc.*, *44*, 1588 (1922).

(21) R. J. Antepenko, F. N. Abercrombie, and A. L. Caskey, "Some Aspects of the Determination of Nitrate in Water Using 1-Naphthol-4-Sulfonic Acid," Abstracts 3rd Midwest Regional Meeting Am. Chem. Soc., Columbia, Mo., 22 (1967).

Chapter 3

SODIUM 2-NITROSO-1-NAPHTHOL-5-SULFONATE AS A REAGENT FOR COBALT IN WATER

Gary D. Carlson* and Albert L. Caskey

I. INTRODUCTION

The first, recorded, man-made object containing cobalt dates back to 1400 BC (1). This was a deep-blue, glass stone which was discovered in Nippur, Mesopotamia. Subsequent analysis revealed that the object contained 0.93 % cobaltous oxide.

Much later, during the early part of the sixteenth century, apparently worthless ore was found in the mines of Saxony. To the extreme displeasure of the miners, it gave off fumes of arsenic, and when roasted, failed to yield copper. As a result, the material was called "kobold," after a gnome who supposedly caused the miners trouble.

It wasn't until a century later that cobalt chemistry and metallurgy actually began. In 1742, Brandt (2) was able to separate a new metallic

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element from kobold ore by fire assay. He called the new element "cobalt," after the parent mineral. Later, in 1780, Bergman (3) obtained cobalt from blue, cobalt glass.

The important cobalt minerals are sulfides, arsenides, sulfoarsenides, and oxidized minerals. The Republic of the Congo is by far the chief supplier, where the main mineral mined is carrollite ($CuCo_2S_4$). The main cobalt arsenides that are mined in Canada, the United States and Morocco are smaltite and safflorite ($CoAs_2$) and skutterudite ($CoAs_3$), along with the sulfo-arsenide, cobaltite (CoAsS). Heterogenite ($CoO \cdot 2Co_2O_3 \cdot 6H_2O$) and absolite ($CoO \cdot 2MnO_2 \cdot 4H_2O$) are among the oxidized cobalt minerals.

Prior to World War I, nearly all cobalt consumed was in the oxide form. This is because it was mainly used as a glaze and coloring agent on pottery, porcelain, china, and glass (4). The development of methods to produce the metal was largely due to the accelerated interest in ferrous-alloying metals during the war. After the war, demand for the metal steadily increased.

The world production of cobalt in 1965 was 17,000 short tons (5), of which 6183 short tons were consumed by the United States. The two leading uses are in the production of magnet materials and high-temperature alloys. Permanent magnets contain 3-36 % cobalt (6), while the content of high-strength, high-temperature alloys is commonly 10-66 %. About 78 % of the 1965 annual consumption in the United States was for metallic purposes.

Cobaltous sulfate is used by the ceramics industry as a clay decolorizer, while cobaltous oxide is used for blueing glass. Organic salts of cobalt are used as driers in paints, inks, and varnishes. Cobalt is used as a catalyst in petroleum processes, and is added to fertilizers and feeds

in the form of cobaltous sulfate or cobaltous chloride to correct cobalt deficiency in livestock (7,8).

Cobalt is not an abundant material. Its average concentration in the lithosphere is only 0.0001-0.022 %, which is only 5-10 % the amount of nickel (4). Being a widely scattered element, it occurs in soils, plants and animals, meteorites, the sun, surface waters, sea water, coal, and minerals. Approximately 60 cobalt-bearing minerals are recorded (4).

Cobalt functions as a key element in vitamin B_{12}, and its essential role in ruminant nutrition gives the element a special place among the rarer heavy metals in the biological sciences.

The increasing importance of cobalt in industrial processes, the wide diversity of the element, and the recognition of its role as a nutrient are all factors which have stimulated the development of analytical methods to quantitatively determine its presence in a wide variety of materials and in many forms. As a result, during the last five decades, hundreds of new and revised colorimetric and spectrophotometric methods have appeared in the chemical literature. These methods employ a variety of reagents and techniques, each having its own characteristic advantages and disadvantages. In some methods, instability of the cobalt complex, low sensitivity, and poor selectivity are undesirable aspects. Some employ reagents that are difficult to prepare and purify, and are relatively unstable. Many procedures require extraction, precipitation, and close control of factors such as pH and reagent concentrations, which provide the opportunity for errors due to the rigor of the required laboratory technique. It should be noted that there are also advantages associated with a water-solvent system that are not present with the organic-solvent systems.

The colorimetric reagent which currently enjoys the widest popularity for the determination of cobalt is nitroso-R-salt (7,9). Other well-known reagents are 2-nitroso-1-naphthol, 1-nitroso-2-naphthol, ammonium thiocyanate, 2-nitroso-1-naphthol-4-sulfonic acid, and 1-(2-pyridylazo)-2-naphthol (PAN).

In 1960, Mossotti (10) investigated a new compound, sodium 2-nitroso-1-naphthol-5-sulfonate (I) as a specific reagent for cobalt. Additional work with (I) was done by Golightly (7) and Rigdon, *et. al.*, (11).

Sodium 2-nitroso-1-naphthol-5-sulfonate is easily prepared and purified and forms solutions that are stable for long periods of time (7). The intense, water-soluble cobalt complex is stable in acid media while complexes formed by other metallic ions are not (11). On the basis of this information, it seemed worthwhile to study (I) as a possible reagent for the spectrophotometric determination of cobalt in natural waters.

II. HISTORICAL REVIEW

For the vast majority of cobalt samples, the selection of a spectrophotometric method can be made from ammonium thiocyanate, nitroso-R-salt, or 2-nitroso-1-naphthol (9). Excellent reviews of these procedures are available by Young (9), Golightly (7), and Banks (12); therefore, only a brief discussion of some important aspects will be presented here.

The classical thiocyanate method is not very sensitive in aqueous solution (3), and steps to increase the color intensity involve extraction of the aqueous solution with organic solvents and subsequent measurement of the absorbance in the ultraviolet region (12, 13). The system conforms to Beer's law between the range 0.2 to 10 ppm cobalt. Diverse ion studies revealed that a host of ions present serious interferences. The permissible amount of Cu(II) is 10 ppm, and only 5 ppm Ni(II) can be tolerated.

The complex formed between 2-nitroso-1-naphthol and cobalt is the basis for an analytical, colorimetric method which has been applied to many materials (14). Once the complex with cobalt has been formed and extracted into an organic solvent, it is stable to moderate concentrations of acids and alkalies, while iron, copper and other metallic complexes are not. Interference from these metals can therefore be eliminated by washing the organic phase with hydrochloric acid and sodium hydroxide. The method is applicable to cobalt concentration in the 0.01-6 ppm range (15). The reagent is somewhat superior to the more popular isomer, 1-nitroso-2-naphthol, as it is obtainable in a more pure form, the color of the cobalt complex is more intense, and it can be more efficiently extracted from water.

There is little doubt that the most popular spectrophotometric method for the determination of cobalt is based on the use of nitroso-R-salt

(disodium 1-nitroso-2-naphthol-3,6-disulfonate). There are, however, several important variables such as quantities of nitric acid, reagent, and time of boiling which must be carefully controlled if reproducibility is to be attained (16). The instability of the complex ion is also a disadvantage.

The general procedure (16) used with this reagent for the determination of cobalt is tedious. After dissolving the sample to be analyzed, phosphoric-sulfuric acid mixture and hydrofluoric acid are added to complex ferric ion. The solution is then buffered with sodium acetate and nitroso-R-salt is added. The solution is boiled to form the complex, 1 ml of concentrated nitric acid is added, and boiling is resumed for one to two minutes to destroy excess reagent and other metal complexes that may have formed. Absorbance measurements are made at 425 mμ for maximum sensitivity.

Young (16) found it necessary to remove manganese, nickel and chromium in the determination of 0.01 to 0.5 mg of cobalt in metallurgical products. Kidson and Askew (17), who were working with quantities of cobalt as low as 0.0001 mg in biological materials, found copper to be a serious interference. This interference, along with that of several other ions can be eliminated by masking with potassium fluoride (18, 19). Young removed large quantities of copper by electrolysis.

Another reagent employing a reagent similar to nitroso-R-salt is based on the formation of the water-soluble red complex formed between cobalt and 2-nitroso-1-naphthol-4-sulfonic acid. The complex is formed at pH 7.0, but is not stable in acid solution. Wise and Brandt (20), who described the method as "convenient, sensitive, reproducible, accurate and precise," reported a concentration range of 0.6 to 6 ppm as the optimum for cobalt. If the concentrations of Fe(III) and Cu(II) are less than

1.00×10^{-3} M, citrate can be used as a masking agent. If these concentrations exceed this value, however, removal of the ions becomes necessary using an extraction and precipitation procedure. Nickel(II) must be removed by dimethylglyoxime precipitation. Komatsu (21) employed an extraction procedure to remove interferences in determining 0.005-0.114 mg cobalt.

The reaction between cobalt(II) and this reagent was studied in detail by Caskey (22) who reported the pKa_2 of 2-nitroso-1-naphthol-4-sulfonic acid to be 6.24 at 25.0 ^{o}C and an ionic strength of 0.1000. Under the same conditions of temperature and ionic strength the logarithm of the formation constant of the complex was given as 14.77 ± 0.21. The ratio of ligand to cobalt in the complex was found to be 3 to 1.

In 1965, it was noted that of the five reported methods used for the determination of cobalt in sea water, two used emission spectroscopy and three used absorption spectroscopy (23). Of the latter three, two used the nitroso-R-complex and one used the thiocyanate method.

Benford (24) used 3-methoxynitrosophenol for the determination of cobalt in water and waste water. The green complex was extracted into chloroform and washed with sodium carbonate solution to remove excess reagent. The sodium carbonate washings were in turn extracted with another portion of chloroform which was combined with the original chloroform extract. The reagent stock solution was stable for three weeks, while the cobalt complex in chloroform was only stable for about two hours. The system conformed to Beer's law in the concentration range of 0.2-1.2 ppm cobalt. Copper(II) and nickel(II) caused serious interference, and rather tedious procedures were described to overcome their effects.

In an effort to develop a simpler method than that described using 3-methoxynitrosophenol, Benford (24) investigated the thiocyanate method.

The blue cobalt thiocyanate complex was extracted into methyl-*iso*-butyl ketone and the absorbance measured at 620 mμ. Copper(II) and iron(III) were found to cause the most serious interference to the method. Copper was removed by sulfite reduction to the cuprous state and precipitation as cuprous iodide. Iron was precipitated as ferric chromate. The method was reported to be applicable in the 0.3-10 ppm cobalt concentration range.

Forster and Zeitlin (23) developed a modified nitroso-R-procedure based on earlier work by Thompson and Leavastu (25) to determine cobalt in sea water. In this modified method, it was necessary to concentrate cobalt to a measurable limit by precipitation as the carbonate from a large volume of sample. The precipitate was aged for a minimum of seven days in order to realize quantitative results. After filtration and dissolution of the precipitate, cobalt was separated from other dissolved ions by a rather tedious extraction procedure using dithizone in carbon tetrachloride. A previously unreported "salt effect" was discovered which was defined as: "the ratio of the absorbance in distilled water to that in sea water, which will always be greater than unity." The salt effect is a result of matrix materials in sea water, such as sodium chloride. Correction was made by constructing the calibration curve from sea water spiked with cobalt or by using a correction factor with distilled water standards. Through careful control of pH, boiling time, development time of complex, and conditions related to the destruction of excess reagent, it was possible to determine 0.5 ppb cobalt in sea water with a 1-2 % relative standard deviation and an accuracy of 3.0 %.

In a later paper studying the salt effect, Forster and Zeitlin (26) found a 32 % difference in cobalt recovery between samples of distilled water and sea water. Using cobalt-60 tracer, they attributed a loss of

18.2 % cobalt to incomplete precipitation as the carbonate during the concentration step. A 10 % loss was accorded the extraction step, while 3 % was due to the color development procedure. Only 0.8 % was lost during filtration.

Riley and Topping (27) used 5,7-dibromo-8-hydroxyquinoline to concentrate trace elements from sea water. They dissolved the precipitate in nitric acid, and separated the metallic ions using an anion-exchange resin. The final measurement of cobalt employed nitroso-R-salt.

Riley and Taylor (28) studied the use of chelating resins of the iminodiacetic acid type. After concentration, the elements, including cobalt, could be determined by spectrophotometry or other techniques. Burrell (29) used coprecipitation with iron(III) hydroxide to concentrate cobalt from sea water.

Friedlander, *et al.*, (30) claimed success in preparing 2-nitroso-1-naphthol-5-sulfonic acid by treatment of the zinc salt of 1-naphthol-5-sulfonic acid with nitrite. Nearly 40 years later, Bogdanov (31) mentioned the preparation of the ammonium salt of 2-nitroso-1-naphthol-5-sulfonic acid by treating 1,2,5-naphthalene-diamine sulfonic acid with hydroxylammonium chloride in an acid solution.

Mossotti (10) found nitrosolation of 1-naphthol-5-sulfonic acid at 0-5 ^{o}C to be the most convenient means of preparing sodium 2-nitroso-1-naphthol-5-sulfonate. Recrystallization from dilute hydrochloric acid solution yielded long, yellow needles of the pure salt. The solid hydrate was not hygroscopic and was slightly soluble in ethanol and insoluble in diethyl ether.

The compound and its water solution were found to be stable. In neutral and basic solutions, the intense-red, water-soluble, cobalt complex

was formed. Brown, *et al.*, (32) reported the system to be adaptable to the spectrophotometric determination of cobalt in the 0.1 to 6 ppm concentration range. Gifford, *et al.*, (33) employed the system to the determination of available-cobalt in soil. It was Rigdon, *et al.*, (11) who first demonstrated that once formed, the cobalt complex is stable in acid solution. He was able to determine cobalt in the presence of low concentrations of iron by first forming the complex at pH 8, followed by acidification of the solution. In this manner, the green, iron complex was destroyed while the cobalt complex was reported to be stable for approximately 40 hours.

It was felt that due to the ease in preparation of the reagent, the stability of the compound and its solutions, and the water solubility of the reagent and the cobalt complex, that an analytical spectrophotometric method for the determination of cobalt in natural waters utilizing sodium 2-nitroso-1-naphthol-5-sulfonate would be near ideal. The ease of formation of the cobalt complex and its stability in acid media would be distinct, additional advantages of this system.

A more complete description of the research reported here, as well as related materials has been prepared by Carlson (34).

III. EXPERIMENTAL

A. Reagents

Reagent-grade chemicals were used whenever they were commercially available. Table 1 lists all commercial compounds used and includes information regarding their source. Table 2 contains details for the preparation of most of the solutions which were used, particularly those used in the interference studies.

Sodium 2-nitroso-1-naphthol-5-sulfonate was not commercially available and was prepared by nitrosolation of 1-naphthol-5-sulfonic acid, sodium salt, according to the method of Mossotti (10). Sodium 1-naphthol-5-sulfonate was dissolved in a very slightly alkaline solution which was cooled to about 1 ^{o}C. An excess of sodium nitrite was added during constant stirring of the solution, followed by dropwise addition of a sufficient quantity of concentrated hydrochloric acid to make the final acid concentration about 0.6 M. The yellow-green product which separated was collected by filtration and purified by recrystallization from 10 % hydrochloric acid solution. Darco G-60 activated carbon was used as a decolorizer. The final solid product was air-dried for two days with filtered air which was drawn through the filter cake. A 2.00×10^{-3} M solution of sodium 2-nitroso-1-naphthol-5-sulfonate was prepared by dissolving 0.6405 g in deionized water and diluting to 1000 ml in a volumetric flask.

A 8.00×10^{-4} M solution of sodium 2-nitroso-1-naphthol-5-sulfonate having an ionic strength of 0.100 was prepared by dissolving 0.1281 g in about 200 ml of deionized water, adding 7.02 g of sodium perchlorate monohydrate and diluting to 500 ml in a volumetric flask using deionized water.

Table 1. Chemicals Used and Chemical Suppliers*

Compound	Vendor**	Vendors Catalog Number
$Al_2(SO_4)_3 \cdot 18H_2O$	2	3208
$AgNO_3$	2	2169
β-naphthol	4	MCB-P2191-NX125
Buffer pH 7	1	SO-B-109
$CdCl_2 \cdot 2\ 1/2\ H_2O$	1	C-9
$CaCO_3$	2	4071
$CrCl_3 \cdot 6H_2O$	3	1575
Cu (electrolytic)	1	C-434
$CuBr_2$	3	1632
EDTA	4	MCW2580
Fe (electrolytic)	5	226
$FeCl_3$	4	MCB-CB382-FX215
$FeSO_4 \cdot 7H_2O$	1	1-146
$HC_2H_3O_2$	3	1019
HCl	1	A-144-C
$HClO_4$	5	66
$HgCl_2$	2	1-146
HNO_3	1	A-200
H_2O_2	1	H-323
H_2SO_4	1	A-300
KBr	7	G-715
KCl	2	6858
KF	2	6844

* Continued on next page

Table 1. Chemicals Used and Chemical Suppliers (Continued)

Compound	Vendor**	Vendors Catalog Number
KSCN	2	7168
$Li_2C_2O_4$	1	L-133
$Mg(NO_3)_2 \cdot 6H_2O$	3	1914
$MnCl_2 \cdot 4H_2O$	2	6126
NaCl	2	7581
$NaClO_4$	5	92
$NaC_2H_3O_2 \cdot 3H_2O$	2	7368
Na_2HPO_4	2	2313
NaK tartrate	2	2367
$NaNO_2$	2	7824
NaOH	1	S318
$Na_4P_2O_7 \cdot 10H_2O$	2	7960
Na_2SO_3	3	2301
$NiCl_2 \cdot 6H_2O$	1	N-54
$ZnCl_2$	1	Z-33
1-Naphthol-5-Sulfonic Acid, Sodium Salt	6	T2807
Darco G-60 Activated Carbon	4	C07384-0L

** 1 - Fisher
2 - Mallinckrodt
3 - Baker & Adamson
4 - Matheson, Coleman & Bell
5 - G. F. Smith
6 - Eastman
7 - Harshaw

Table 2. Solutions Used and Details of Their Preparation

Compound	Weight (g)	Volume diluted to (ml)	Specie present	Concentration
$FeCl_3 \cdot 6H_2O$	0.483	100	Fe^{++}	1.00 mg/ml
$Al_2(SO_4)_3 \cdot 18H_2O$	1.11	100	Al^{+++}	1.00 mg/ml
$NiCl_2 \cdot 6H_2O$	0.405	100	Ni^{++}	1.00 mg/ml
$HgCl_2$	0.135	100	Hg^{++}	1.00 mg/ml
$ZnCl_2$	0.209	100	Zn^{++}	1.00 mg/ml
$CuBr_2$	0.351	100	Cu^{++}	1.00 mg/ml
$CrCl_3 \cdot 6H_2O$	0.511	100	Cr^{+++}	1.00 mg/ml
$MnCl_2 \cdot 4H_2O$	0.360	100	Mn^{++}	1.00 mg/ml
$CaCO_3$	2.4950	100	Ca^{++}	10 mg/ml
KCNS	0.972	50	SCN^-	0.2 M
KCl	0.764	50	Cl^-	0.2 M
$NaC_2H_3O_2$	0.820	50	$C_2H_3O_2^-$	0.2 M
$CdCl_2$	1.83	50	Cd^{++}	0.2 M
$Li_2C_2O_4$	1.02	50	$Li^+, C_2O_4^{--}$	0.2 M
KF	0.581	50	F^-	0.2 M
EDTA	0.2	50	EDTA	0.01 M
$NaKC_4H_4O_6 \cdot 4H_2O$	4.000	100	$C_4H_4O_6^{--}$	40 mg/ml
NaCN	0.490	100	CN^-	0.1 M
$Na_4P_2O_7 \cdot 10H_2O$	8.9	100	$P_2O_7^{4-}$	0.2 M
$Mg(NO_3)_2 \cdot 6H_2O$	5.27	50	Mg^{++}	10 mg/ml
$NaClO_4 \cdot H_2O$	28.10	2000	Na^+, ClO_4^-	0.1000 M

A 1.60×10^{-4} M solution of sodium 2-nitroso-1-naphthol-5-sulfonate having an ionic strength of 0.100 was prepared as described above, except that 40.00 ml of 2.00×10^{-3} M sodium 2-nitroso-1-naphthol-5-sulfonate was used.

Pure, anhydrous cobalt(II) sulfate, prepared by Caskey (22), following the method of Diehl and Butler (35), was used by Golightly (7) to prepare a stock 1.9991×10^{-2} M solution of cobalt(II) sulfate. For this purpose, 3.0987 g of cobalt(II) sulfate was dissolved in deionized water and diluted to 1000 ml.

A 1.9991×10^{-4} M solution of cobalt(II) sulfate was prepared by diluting 10.00 ml of the 1.9991×10^{-2} M solution to 1000 ml using deionized water.

A 7.996×10^{-6} M cobalt(II) sulfate solution was prepared by diluting 10.00 ml of 1.9991×10^{-4} M cobalt(II) sulfate solution to 250 ml using deionized water.

A 8.00×10^{-4} M solution of cobalt(II) sulfate having an ionic strength of 0.100 was prepared by dissolving 7.02 g of sodium perchlorate monohydrate in about 100 ml deionized water, adding 20.00 ml of 1.9991×10^{-2} M cobalt(II) sulfate solution and diluting to 500 ml in a volumetric flask with deionized water.

A 1.60×10^{-4} M solution of cobalt(II) sulfate having an ionic strength of 0.100 was prepared as described above, except that 4.00-ml 1.9991×10^{-2} M cobalt(II) sulfate solution was used.

A 0.1 N solution of perchloric acid was prepared by diluting 1.00 ml of concentrated perchloric acid to 120 ml using deionized water.

A buffer solution of pH 8.00 having an ionic strength of 0.100 was prepared by dissolving 4.959 g of dibasic sodium phosphate in about 600 ml of deionized water and titrating with 0.1 N perchloric acid to pH 8.00, as

indicated by a pH meter. The solution was then diluted to 1000 ml using deionized water and stirred overnight with a teflon stirring bar and a magnetic stirrer. The pH was again checked and found to be 8.00.

All water used was deionized by passing distilled water through a 45 x 400 mm column of monobed self-indicating, ion-exchange resin, Rohm and Haas Amberlite MB 3 (Mallinckrodt 332G). The water was stored free from carbonate.

B. Equipment

A Corning Model 12 pH meter equipped with a general-purpose, glass electrode and a fiber-type, saturated-calomel electrode was used for all pH measurements.

Beckman Model DB(1401) and DK-1A recording spectrophotometers were used with 1.000- and 10.00-cm, matched, silica, absorption cells in all spectrophotometric work. The Model DB was equipped so that the sample cell compartment could be maintained at constant temperature with water from the constant temperature bath, which was pumped through jackets surrounding the compartment.

The constant temperature bath was equipped with a Precision Scientific Co. Porta-Temp regulator (Sargent 84875). Temperatures could be maintained to within $\pm$ 0.25 ^{o}C.

A Perkin Elmer Model 137B Infracord was employed to obtain infrared spectra. The potassium bromide pellet technique was used.

All glassware was borosilicate. All volumetric glassware was of NBS Class A quality. Glassware was washed with a hot water solution of Alconox and rinsed six times with distilled water. Drying was done in an air oven at 120 ^{o}C.

C. General Procedure

All work done was based on the same procedure, with only slight modifications occurring when necessary. An accurately measured volume (15.00 ml) of 1.9991 x 10^{-4} M cobalt(II) sulfate was pipetted into a 100-ml beaker, and 15-drops of 0.1 M perchloric acid added. After addition of excess 2.00 x 10^{-3} M reagent solution (10.00 ml), the pH of the system was brought to 8.0 using 0.1 M NaOH and a pH meter. The solution was transfered to a 100-ml volumetric flask containing 25.00-ml 2.0 M perchloric acid, and diluted to the mark with deionized water. The absorbance was measured at 540 mμ versus a reagent blank.

D. Recommended Procedure for the Determination of Cobalt in Natural Waters

After collection of samples, add approximately 5 ml of concentrated perchloric acid to each liter of sample to prevent algae growth and hydrolysis of metals present. If needed, clarify the samples by filtering them through Whatman number 42 filter paper.

Pipet 25.00 ml (or any suitable aliquot) of water sample into a 100-ml beaker and add about 20 drops of 0.1 M perchloric acid to bring the pH of the sample to about 2. If sulfite or nitrite are present at concentrations greater than 50 ppm and 1000 ppm, respectively, add 1 ml of 30 % hydrogen peroxide and apply gently warming for about 1 minute. Add 10 ml of 4 % sodium potassium tartrate solution to mask iron and aluminum, and if manganese is present, add 10 ml of 0.2 M sodium pyrophosphate. Then add 25.00 ml of 2.00 x 10^{-3} M sodium 2-nitroso-1-naphthol-5-sulfonate and adjust the pH to 8.0, using a pH meter and 0.1 N sodium hydroxide added dropwise with stirring. Quantitatively transfer the solution to a 100-ml volumetric flask containing 25 ml of 0.5 M perchloric acid, dilute

to the mark using deionized water and measure the absorbance at 540 mμ against a reagent blank using either 10.00- or 1.00-cm cells depending upon the concentration.

IV. RESULTS AND DISCUSSION

The infrared spectrum of the sodium 2-nitroso-1-naphthol-5-sulfonate was identical to that obtained by Golightly (7).

A potentiometric titration of 1.5693 g of the air-dried product required 39.21 ml of 0.1250 N (ave. of 4 trials, rel. std. dev. 1.8 ppt) sodium hydroxide solution. A typical titration curve of a weak acid was obtained: neutralization equivalent, 320.9; pKa 7.15. The calculated neutralization equivalent for the two and one-half hydrate is 320.263.

Three reagent samples, weighing 0.5325, 0.5710, and 0.6071 g, were treated with sulfuric acid and nitric acid using the classical techniques in order to determine sodium as the sulfate. Weights of sodium sulfate of 0.1160, 0.1233, and 0.1305 g, and percent sodium values of 6.96, 6.99, and 7.05, respectively, were obtained. These results are in agreement with the calculated value of 7.18 for the two and one-half hydrate.

A. Effect of pH on Formation of Complex

In order to determine an optimum pH at which the complex was quantitatively formed, a series of solutions was prepared and treated as in the general procedure except that the pH to which each solution was adjusted was varied. In order to minimize localized, high-pH effects upon the dropwise addition of base, the solutions were initially buffered with acetate-acetic acid.

From the data in Table 3, which is displayed graphically in Figure 1, it was apparent that the complex formed completely at pH 4.7 or above. There was evidence that at pH 10 or greater some completing reaction caused low results. A pH of 8.0 was therefore chosen for the continuous variations study and for all other work. At this pH, the naphthol hydrogen of

Table 3. Effect of pH on Formation of Complex

Solution Number	pH	A @ 540 mμ
514	6.80	.406
515	8.00	.405
516	9.70	.407
517	10.84	.400
519	11.50	.401
522	10.10	.407
523	11.80	.399
722	4.70	.409
723	3.60	.100
724	4.10	.284
725	5.34	.409
726	5.92	.410
727	6.35	.402
728	3.35	.005
729	4.39	.353
730	3.90	.152
731	3.45	.009
732	4.00	.283
733	4.21	.255
734	3.71	.071
512	5.80	.406

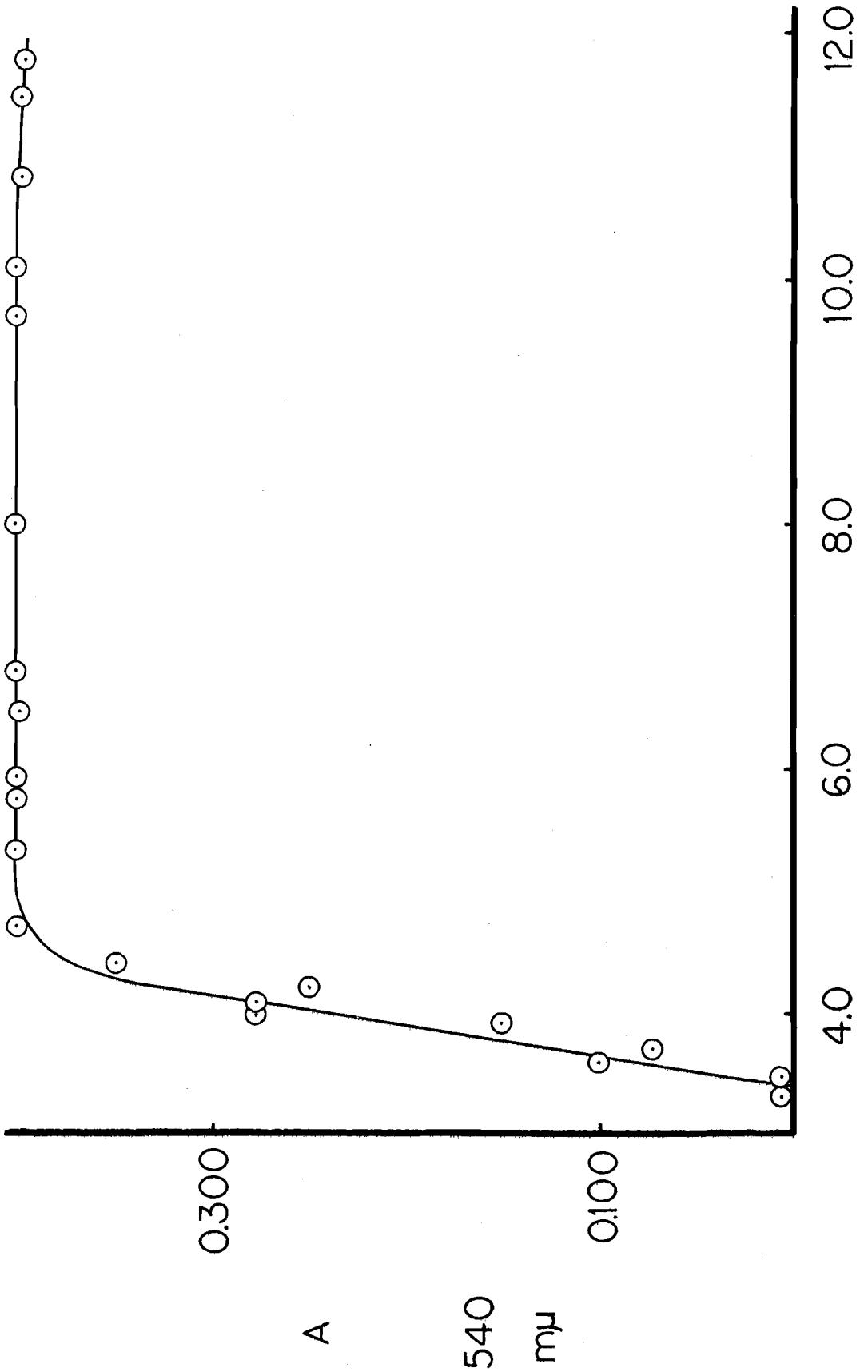

Figure 1. Effect of pH on the formation of the cobalt complex

2-nitroso-1-naphthol-5-sulfonic acid was calculated to be 87.7 % ionized. When the pH was increased, the precipitation of cobalt hydroxide became a problem in solutions containing relatively high concentrations of cobalt. For routine work, it was found that a pH range of 7.0-8.5 was generally satisfactory.

B. Effect of Perchloric Acid and Time on the Stability of Cobalt Complex

The stability of the complex was studied with respect to acidity and time. A series of samples was processed according to the general procedure except that the final perchloric acid concentration was varied. Absorbance measurements were made over a time period of 58 hours.

In general, the system was found to be stable for at least 10 hours at perchloric acid concentrations as high as 4 molar. As can be seen in Table 4 and Figure 2, absorbance began to decrease significantly when either the time or acid concentration was increased beyond these values. Although not shown, it was observed that the complex formed almost instantaneously and that the lines in Figure 2 could be extended to nearly zero on the time axis. This meant that measurements were possible immediately after final dilution and mixing. For the remaining studies the final perchloric acid concentration was selected to be 0.5 M, which was well within the range of stable conditions.

C. Conformance of the Cobalt Complex to Beer's Law in Acid-Aqueous Media

A series of solutions was prepared containing varying amounts of cobalt(II) sulfate according to the general procedure. The reagent concentration was such that an excess was present in all cases. The study was extended to lower concentrations using 7.996×10^{-6} M cobalt(II) sulfate solution and 10-cm cells.

Table 4. Stability-Study Data

Solution Number	M $HClO_4$ after Dilution	Absorbance after				
		1 hr	9 hr	19 hr	30 hr	58 hr
470	0.0	Reference				
471	0.0	0.410	0.411	0.411	0.412	0.412
472	1.00	0.411	0.400	0.399	0.400	0.365
473	2.00	0.411	0.397	0.397	0.398	0.353
474	3.00	0.400	0.400	0.400	0.401	0.367
475	4.00	0.404	0.400	0.398	0.395	0.364
476	5.00	0.393	0.393	0.393	0.396	0.353
477	6.00	0.388	0.387	0.388	0.384	0.337
478	0.04	0.405	0.398	0.398	0.398	0.363

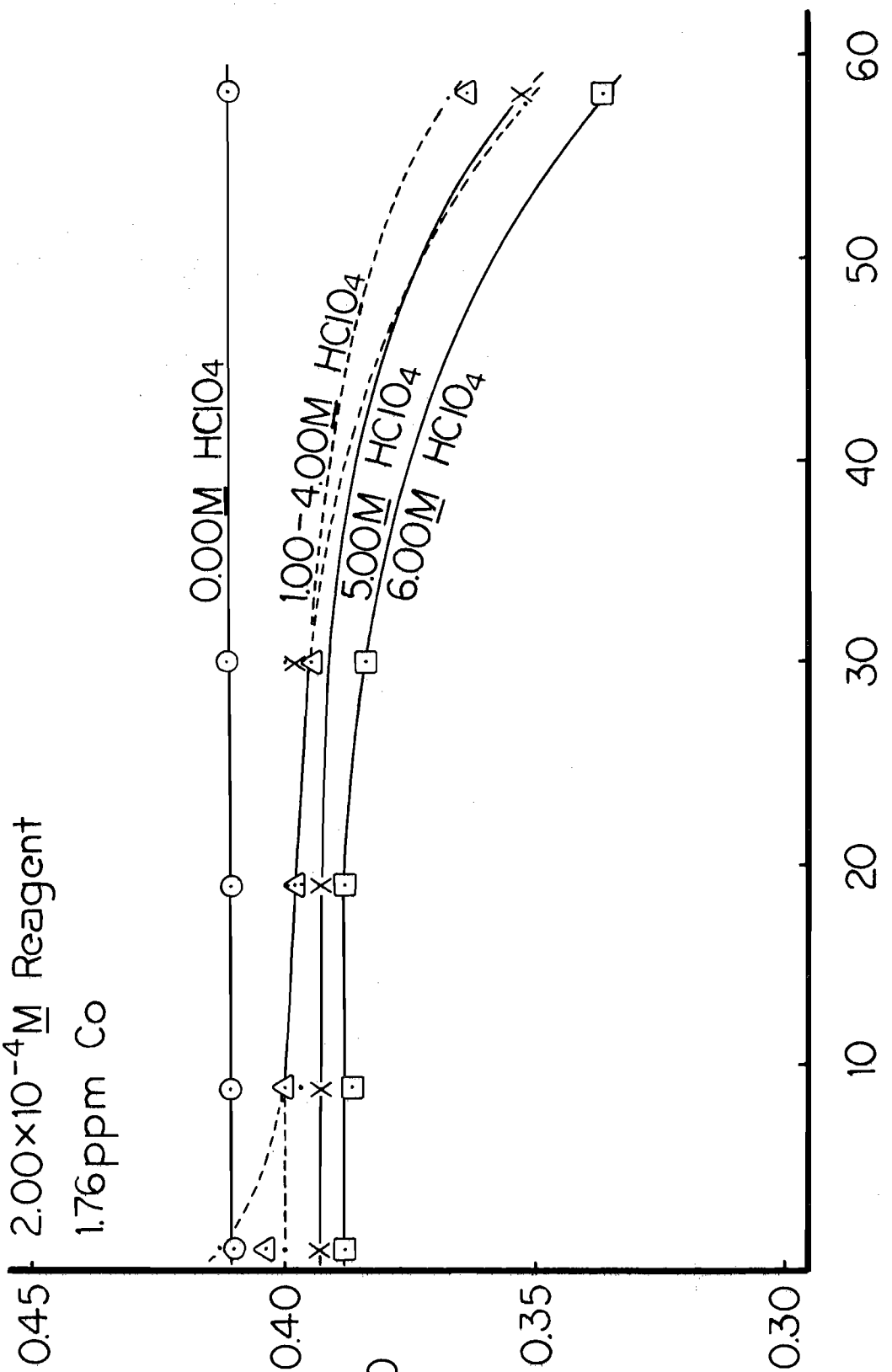

Figure 2. The stability of the cobalt complex with respect to time and perchloric acid concentration

Table 5 and Figures 3 and 4 show that Beer's law was closely followed over a cobalt-concentration range of 0.02-4.7 ppm. This range can most likely be extended using spectrophotometers that give accurate readings above 1 absorbance unit. The molar absorptivity of the complex was found by calculation to be 1.36×10^4.

As indicated by Table 5 the use of 10-cm cells facilitated dealing with solutions containing relatively low concentrations of cobalt, as was the case in the analyses of the natural waters described later in this report. Under the conditions of the general procedure, a 50-ml aliquot of sample was the maximum volume which could be conveniently analyzed. As a general guideline, 10-cm cells were used to measure the absorbance of solutions containing less than 0.2 ppm cobalt. In this manner, the region of optimum accuracy of the spectrophotometer was utilized.

D. Precision Study

Prior to an examination of possible interferences, it was necessary to determine the precision of the method so that an actual interference could be distinguished from normal variations in the spectrophotometric procedure. This was accomplished by treating 56 solutions according to the general procedure. Solutions were prepared and measured in sets of 8 on 7 different days.

The data, as shown in Table 6 indicated that the procedure was quite precise. Factory specifications for the Beckman DB include a precision of 4.0×10^{-3} (standard deviation) at absorbance values of 0.400.

E. Interfering Species

Several ions which might be present as impurities in natural waters or as additives during the course of analysis were examined as possible

Table 5. Beer's-law Data

Solution Number	1.999×10^{-4} M $CoSO_4$ (ml)	2.00×10^{-3} M Reagent (ml)	A @ 540 mμ
8a	0.00	10.00	Blank
8b	1.00	10.00	0.019
8c	3.00	10.00	0.073
8d	5.00	10.00	0.134
8e	10.00	10.00	0.270
8f	15.00	10.00	0.407
8g	20.00	10.00	0.540
8h	25.00	10.00	0.675
227	0.00	20.00	Blank
228	25.00	20.00	0.680
229	29.00	20.00	0.780
232	32.00	20.00	0.864
231	35.00	20.00	0.940
230	40.00	20.00	1.07
	7.9996×10^{-6} M $CoSO_4$ (ml)	2.00×10^{-3} M Reagent (ml)	
219	0.00	5.00	Blank
220	5.00	5.00	0.044
221	7.00	5.00	0.070
222	10.00	5.00	0.101
223	15.00	5.00	0.160
224	30.00	5.00	0.318
225	50.00	5.00	0.531

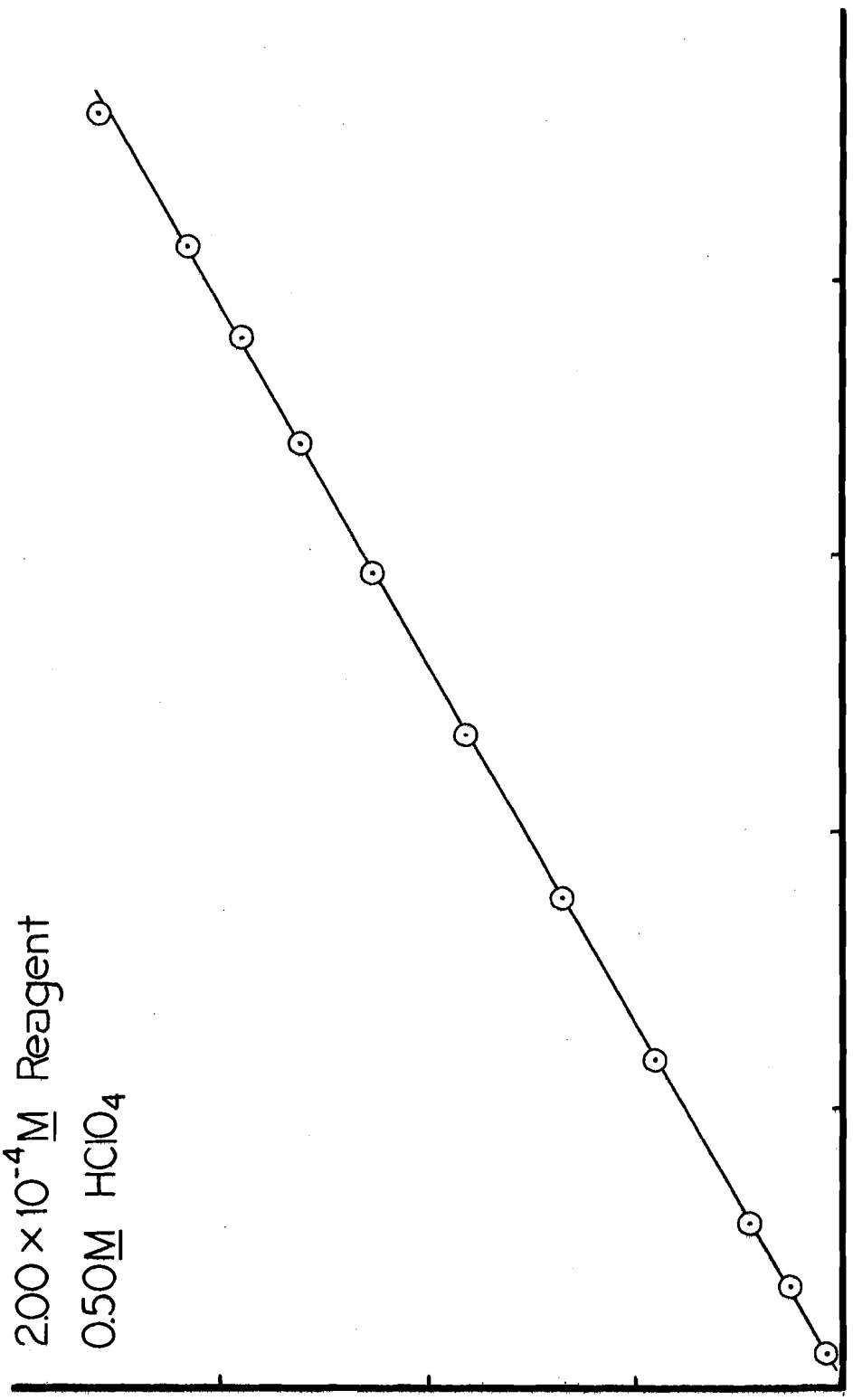

Figure 3. Beer's-law plot of the cobalt complex at high concentrations

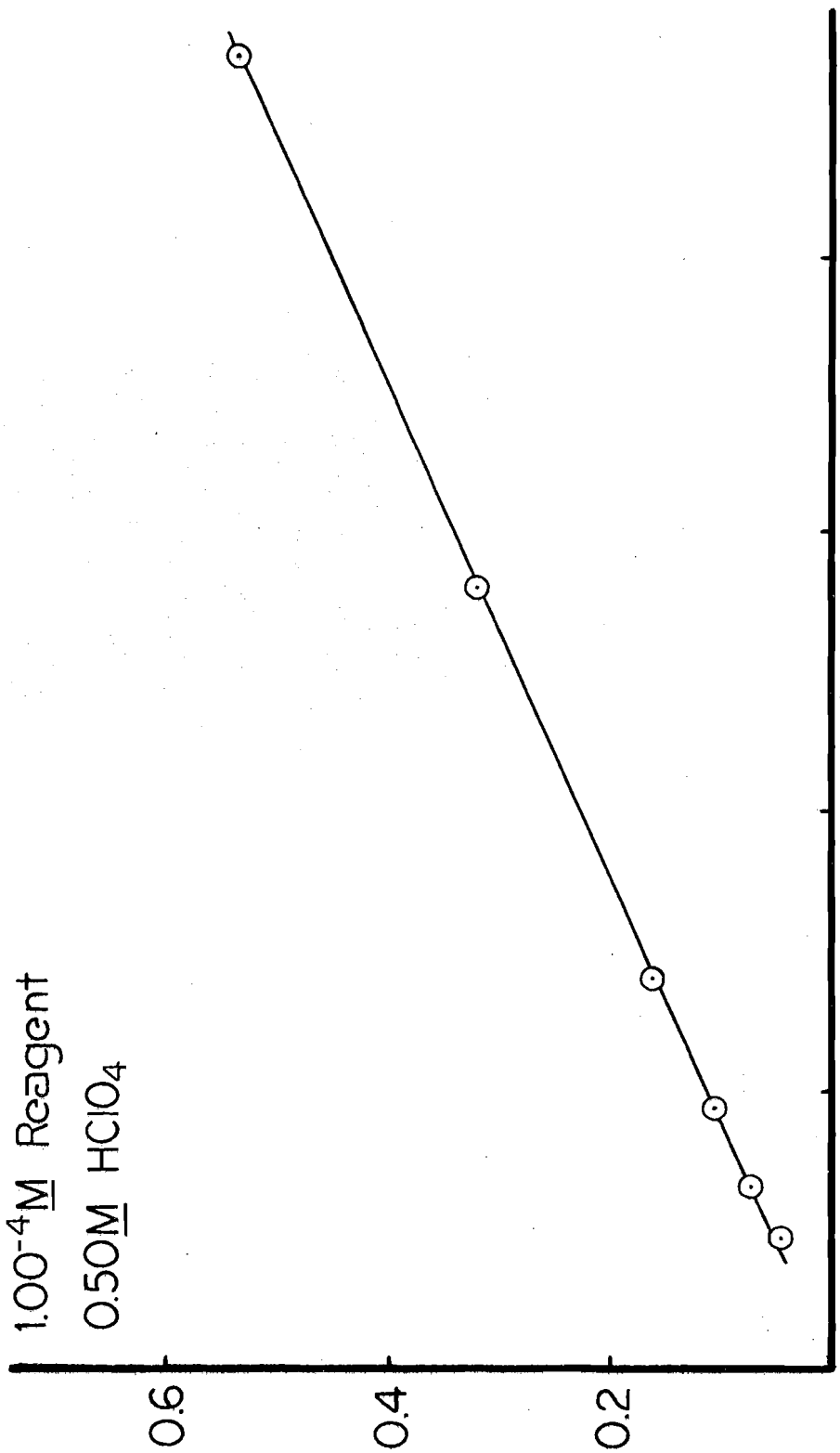

Figure 4. Beer's-law plot of the cobalt complex at low concentrations

Table 6. Precision Data

Solution Number	Absorbance at 540 mμ							
1-8	0.413	0.418	0.420	0.420	0.419	0.415	0.421	0.421
56-63	0.419	0.420	0.418	0.418	0.419	0.419	0.418	0.418
64-71	0.409	0.410	0.409	0.409	0.409	0.410	0.408	0.409
100-107	0.416	0.419	0.418	0.418	0.420	0.418	0.417	0.418
108-115	0.412	0.411	0.416	0.411	0.411	0.413	0.411	0.412
117-124	0.414	0.415	0.412	0.414	0.412	0.413	0.413	0.414
125-132	0.412	0.406*	0.411	0.411	0.410	0.414	0.412	0.412

Mean absorbance - 0.416

Average deviation - 3.6×10^{-3}

Standard deviation - 4.1×10^{-3}

* discarded

interferences, by adding the diverse specie to the test solution prior to the addition of reagent and proceeding as in the general procedure. Several ions of interest were also examined in detail and interference thresholds were determined for these by adding varying concentrations of diverse specie to a series of solutions.

When repeated, independent measurements of a single quantity are made, 99.7 % of the results on the measurement should fall within the range of the average plus and minus three times the standard deviation (37). Therefore, the interference threshold was defined in this work as the concentration of a diverse ion which created a deviation in the absorbance measurement of 0.012 units. In most cases, as shown in Table 7, threshold values were expressed as "greater than" some arbitrary value which one would not ordinarily expect to encounter in natural water samples. For certain species which interfered at low concentrations, namely nickel(II), copper(II), iron(II), and iron(III), the threshold values were more accurately defined by treating solutions according to the general procedure, several at various concentrations of interfering specie. The results of these studies are exemplified in Table 8 and Figure 5 which show that absorbance of the system began to decrease when iron(III) was present at 1.5 ppm or greater.

Other selected species were also studied in some detail. Sodium chloride was examined at high concentrations such as one might encounter in the analysis of sea water. The threshold values of tartrate ion and the iron(III)-tartrate complex are of interest in relation to work with steels and metal alloys where iron is present in large amounts.

Table 7. Interference Threshold Study

Specie	Threshold Concentration
Li^{+}	>200 ppm
$Na^{+}Cl^{-}$	50,000 ppm (5.0%)
K^{+}	1,000 ppm
Ca^{++}	>500 ppm
Hg^{++}	>50 ppm
Zn^{++}	>50 ppm
Mn^{++}	>50 ppm
Ni^{++}	5.0 ppm
Cu^{++}	8.0 ppm
Fe^{+++}	1.0 ppm
Fe^{++}	1.0 ppm
Al^{+++}	>10 ppm
Cr^{+++}	>20 ppm
CNS^{-}	>1.500 ppm
F^{-}	>500 ppm
$C_2H_3O_2^{-}$	>1,170 ppm
$C_2O_4^{--}$	>2,000 ppm
$P_2O_7^{----}$	>5,000 ppm
$C_4H_4O_6^{--}$	11,000 ppm (1.1%)
EDTA	7.5×10^{-5} M
SO_3^{--}	50 - 150 ppm
NO_2^{-}	1,000 -2500 ppm
Fe(III) tartrate	1000 ppm

Table 8. Iron(III) Threshold Data

Solution Number	Iron(III) (ppm)	A @ 540 mμ
301	0	0.407
313	0.20	0.407
312	0.50	0.406
309	1.00	0.406
314	1.00	0.407
315	1.00	0.407
318	1.00	0.406
319	1.00	0.407
320	1.00	0.405
321	1.00	0.406
317	1.50	0.403
323	1.50	0.399
302	2.00	0.388
310	2.00	0.399
316	2.00	0.407
303	3.00	0.392
311	3.00	0.389
304	4.00	0.390
305	5.00	0.389
306	6.00	0.380
307	7.00	0.380
308	8.00	0.362

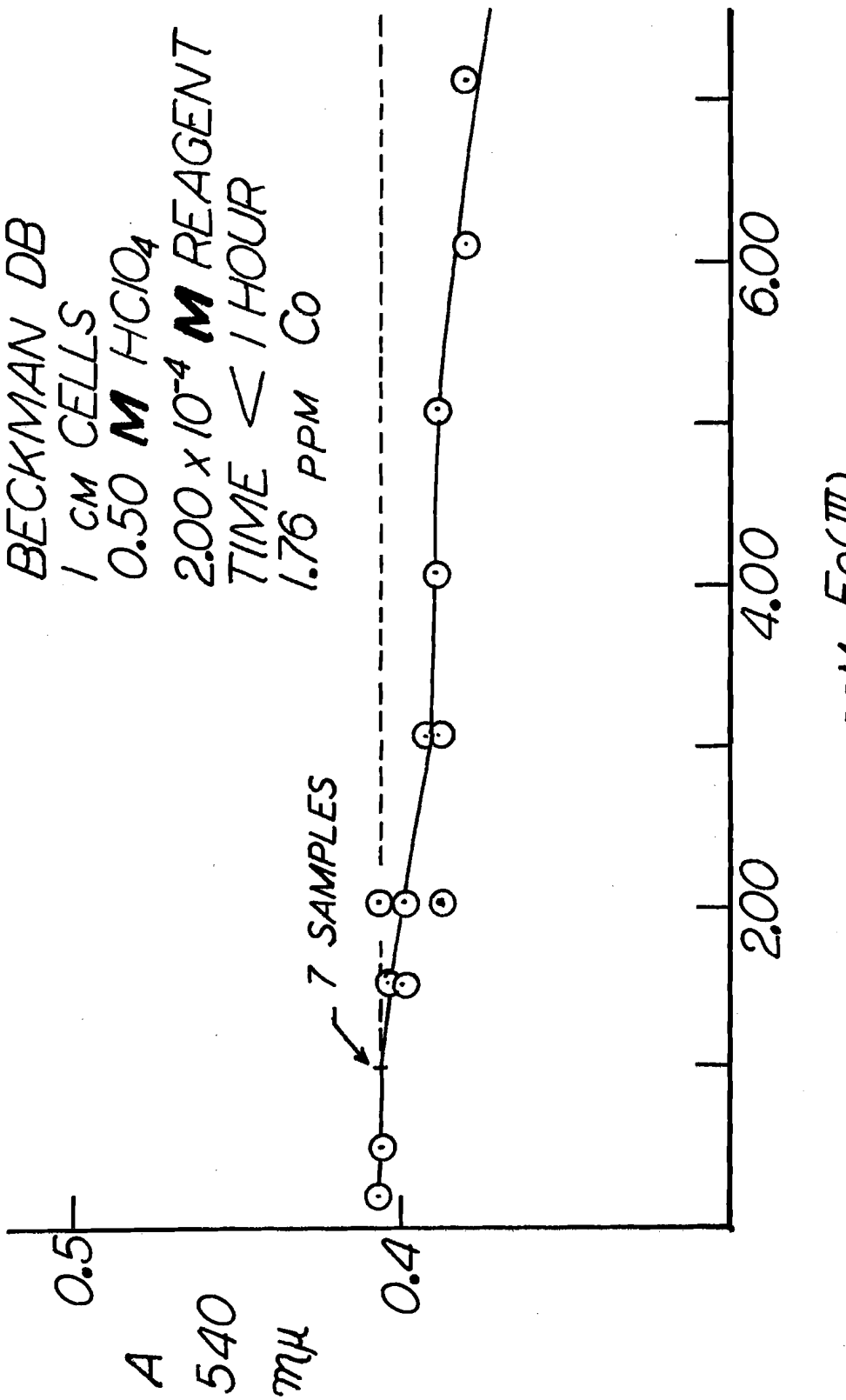

Figure 5. The interference threshold of iron(III)

F. Elimination of Interferences

After the preliminary interference studies were made, it was believed that three general mechanisms were present by which interference reactions occurred. The first, as expressed by (1) below, involved the precipitation of a diverse ion, such as aluminum or ferric ion when the system was adjusted to pH 8. The hydrous aluminum or ferric oxides, $M(OH)_3$, precipitate.

$$n\ Co^{2+} + M^{3+} + 3n\ R^{-2} \xrightarrow{1.\ NaOH} (n-x)\ CoR_3^{-4} + M(OH)_3 \cdot x\ Co^{2+} + 3x\ R^{2-}$$

$$(n-x)\ CoR_3^{-4} + M^{+3} + x\ Co^{2+} + 3x\ R^{2-} \xleftarrow{2.\ HClO_4} \qquad (1)$$

When the precipitate formed, a quantity of Co^{2+} was occluded and was prevented from complexing with available reagent molecules. During the reacidification step, the occluded Co^{2+} was liberated as the precipitate dissolved but was not converted into the complex under these acidic conditions. Therefore, low results were obtained.

A second general mechanism of interference was encountered when a specie which was also capable of forming a complex with the reagent, was present in large concentration. As shown in (2), this specie competed with Co^{2+} for available reagent molecules, thus preventing quantitative results. When the system was then acidified, the interfering complex dissociated, but the uncomplexed cobalt was unable to react with the freed reagent and low results were obtained.

$$n\ Co^{2+} + y\ M^{2+} + R^{2+} \xrightarrow{1.\ NaOH} (n-z)\ CoR_3^{4-} + y\ MR_3^{4-} + x\ Co^{2+}$$

$$(n-z)\ CoR_3^{4-} + y\ M^{2+} + 3y\ R^{2-} + x\ Co^{2+} \xleftarrow{2.\ HClO_4} \qquad (2)$$

A third mechanism of interference was caused by species such as nitrite and sulfite which most likely entered into oxidation-reduction reactions with the system. The reagent molecule can perhaps be reduced

to several compounds, including the 2-amino derivative, and can be oxidized to the 2-nitro derivative.

1. Masking Agent

An attempt was made to eliminate the interferences by aluminum and iron(III) by a recycling procedure similar to that employed by Shipman, *et.al.*,(19). This attempt involved the preparation of solutions, containing a sufficient quantity of diverse ion to create a significant interference, according to the general procedure. Instead of measuring the absorbance at that point, however, the solutions were again made basic (pH 8) and reacidified. This procedure was repeated a number of times before the final absorbance measurements were made. The process was somewhat analogous to the method of reprecipitation described by Walton (38) and even though results were much improved by using this technique, quantitative recoveries were not attained. This was due to the fact that as the concentration of an adsorbed impurity decreased the relative amount adsorbed increased (38).

If the mechanism outlined by (1) above was correct, it should have been possible to eliminate this type of interference by the technique of masking of the hydroxide-forming metal, thereby preventing the formation of a precipitate. To solutions containing 15.00 ml of 1.9991×10^{-4} M cobalt(II) sulfate and a sufficient quantity of diverse ion to effect a significant interference were added varying quantities of masking agent. The solutions were then handled according to the general procedure. No precipitates were observed, and the results shown for aluminum(III) and iron(III) in Table 9 indicated successful elimination of interference using tartrate as masking agent.

Table 9. Tartrate as Masking Agent

Ion	Solution Number	Tartrate salt (ml) 40 mg/ml	A @ 540 mμ
Fe^{+++}	77 (standard)	--	0.403
(100 ppm)	76 (control)	0	0.300
	74	5	0.405
	75	5	0.400
Al^{+++}	86 (standard)	--	0.405
(100 ppm)	85 (control)	0	0.389
	83	10	0.406
	84	10	0.406

Similar results were obtained when 100-ppm manganese(II) was masked using 10 ml of 0.2 M sodium pyrophosphate.

2. Excess Reagent

Mechanism (2) outlined above indicated that low results might be obtained due to a competition between cobalt and another metallic ion for reagent molecules with the result that some cobalt may remain uncomplexed. To a series of solutions containing 15.00 ml of 1.999×10^{-4} M cobalt(II) sulfate and a sufficient quantity of diverse ion to create a significant interference were added varying amounts of reagent solution. The solutions were then handled according to the general procedure. Table 10 illustrates this situation when nickel(II), copper(II), and chromium(III) were present in sufficient concentration to compete for reagent molecules. As shown, quantitative results were obtained when additional reagent was added, 25-30 ml 2.00×10^{-3} M reagent being sufficient at the concentrations of interfering species examined.

3. Oxidation

It was felt that the third type of interference might be eliminated if the oxidation state of the interfering specie was altered. It was already known that the system could tolerate high concentrations of sulfate and nitrate. To study this effect, to solutions containing 15.00 ml of 1.9991×10^{-4} M cobalt(II) sulfate and 30 mg $SO_3^=$ were added 1 ml of 30 % H_2O_2. The solutions were then treated according to the general procedure. If sulfite was interfering by reducing reagent molecules, the hydrogen peroxide treatment should remedy this by oxidizing sulfite to sulfate.

Table 10. Effect of Excess Reagent on Interfering Metal Ions

Ion	Solution Number	2.000×10^{-3} M reagent (ml)	A @ 540 mμ
Ni^{++} (20 ppm)	144 (standard)	10	0.412
	146 (control)	10	0.241
	147	20	0.395
	148	30	0.413
Cu^{++} (50 ppm)	156(standard)	10	0.414
	157 (control)	10	0.370
	158	15	0.401
	159	25	0.414
Cr^{+++} (50 ppm)	161 (standard)	10	0.411
	162	10	0.403
	165	20	0.399
	166	30	0.413

Similarly the oxidation of nitrite to nitrate would eliminate nitrite interference. A similar study was carried out, but in the presence of 2500 ppm nitrite instead of sulfite.

The results of the oxidation treatment on sulfite and nitrite, reported in Table 11, indicated that their interference was eliminated by hydrogen peroxide oxidation. One-ml 30 % hydrogen peroxide was sufficient in the samples examined.

G. Determination of Cobalt in Natural Waters

Six natural-water samples were taken, two liters each from the Mississippi River, Big Muddy River, Crab Orchard Lake, Southern Illinois University at Carbondale Campus Lake, and two wells. After addition of perchloric acid to prevent algae growth, the samples were clarified by filtration and cobalt determined in them according to the recommended procedure. Details of the development of the method were earlier reported by Rigdon, Carlson and Caskey (11). The utilization of the proposed procedure was recently discussed by Carlson and Caskey (39).

In order to examine the system for the presence of possible natural-occurring interferences, three of the natural water samples were used for recovery studies. Aliquots of 50.00 ml from Crab Orchard Lake, Big Muddy River, and Well #1 were first analyzed for cobalt according to the recommended procedure for determining cobalt in water. The low concentration of cobalt in these waters required the use of 10-cm cells and the Beckman DK-IA spectrophotometer. After the waters were analyzed for cobalt, additional 50.00-ml aliquots were taken and to these were added various quantities of 7.996×10^{-6} M cobalt(II) sulfate. These solutions were then analyzed according to the recommended procedure for determining cobalt in water and the amounts of cobalt recovered were calculated. The recovery

Table 11. Oxidation of Interfering Species

Solution Number	SO_3^{2-} (ppm)	30 % H_2O_2 (ml)	A @ 540 mμ
199	50	0	0.409
200	150	0	0.398
201	300	0	0.362
205	300	1	0.410
205a	300	1	0.408
	NO_2^- (ppm)		
212	500	0	0.410
210	1000	0	0.403
211	2500	0	0.362
212a	2500	1	0.408
212b	2500	1	0.410

data shown in Table 12 was indicative that no significant interferences were encountered in these waters. No cobalt was found in the remaining three waters, i.e., Mississippi River, Well #2, and Southern Illinois University at Carbondale Campus Lake.

Carlson and Caskey have recently reported (40) the application of the method to the determination of cobalt in steels. Excellent results were obtained on the steel samples, showing that the method has few interferring species and can be adapted to very complex systems. Excess reagent and sodium potassium tartrate were used to eliminate interferences.

A more complete description of the research described in this chapter of this report, as well as related materials, has been prepared by Carlson (34).

Table 12. Determination of Cobalt in Natural-Water Samples

Crab Orchard Lake	Solution Number	Cobalt Added (ppm)	Cobalt Found (ppm)	Cobalt Recovered (ppm)	Cobalt Recovered (%)
	252		0.028		
	253		0.029		
	254		0.029		
	255		0.028		
	256		0.033		
	Average		0.029		
	257	0.0235	0.0518	0.0228	97
	258	0.0235	0.0525	0.0235	100
	259	0.0235	0.0525	0.0235	100
	260	0.0235	0.0506	0.0216	92
	261	0.0235	0.0558	0.0268	114
	Average	0.0235	0.0526	0.0236	100
Big Muddy River					
	360		0.012		
	361		0.013		
	362		0.009		
	363		0.013		
	364		0.012		
	Average		0.012		
	376	0.0047	0.0166	0.0046	97
	377	0.0047	0.0177	0.0055	119
	378	0.0094	0.0183	0.0063	67
	379	0.0470	0.0605	0.0485	103
	Average				94
Well Number 1					
	433		0.010		
	434		0.014		
	435		0.012		
	436		0.013		
	437		0.013		
	Average		0.012		
	423	0.0470	0.0580	0.0460	98
	424	0.0470	0.0620	0.0500	106
	425	0.0470	0.0614	0.0494	105
	426	0.0470	0.0614	0.0494	105
	427	0.0470	0.0614	0.0494	105
	Average	0.0470	0.0608	0.0488	104

V. SUMMARY AND CONCLUSION

Sodium 2-nitroso-1-naphthol-5-sulfonate was prepared by the method of Mossotti by nitrosylation of sodium 1-naphthol-5-sulfonate. Results of elemental analysis, the neutralization equivalent, and the infrared spectrum indicated that the product was in a very pure form and existed as a two and one-half hydrate. The pKa_2, which was calculated from the neutralization titration, was found to be 7.15 at 25 ^{o}C.

The reaction between cobalt(II) and sodium 2-nitroso-1-naphthol-5-sulfonate to form a red, water-soluble complex was utilized in a proposed, excellent method for the determination of cobalt in natural waters. The system was followed in a perchloric acid medium which removed many interferences. The complex, containing three organic ligands, formed quantitatively in the pH 4.7-10 range and was stable for 10 hours in perchloric acid solutions as high as 4 molar. The system conformed to Beer's law over a cobalt-concentration range of 0.02 - 4.7 ppm, and was quite reproducible, yielding a standard deviation of 4×10^{-3} absorbance units.

The system exhibited excellent selectivity and it should be noted that several ions of interest could be tolerated at relatively high concentrations. The presence of five-percent sodium chloride caused no interference, which indicated that the method should be applicable to sea water. An interference-threshold value of greater than 500 ppm for fluoride was observed, which should be of interest to those working with municipal-water supplies. The high interference threshold for tartrate and its complex with iron(III) facilitated the analysis of steels.

Species which interfered at low concentrations were dealt with using masking techniques, excess reagent, or alteration of the oxidation state of the interfering specie. Iron(III) and aluminum(III) were masked

using tartrate, while pyrophosphate was used to sequester manganese(II). Chromium(III), nickel(II), copper(II), and iron(II) interferences were eliminated by adding excess reagent. Nitrite and sulfite were oxidized using hydrogen peroxide. Successful recovery studies were carried out on three natural-water samples. That the method is accurate, specific and precise has been demonstrated by the successful determination of cobalt in standard-steel samples.

VI. LITERATURE CITED

(1) M. E. Weeks, "Discovery of the Elements", 6th Ed., Journal of Chemical Education, Easton, Pa., 1956.

(2) W. J. Williams, *Talanta, 1,* 88 (1958).

(3) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. 2, D. Van Nostrand, New York, 1949.

(4) R. W. Young, *Cobalt,* A.C.S. Monograph No. 108, Reinhold, New York (1948).

(5) Anonymous, *Cobalt,* No. 30, 39 (1966).

(6) M. Urbain, *Cobalt,* No. 1, 13 (1958).

(7) D. Golightly, *Honors Dissertation,* Southeast Missouri State College, 1962.

(8) Anonymous, *Cobalt,* No. 1, 5 (1958).

(9) R. S. Young, "The Analytical Chemistry of Cobalt," 1st ed., Vol. 27, Pergamon Press Inc., New York, 1966.

(10) V. G. Mossotti, *Honors Dissertation,* Southeast Missouri State College, 1960.

(11) J. A. Rigdon, G. D. Carlson, A. L. Caskey, *Abstracts 4th Midwest Reg. Meet., Am. Chem. Soc.,* Manhattan, Kansas (1968).

(12) C. V. Banks and J. M. Dale, *Treatise on Analytical Chemistry, Part II,* "Analytical Chemistry of the Elements," Vol. 2, Interscience Publications, New York, 1962.

(13) R. Lundquist, G. E. Markle, and D. F. Boltz, *Anal. Chem., 27,* 1731 (1955).

(14) H. Schuller, *Mikrochim. Acta, 31,* 33 (1964).

(15) H. Baron, Z. *Anal. Chem., 140,* 173 (1953).

(16) R. S. Young, E. T. Pinkney and R. Dick, *Ind. Eng. Chem., Anal. Ed., 18,* 474 (1946).

(17) E. B. Kidson and H. O. Askew, *New Zealand J. Sci. Tech., 21,* 1788 (1940).

(18) W. H. Shipman and J. R. Lai, *Anal. Chem., 28,* 1151 (1956).

(19) W. H. Shipman, S. C. Foti, and W. Simon, *Anal. Chem.*, *27*, 1240 (1955).

(20) W. M. Wise and W. Brandt, *Anal. Chem.*, *26*, 693 (1954).

(21) S. Komatsu, *Nippon Kagaku Zasshi*, *82*, 1064 (1961).

(22) A. L. Caskey, *Dissertation Abstr.*, *22*, 61-6156 (1962).

(23) W. Forster and H. Zeitlin, *Anal. Chim. Acta*, *34*, 211 (1966).

(24) K. Benford, M. Gilbert, and S. H. Jenkins, *Water Research*, *1*, 695 (1967).

(25) T. G. Thompson and T. Laevastu, *J. Marine Res.*, *18*, 189 (1960).

(26) W. Forster and H. Zeitlin, *Limnol. Oceanogr.*, *12*, 359 (1967).

(27) J. P. Riley and G. Topping, *Anal. Chim. Acta*, *44*, 234 (1969).

(28) J. P. Riley and D. Taylor, *Anal. Chim. Acta*, *40*, 479 (1968).

(29) D. C. Burrell, *Anal. Chim. Acta*, *38*, 447 (1967).

(30) P. Friedlaender and R. Faussig, *Ber. deut. chem. Ges.*, *30*, 1456 (1897).

(31) S. V. Bogdanov and L. L. Teckoev, *J. Gen. Chem.* (U.S.S.R.), *4*, 1353 (1934).

(32) G. E. Brown, A. L. Caskey, V. G. Mossotti and D. W. Golightly, *Abs. 139th Nat. Meet.* A.C.S., St. Louis, p. 27B, (1961).

(33) W. A. Gifford, C. E. Williams, and A. L. Caskey, *Prog. 62nd Ann. Meet. Ill. State Acad. Sci.*, p. 10 (1969).

(34) G. D. Carlson, *Masters Thesis*, Southern Illinois University, 1970.

(35) H. Diehl and J. P. Butler, *Anal. Chem.*, *27*, 777 (1955).

(36) H. Diehl and F. Lindstrom, *Anal. Chem.*, *30*, 414 (1958).

(37) H. Diehl and G. F. Smith, "Quantitative Analysis," J. Wiley & Sons Inc., New York, 1952.

(38) H. F. Walton, "Principles and Methods of Chemical Analysis," 2nd Ed., Prentice-Hall, Inc., Englewood Cliffs, N.J., 1964.

(39) G. D. Carlson and A. L. Caskey, *61st Ann. Conf., Ill. Sect., Am. Water Works Assoc.*, Chicago, Illinois (1970).

(40) G. D. Carlson and A. L. Caskey, *Abs. 5th Ann. Midwest Reg. Meet. Am. Chem. Soc.*, Kansas City, Missouri, 116 (1969).

Chapter 4

STUDY OF THE VALUES OF SOME THERMODYNAMIC FUNCTIONS OF NAPHTHOL SULFONIC ACID DERIVATIVES

Raymond A. Cox and Albert L. Caskey

I. INTRODUCTION

Lambert in 1760, and later Beer, observed and investigated certain optical phenomena (1). Lambert noted that when monochromatic or multi-colored light passed through some absorbing medium, the intensity of the incident light was greater than the intensity of the transmitted light. The intensity of the incident light, I_o, was related to the sum of the intensities of the reflected light, I_r, the absorbed light, I_a, and the transmitted light, I_t. By using a control to measure the reflected light, Lambert eliminated that term and obtained

$$I_o = I_a + I_t \quad \text{and} \quad \frac{dI}{db} = -K_1 I$$

which when integrated yielded

$$I_t = I_o \cdot e^{-k_1 b} \quad \text{or} \quad I_t = I_o \cdot 10^{-k_2 b}$$

where b was the thickness of the medium and K_1 and K_2 were constants, called absorption coefficients, which were dependent on the wavelength of the light and the nature of the absorbing medium used.

Beer extended Lambert's studies and determined the effect of the concentration of colored species in solution on the intensity of the light transmitted. The intensity of a beam of monochromatic light decreased exponentially as the concentration of the absorbing substance increased arithmetically, or

$$I_t = I_o \cdot e^{-k_3 c} \quad \text{or} \quad I_t = I_o \cdot 10^{-k_4 c}$$

where k_3 and k_4 were constants and c was concentration of the light-absorbing species.

The combined Lambert's and Beer's laws related both the path length of the transmitted light and the concentration of the absorbing species to the incident and transmitted intensities, which in modern nomenclature have been referred to as the incident and transmitted power, P_o and P_t, respectively, and yielded the expression

$$P_t = P_o \cdot 10^{-\varepsilon c b}$$

where ε was the molar absorptivity, c the concentration expressed in moles per liter, and b the path length expressed in centimeters. The absorbance, A, was defined by

$$A = \log (P_o/P_t) = \varepsilon c b$$

allowing the molar absorptivity to be calculated when the absorbance of a solution of known concentration was measured in an absorption cell of known dimension.

Suppose that an undissociated, weak acid, HX, absorbs visible or ultraviolet radiation over a wavelength range, $\Delta\lambda$, including a maximum absorbance at λ_1, and suppose that the anion of the acid, X^-, does not absorb light over this wavelength range. Measurement of the absorbance values at λ_1 of each of two, equal-formal, standard solutions of this acid, one in an acidic medium to ensure that HX is 100 percent undissociated, and the other in a buffered solution of intermediate pH, allows calculation of the concentration of the undissociated acid, HX, in the buffered medium. The concentration of the anion, X^-, present in the buffered solution can be calculated by substracting this concentration from the formal, standard concentration of the acid.

Therefore, if the pH of the buffered solution is measured or if a buffer of known pH is used, the ionization constant for the acid can be calculated by the equation

$$K_a = \frac{[H^+]\,[X^-]}{[HX]}$$

where the ratio $[X^-]/[HX]$ is obtained spectrophotometrically.

II. HISTORICAL

Knowledge of the thermodynamic values of ionization constants of new acids is a prerequisite for completely understanding their chemistry. Without knowing the strength of acids, and the effects substituents have upon those strengths, the chemist cannot hope to explain the behavior of the acids, let alone predict what the acids will do in any given chemical system. Halban and Ebert (2) first proposed the possibility of determining ionization constants colorimetrically and made some rough determinations. Since then, instrumentation has improved to such an extent that in 1954, Bates and Schwarzenbach (3) proposed that the accurate determination of thermodynamic values of ionization constants could be obtained by a combination of spectral absorption and e.m.f. data by an extrapolation to zero ionic strength to eliminate all salt effects. To verify this, they determined the ionization constants of three, uncharged acids (4-nitrophenol, 2,4-dinitrophenol and 4-chloro-2,6-dinitrophenol) and of three, cationic acids (3-nitroanilinium ion, 4-chloroanilinium ion, and N,N-diethyl-4-toluidinium ion). The results they obtained agreed very well with the accepted literature values.

In 1955 Robinson and Biggs (4) described a procedure for the accurate determination of the ionization constant of 4-nitrophenol by a spectrophotometric method. Buffers of known pH were prepared according to procedures described by Bates and Acree (5) and the pH values of the buffers checked with a pH meter. Then by measuring the absorbance of three solutions containing equal-formal concentrations of an unknown acid when it was completely undissociated, completely dissociated, and in a buffer solution of intermediate known pH, the ratio of the concentration of the dissociated acid to the

undissociated acid was evaluated and the ionization constant calculated. The thermodynamic value of the ionization constant of 4-nitrophenol was reported to be 7.149. This compared with the values of 7.02 (6), 7.16 (7), and 7.19 (8) measured by other authors using other methods of determination.

In 1961, Bates and Gary (9) published the results of work that greatly improved the spectrophotometric method for the determination of thermodynamic values of ionization constants of weak acids and bases. A thermodynamic acidity function, $p(a_{H^+}\gamma_{Cl^-})$, was defined for use in measuring the activity of the hydrogen ion in solution where $p(a_{H^+}\gamma_{Cl^-}) \equiv -\log_{10}(m_{H^+}\gamma_{H^+}\gamma_{Cl^-})$ in accordance with the convention set forth by Bates and Guggenheim (10). An electromotive cell of the type

$$Pt;\ H_2(g,\ 1\ atm),\ buffer\ solution\ containing,\ AgCl;\ Ag$$
$$soluble\ chloride$$

was used for the determination of $p(a_{H^+}\gamma_{Cl^-})$ by the equation

$$p(a_{H^+}\gamma_{Cl^-}) = \frac{E - E^\circ}{2.30259RT/F} + \log m_{Cl^-}$$

where E was the electromotive force of the above cell, E° was the standard potential of the cell, R was the gas constant, T was the absolute temperature in degrees Kelvin, and F was the faraday. In order to extrapolate back to zero ionic strength for determining thermodynamic data, the ionic strength, μ, of the buffer solution must be known and potential measurements made at different ionic strengths, since $p(a_{H^+}\gamma_{Cl^-})$ was used for determining thermodynamic data at an ionic strength of zero. This acidity function was measured by Bates and Gary for a series of buffers over a wide range of temperatures and the values reported (9). This made it possible for other workers to prepare a buffer solution with an

accurately known acidity function; the thermodynamic value of the ionization constant of an acid could now be measured by carefully preparing three, equal-formal solutions of the acid being studied and then measuring the absorbance of each solution at one wavelength. In one solution the acid must be completely undissociated, in one solution the acid must be completely dissociated, and in the third solution, which must be one of the buffered solutions described by Bates and Gary (9), the acid must be partially dissociated. As long as the concentration of the acid being studied was kept very small so as not to appreciably change the ionic strength of the solution, or to exceed the buffer capacity of the buffer, the reported acidity function could be used and no pH measurement needed to be taken.

Robinson (11) used the values of Bates and Gary (9) to spectrophotometrically determine the thermodynamic values of the ionization constants of six dichloroanilines and six dichlorophenols in aqueous solutions at 25 °C with very good results. An approximately linear relationship was found to exist between the pK_a° values of the dichloroanilines and the pK_a° values of the corresponding dichlorophenols. Relationships like this made it possible to predict the behavior of related compounds by knowing the behavior of one of them.

Srivastava (12) determined spectrophotometrically the values of the ionization constant of 1-nitroso-2-naphthol at seven different temperatures from 25 °C to 55 °C and used these values to calculate the values of free energy, enthalpy, entropy, and heat capacity of ionization. Since 1-nitroso-2-naphthol was used as an analytical reagent for precipitating cobalt in hot 0.2 N hydrochloric acid solution (13) and

Fe(III), Cr(III), W(VI), V(V), Sn(IV), Ti, Ag, and Bi precipitated under these same conditions, it might be possible to choose better conditions by knowing the values of the thermodynamic functions of 1-nitroso-2-naphthol so that the interferring cations would not first have to be removed. If the values of formation constants of the complexes of 1-nitroso-2-naphthol with all of the cations were also measured accurately, then a reliable prediction of the feasibility of such a separation would be possible. The work done by Srivastava is only one example of the increased use of the spectrophotometric method to evaluate values of other thermodynamic functions of acids from the values of the ionization constant measured spectrophotometrically at different temperatures.

Wilson, Gore, Sawbridge and Cardenas-Cruz (14) calculated the thermodynamic values of the ionization constants of a series of substituted benzoic acids, and also calculated the values of other thermodynamic functions and explained the correlation of acid strength with molecular structure. An advance in the technique was a computer program which calculated the values of the thermodynamic quantities ΔG°, ΔH°, and ΔS° at a number of selected reference temperatures over a temperature range. They explained the effects that methyl substituents had upon the acid strength of benzoic acid and found that benzoic acid and its derivatives seemed to fall in four distinct classes when the ionization constant was plotted against temperature. They then explained the substituent effects on the basis of resonance effects and a delocalization effect.

Of course, thermodynamic functions of acids are not the only important chemistry of acids, but they are important enough to merit careful consideration and understanding.

It was desired to use the improved, spectrophotometric method proposed by Bates and Gary (9), directly deducible from the method of Robinson and Biggs (4), to determine the thermodynamic ionization constants of 1-naphthol and 2-naphthol and their sulfonic acid derivatives and use the determined values to calculate the other thermodynamic functions of these acids so that the complexing ability of the hydroxynaphthalene sulfonic acids might better be explained and their specific behavior predicted. The preliminary work using a model compound is described in this chapter of this report. A more comprehensive study of naphthol sulfonic acid derivatives was presented by Cox (15).

III. EXPERIMENTAL

A. Reagents

Reagent-grade chemicals, meeting American Chemical Society specifications were used whenever they were commercially available, including *tris*-(hydroxymethyl)-aminomethane (Fisher T-395), hydrochloric acid (Fisher A-144-C), sodium hydroxide (Fisher S-318), potassium dihydrogen phosphate (Fisher P-285), disodium phosphate (Baker and Adamson 2313), sodium borate decahydrate (Fisher S-249), and sodium chloride (Matheson, Coleman and Bell SX645).

Primary-standard potassium hydrogen phthalate (Fisher P-243) was used.

The 4-nitrophenol (Matheson, Coleman and Bell NX 645), was purified by sublimation: mp 113 - 114 °C, [lit, mp 114 °C (16)].

The water used was deionized water which was prepared from distilled water by passing it through a 45 x 400-mm column of monobed, self-indicating, ion-exchange resin, Rohm and Haas Amberlite MB 3 (Mallinckrodt 332G). The deionized water was stored carbonate free.

B. Equipment

A Beckman Research Model pH meter, equipped with a general-use, glass electrode and a fiber-type, saturated-calomel electrode was used. The pH meter was calibrated by making up buffers of known pH according to the procedures of Bates (17).

A Beckman Model DB (1401) recording spectrophotometer was used for all absorbance measurements. A pair of matched, silica, absorption cells of 1.00-cm path length was used. To ensure that the temperature within

the cell compartment was correct, a total-immersion thermometer was placed in an insulated glass tube attached to the inlet and another thermometer was placed in an insulated glass tube attached to the outlet. Each thermometer was calibrated against an NBS calibrated thermometer, test number 186179. The proper correction was applied. The magnitude of the correction needed for six different temperatures is presented in Table 1. The temperature drop between the inlet and outlet of the cell compartment was less than 0.10 °C.

The melting points were measured with a Thomas Hoover Unimelt Capillary Melting Point Apparatus (Thomas 6406-M) calibrated with acetanilide: mp 112.5 - 113.5 °C, [lit, mp 113-114 °C (17)].

Borosilicate glassware was used exclusively. All volumetric glassware used was NBS Class A quality. The glassware was cleaned by washing first with hot water containing Dreft and finally rinsing at least six times with distilled water. The glassware was then dried at 110 °C in an oven. Any glassware which did not drain properly was washed with a solution of potassium hydroxide in ethanol, and then washed again in hot water containing Dreft.

Purification by vaccum sublimation was accomplished using an Ace-6684, standard-taper unit, and a Duo-Seal vacuum pump (Model 1405).

Control of the temperature of the solutions and the cell compartment of the spectrophotometer to within $\pm$ 0.10 °C was obtained using two constant temperature baths equipped with Sargent-Welch thermonitors (Model ST), and a Cole-Parmer Variable Speed Masterflex Tubing pump.

Table 1. Calibration of Thermometers

Thermometer Reading for RI655	Correction[a]	Thermometer Reading for 674	Correction[a]
16.12 °C	+0.08 °C	16.05 °C	+0.15 °C
22.51 °C	+0.06 °C	22.51 °C	+0.06 °C
31.90 °C	+0.03 °C	31.93 °C	+0.04 °C
40.06 °C	+0.01 °C	40.06 °C	+0.00 °C
43.41 °C	+0.04 °C	43.41 °C	+0.01 °C
50.00 °C	+0.00 °C	50.00 °C	+0.00 °C

[a]The plus sign means that the true temperature is higher than the indicated temperature.

C. Special Stock Solution

Standard hydrochloric acid, 0.1173 N, was prepared by buretting 41.5 ml of concentrated hydrochloric acid, sp. gr. 1.19, into a 5-liter polypropylene bottle, filling the bottle with deionized water, and magnetically stirring the solution for one-half hour. The solution was standardized potentiometrically against primary-standard, *tris*-(hydroxymethyl)-aminomethane which had been dried at 100 °C for one-and-one-half hours (0.1173 N, rel. std. dev. 0.07 %, 6 trials).

Standard sodium hydroxide, 0.0900 N, was prepared by buretting 20.0 ml of concentrated sodium hydroxide (1 g/ml) into a 5-liter polypropylene bottle and filling the bottle with carbonate-free, deionized water and magnetically stirring the solution for thirty minutes. The solution was standardized against primary-standard potassium hydrogen phthalate, previously dried at 120 °C for two hours, using phenolphthalein as indicator (0.0900 N, rel. std. dev. 0.13 %, six trials).

A stock solution of 1.00×10^{-3} M 4-nitrophenol was prepared by placing 0.13911 g of this substance into a 1-liter volumetric flask, and diluting to volume with deionized water.

A solution, 0.2500 m in both potassium dihydrogen phosphate and disodium hydrogen phosphate buffer, was prepared by placing 35.4950 g of disodium hydrogen phosphate and 34.0225 g of potassium dihydrogen phosphate in 998.95 g of water weighed at 25.0 °C and atmospheric pressure. This mass of water was equivalent to 1000.0 g of water at 25.0 °C weighed in vacuum. Bates and Gary (9) reported $p(a_{H^+}\gamma_{Cl^-})$ values for this buffer at different temperatures.

D. Procedure

Five sets of six solutions each were prepared by pipeting various volumes of 1.000×10^{-3} M 4-nitrophenol into each of several 100-ml, volumetric flasks. Then 10.00-ml 0.1173 N hydrochloric acid, 10.00-ml 0.0900 N sodium hydroxide, 5.00-ml, 10.00-ml, and 15.00-ml of buffer were added to each flask in sets 1, 2, 3, 4, and 5, respectively. The solutions were diluted to volume with deionized water, shaken, and placed in the constant-temperature bath at 25.0 °C for thirty minutes. The absorbance of each solution was measured at 399 mμ against a deionized water blank.

IV. DISCUSSION AND RESULTS

A. Derivation of Working Equation

If one considers a weak acid, HX, the negative logrithm of the thermodynamic value of the ionization constant, pK_a°, for the ionization reaction

$$HX \rightleftharpoons H^+ + X^-$$

can be expressed by the mathematical equation

$$pK_a^\circ = p(a_{H^+}\gamma_{Cl^-}) - \log\left[\frac{(A-A_1)}{(A_2-A)}\right] + \log\left[\frac{\gamma_{HX}\gamma_{Cl^-}}{\gamma_{X^-}}\right] \qquad \{1\}$$

where $p(a_{H^+}\gamma_{Cl^-})$ is an "acidity function" which designates the quantity $-\log(m_{H^+}\gamma_{H^+}\gamma_{Cl^-})$; $\log\left[\frac{(A-A_1)}{(A_2-A)}\right]$ is a function giving the fraction of the acid in the anionic state in terms of spectrophotometric absorbance values; and $\log\left[\frac{\gamma_{HX}\gamma_{Cl^-}}{\gamma_{X^-}}\right]$ is a function of certain activity coefficients [a = activity, γ = activity coefficient, A = absorbance, m = molality]. This approach for determining pK_a° values is much easier and quicker than older methods thanks to the work of R. G. Bates and R. Gary (9), and M. Paabo, R. G. Bates, and R. A. Robinson (18), who have evaluated the $p(a_{H^+}\gamma_{Cl^-})$ values for a series of buffer solutions over a wide range of temperatures. Since $pK_a^\circ = -\log K_a^\circ$, therefore

$$-\log K_a^\circ = -\log\left[\frac{a_{H^+}a_{X^-}}{a_{HX}}\right] = -\log\left[\frac{m_{H^+}\gamma_{H^+}m_{X^-}\gamma_{X^-}}{m_{HX}\gamma_{HX}}\right].$$

Multiplying the term inside the brackets by $\left[\frac{\gamma_{Cl^-}}{\gamma_{Cl^-}}\right]$ and rearranging terms gives

$$- \log K_a^\circ = - \log (m_{H^+}\gamma_{H^+}\gamma_{Cl^-}) - \log \left[\frac{m_{X^-}}{m_{HX}}\right] - \log \left[\frac{\gamma_{X^-}}{\gamma_{HX}\gamma_{Cl^-}}\right],$$

and

$$- \log K_a^\circ = p(a_{H^+}\gamma_{Cl^-}) - \log \left[\frac{m_{X^-}}{m_{HX}}\right] + \log \left[\frac{\gamma_{HX}\gamma_{Cl^-}}{\gamma_{X^-}}\right].$$

Then, $- \log \left[\frac{m_{X^-}}{m_{HX}}\right] = - \log \left[\frac{(A-A_1)}{(A_2-A)}\right]$, where A_1 is the absorbance of a solution containing only HX, A_2 is the absorbance value of a solution containing only X^-, and A is the absorbance of a solution buffered so that both X^- and HX exist. The sum of the concentrations of X^- and HX is constant in each of the three solutions.

Proof that the term $\left[\frac{A-A_1}{A_2-A}\right]$ will actually give the ratio of the concentration of anion to the concentration of undissociated acid can be given. A, A_1 and A_2 have already been defined. Also, let m_{HX} equal the molal concentration of HX in solution, and m_{X^-} the molal concentration of X^- in solution, and $c = m_{HX} + m_{X^-}$. Then, substituting into the Beer-Lambert law,

$$A = \varepsilon bc$$

where ε is the molal absorptivity, one obtains,

$$A_2 = \varepsilon_{X^-} bc,$$

$$A_1 = \varepsilon_{HX} bc,$$

$$A = \varepsilon_{HX} b m_{HX} + \varepsilon_{X^-} b m_{X^-},$$

$$\frac{A-A_1}{A_2-A} = \frac{\varepsilon_{HX}bm_{HX} + \varepsilon_{X^-}bm_{X^-} - \varepsilon_{HX}bc}{\varepsilon_{X^-}bc - \varepsilon_{HX}bm_{HX} - \varepsilon_{X^-}bm_{X^-}} ,$$

and

$$\frac{A-A_1}{A_2-A} = \frac{b[m_{X^-}\varepsilon_{X^-} + \varepsilon_{HX}(m_{HX} - c)]}{b[\varepsilon_{X^-}(c - m_{X^-}) - m_{HX}\varepsilon_{HX}]} .$$

Since $c = m_{X^-} + m_{HX}$,

then

$$\frac{A-A_1}{A_2-A} = \frac{m_{X^-}\varepsilon_{X^-} - m_{X^-}\varepsilon_{HX}}{m_{HX}\varepsilon_{X^-} - m_{HX}\varepsilon_{HX}} ,$$

$$\frac{A-A_1}{A_2-A} = \frac{m_{X^-}(\varepsilon_{X^-} - \varepsilon_{HX})}{m_{HX}(\varepsilon_{X^-} - \varepsilon_{HX})} ,$$

and

$$\frac{A-A_1}{A_2-A} = \frac{m_{X^-}}{m_{HX}} .$$

Therefore, the negative logrithm of the thermodynamic value of the ionization constant of a weak acid is given by:

$$pK_a^\circ = \rho(a_{H^+}\gamma_{Cl^-}) - \log\left[\frac{(A-A_1)}{(A_2-A)}\right] + \log\left[\frac{\gamma_{HX}\gamma_{Cl^-}}{\gamma_{X^-}}\right] . \qquad \{1\}$$

The $\rho(a_{H^+}\gamma_{Cl^-})$ values can be obtained from literature data (5,9), the absorbance values A, A_1, and A_2 can be measured in the laboratory, but the activity-coefficient term must be evaluated.

By using the Debye-Hückel equation (19),

$$-\log \gamma_i = \frac{Az_i^2\sqrt{\mu}}{1 + Ba_i\sqrt{\mu}} \qquad \{2\}$$

where

$$B = \left[\frac{8\pi\epsilon^2 N}{1000\ Dkt}\right]^{1/2} = 0.33 \times 10^{8}$$

for water at 25 °C, the activity coefficient γ_i of an ionic species can be calculated. Since a_i, the ion size parameter, is of the order of 3×10^{-8} cm for many ions, the Debye-Hückel equation reduces to

$$-\log \gamma_i = \frac{Az_i^2\sqrt{\mu}}{1 + \sqrt{\mu}} \qquad \{3\}$$

where μ is the ionic strength, z_i is the charge on the ion, and A, the Debye-Hückel slope which has a value of 0.5108 $mole^{-1/2}\ kg^{1/2}$ at 25 °C. Values of parameters in the Debye-Hückel-Onsage equations for aqueous 1:1 electrolytes over a wide temperature range can be obtained from tables (20). As stated by R. G. Bates (21), the magnitude of the activity coefficient term depends not only on the ionic strength but on the charge type of the acid-base conjugate pair and, particularly at moderate and high ionic strengths, on specific effects not easily evaluated. It is therefore desirable to work at relatively low ionic strengths.

The extended Debye-Hückel equation was discussed by Bates and Acree (5) when they determined the second dissociation constant of phosphoric acid from 0 to 60 °C. They used the extended Debye-Hückel equation, also known as the Guggenheim equation, in the form

$$-\log \gamma_i = \frac{Az_i^2\sqrt{\mu}}{1 + Ba_i\sqrt{\mu}} - \beta\mu \qquad \{4\}$$

where A and B were constants dependent upon the dielectric constant and the temperature of the solvent, z_i was the charge on any i^{th} ion, and a_i and β were adjustable parameters. Bates, Siegel and Acree (22) explained the term $\beta\mu$ as resulting from the change of dielectric constant with concentration of ionized solutes as well as interactions among resonant dipolar ions and nonpolar ions. The term a_i ($cm \times 10^{-8}$) was related to the ion size or the effective-charge radius of the ion in solution.

Therefore, to calculate the activity coefficients of the ions in dilute solutions, the simple Debye-Hückel equation, equation 2, can be used for each ion (i) and the resulting term calculated.

B. Relationship of Molality and Molarity

The $p(a_{H^+}\gamma_{Cl^-})$ values determined by Bates and Gary (9) were evaluated using buffer solutions prepared on the basis of molality, where molality was defined as the number of moles of solute dissolved in one kilogram of solvent. Therefore, in this study all stock buffer solutions were prepared on the basis of molality. Dilution of stock molal solutions to prepare other more dilute molal solutions required weighing the correct masses of solvent needed. Such processes would have been very tedious for making the large number of dilutions required. Further solution preparations were facilitated using dilutions by molarity of the stock molal solutions. It can be shown that such dilutions were justified, and did not introduce large relative errors.

By definition, $m^\circ = n/W_1$, $M^\circ = n/V^\circ$, $n = W_2/M$, $V^\circ M^\circ = VM$, and $D^\circ = [W_1 + (W_2/1000)]V^\circ$ where

m° = molality, initial conditions
m = molality, final conditions

W_1 = mass solvent, kg
W_2 = mass solute, g
n = number of moles of solute
V° = volume, liters, initial conditions
V = volume, liters, final conditions
D° = density, initial conditions
D = density, final conditions
M° = molarity, initial conditions
M = molarity, final conditions

and M is the molecular weight of the solute. The initial molarity of a solution is given by the equation $M° = n/V°$, but by substituting for $V°$ the value $[W_1 + (W_2/1000)]/D°$ a new equation

$$M° = D°n \,/\, [W_1+(W_2/1000)] \qquad \{5\}$$

is obtained. Now, if nM is substituted for W_2, the molarity can be expressed by the equation

$$M° = D°n \,/\, [W_1 + (Mn/1000)] = D°(n/W_1) \,/\, [1+(Mn/1000W_1)].$$

Since $m° = n/W_1$, the molarity of the solution is given by

$$M° = D°m° \,/\, [1 + (Mm°/1000)], \qquad \{6\}$$

an equation which relates molarity to molality. The molality can then be calculated by rearranging and solving for $m°$ to get

$$m° = M° \,/\, [D° - (MM°/1000)]. \qquad \{7\}$$

The molarity of the final solution can be calculated by equation $M = V°M°/V$. But, by inspection of equation 6, the molality of the diluted solution is also given by the equation

$$M = Dm \,/\, [1 + (Mm/1000)]. \qquad \{8\}$$

Equations 7 and 8 can be equated to obtain

$$V°M°/V = Dm / [1 + (Mm/1000)]. \quad \{9\}$$

Substituting into equation 9, the result obtained for $M°$ from equation 6, a new equation

$$V°/V = \left[\frac{Dm}{1 + (Mm/1000)}\right] \Big/ \left[\frac{D°m°}{1 + (Mm°/1000)}\right] \quad \{10\}$$

is obtained, which after solving for the final molality m, yields

$$m = \frac{1000\ D°m°V°}{1000\ DV + DVMm° - D°m°V°M} \quad . \quad \{11\}$$

All stock buffer solutions were prepared on the basis of molality, but the dilutions of the buffer solutions were made on the basis of molarity. A calculation of the molality of a sample solution of the buffer, potassium dihydrogen phosphate - disodium hydrogen phosphate, handled in this manner was made and the effect on the corresponding $p(a_{H^+}\gamma_{Cl^-})$ value given by Bates and Gary (9) was determined.

The density of the initial stock solution of the buffer was measured at 25.0 °C using standard, careful techniques. A clean, dry, 5-ml volumetric flask was first weighed empty at 25.0 °C, the flask was filled to the mark with stock buffer solution, cooled to 25.0 °C, and then reweighed. The weight of 5.00 ml of the stock buffer solution was 5.2463 g at 25.0 °C. Next, a 15.00-ml aliquot of the stock buffer solution was diluted to the mark in a 100-ml volumetric flask and thoroughly shaken. Another clean, dry, 5-ml volumetric flask was weighed empty at 25.0 °C, filled to the mark with the diluted buffer solution at 25.0 °C, and then reweighed. The weight of the 5.00 ml of diluted buffer was 5.0060 g. The density of the stock solution of the buffer was [5.2463 g / 5.00 ml] = 1.0493 g/ml and

the density of the diluted buffer solution was [5.0060 g/ 5.00 ml] = 1.0010 g/ml. The molality of the diluted buffer solution was than calculated using equation *11*, where

D° = 1.0493 g/ml D = 1.0010 g/ml
m° = 0.2500 m V = 0.1000 liter
V° = 0.0150 liter

and M was 139.04, the average molecular weight since the solution was 0.2500 m in both potassium dihydrogen phosphate and disodium hydrogen phosphate. Substituting these values into equation *11*, and solving, gave

$$m = \frac{3.9349}{100.1 + 3.4795 - 0.54705}$$

$$= 0.03819$$

According to Bates and Gary (9), m should have been 0.03750 giving 1.8 % relative error in the molality. The $\rho(a_{H^+}\gamma_{Cl^-})$ value for m = 0.03750 is 6.940 at 25.0 °C and by a graphical extrapolation of $\rho(a_{H^+}\gamma_{Cl^-})$ verses m, the experimental value of 0.03819 m gave a value of 6.938 for $\rho(a_{H^+}\gamma_{Cl^-})$ at 25.0 °C. An absolute error of -0.002 was observed, which was of the same order as the experimental error in the determination of $\rho(a_{H^+}\gamma_{Cl^-})$ and was insignificant even though it might be used as a correction in the evaluation of pK_a°; the small relative error of 0.03 % which was obtained further indicated that the error was insignificant.

C. Calculation of the Average Value of the Ionization Constant

Solutions containing ten different concentrations of an acid, HA, at a minimum of three different ionic strengths were used to evaluate the thermodynamic values of the ionization constant by the equation

$$pK_a^\circ = \rho(a_{H^+}\gamma_{Cl^-}) - \log\left[\frac{A-A_1}{A_2-A}\right] + \log \gamma_{Cl^-}/\gamma_{X^-} \qquad \{12\}$$

where the activity coefficient term was a constant at any particular ionic strength and temperature once it was evaluated. The solution of the equation involved the addition or substraction of a constant term from the sum of two other terms, $\rho(a_{H^+}\gamma_{Cl^-}) - \log [(A-A_1)/(A_2-A)]$, which is $\rho(K_a^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-})$, as will be seen later. The average value of pK_a° at each ionic strength was equal to

$$pK_a^\circ = \sum_{i=1}^{n} [\rho(K_{ai}^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-}) - a]/n$$

where n was the total number of $\rho(K_a^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-})$ values at each ionic strength and a was equal to $\log_{10} (\gamma_{Cl^-}/\gamma_{X^-})$. This can be expanded to yield

$$pK_a^\circ = \frac{[\rho(K_a^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-})-a] + [\rho(K_{a2}^\circ \gamma_{Cl^-}/\gamma_{X^-})-a] + \ldots + [\rho(K_{an}^\circ \gamma_{Cl^-}/\gamma_{X^-})-a]}{n}$$

$$= \frac{[\rho(K_{a1}^\circ \gamma_{Cl^-}/\gamma_{X^-})-a]}{n} + \frac{[\rho(K_{a2}^\circ \gamma_{Cl^-}/\gamma_{X^-})-a]}{n} + \ldots + \frac{[\rho(K_{an}^\circ \gamma_{Cl^-}/\gamma_{X^-})-a]}{n}$$

$$= \frac{\rho(K_{a1}^\circ \gamma_{Cl^-}/\gamma_{X^-})}{n} + \frac{\rho(K_{a2}^\circ \gamma_{Cl^-}/\gamma_{X^-})}{n} + \ldots + \frac{\rho(K_{an}^\circ \gamma_{Cl^-}/\gamma_{X^-})}{n} - \frac{a}{n} - \frac{a}{n} - \ldots - \frac{a}{n},$$

an equation where the constant has been separated from the initial equation without changing the value of the equation. The terms can now be recombined to yield

$$pK_a^\circ = \sum_{i=1}^{n} [p(K_{ai}^\circ \gamma_{Cl^-}/\gamma_{X^-})/n] - na/n$$

$$= \sum_{i=1}^{n} [p(K_{ai}^\circ \gamma_{Cl^-}/\gamma_{X^-})/n] - a, \qquad \{13\}$$

a much simplified way to evaluate the average value of the thermodynamic ionization constant. A similar relationship holds for acids of other charge types, such as HX^-.

D. Calculation of the Standard Deviation of Thermodynamic Values of the Ionization Constants

The standard deviation of a series of groups of numbers can be calculated for that series if the standard deviation of each of the groups of numbers is known. If each group is composed of i numbers then the standard deviation of the kth group is given by

$$s_k = \left[\frac{\sum_i (xi-\bar{x}i)^2}{n-1}\right]^{1/2}$$

where s is the standard deviation of group k, x_i is any number in group k, $\bar{x}_i$ is the average of the numbers of group k, and n is the total number of variables in group k. The variance, V, for one group is

$$V = s^2$$

and the variance for k groups, V_t, is

$$V_t = \frac{\sum_k \sum_i (x_i - \bar{x}_i)^2}{N-k}$$

where N is the sum of all the variables and k is the number of groups. If one substitutes

$$\sum_i (x_i - \bar{x}_i)^2 = (n-1)\, s_k^2,$$

then

$$V_t = \frac{\sum_k [(n-1)s_k^2]}{N-k}, \quad \text{which when expanded yields}$$

$$V = \frac{(n-1)\, s_1^2 + (n-1)\, s_2^2 + \ldots + (n-1)\, s_k^2}{N-k} .$$

The standard deviation for k groups, s_t, is given by

$$S_t = \sqrt{V_t} = \left[\frac{(n-1)\, s_1^2 + (n-1)\, s_2^2 + \ldots + (n-1)\, s_k^2}{N-k} \right]^{1/2}$$

The pK_a° value for 4-nitrophenol at ionic strength μ_1, was calculated using all the $\rho(K_a^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-})$ values obtained at ionic strength μ_1. Then

the pK_a° value for 4-nitrophenol at ionic strength μ_1, was calculated using the average value of $\rho(K_a^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-})$ obtained at ionic strength μ_1. These two values for the pK_a° were exactly the same. It was then shown that using the average value of $\rho(K_a^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-})$ at each ionic strength was just as valid for the calculation of the pK_a° value at that ionic strength as using all of the values of $\rho(K_a^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-})$ at each ionic strength for the calculation of the pK_a° value at each ionic strength. Also, since the standard deviation for all the $\rho(K_a^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-})$ values at each ionic strength was calculated, it was shown that the standard deviation for the pK_a° value at ionic strength μ_1 was the same as the standard deviation for the $\rho(K_a^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-})$ values at ionic strength μ_1. The standard deviation for the average pK_a° value for all the ionic strengths was then calculated with the equation *15* where s was the standard deviation of the pK_a° values for the ionic strength indicated by the subscripts, n was the number of $\rho(K_a^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-})$ values obtained at each ionic strength, N was the total number of $\rho(K_a^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-})$ values at all ionic strengths, and k was the number of different ionic strengths.

E. A Model Compound, 4-Nitrophenol

A model compound, 4-nitrophenol, was studied to ensure that the experimental system could property be handled.

Spectral characteristics of 4-nitrophenol: found; solvent, wavelength, mμ [molar absorbitivity]; in acidic aqueous solution, 319 maximum; in basic aqueous solvent, 401 [25,00] maximum; in aqueous solution, 347 isobestic point. The absorption spectra was graphically reported by Biggs (23).

The wavelength of maximum absorption of the completely dissociated 4-nitrophenolate anion was reported by Robinson and Biggs (4) to be 407

mμ, while in this study, that wavelength of maximum absorption was first observed at 399 mμ. In order to ascertain which wavelength was correct, the spectra of 4-nitrophenol in both its completely dissociated and undissociated forms was recorded from 550 mμ to 280 mμ on two different Beckman DB spectrophotometers and one Beckman DK-IA spectrophotometer. The wavelength of the maximum absorption of the 4-nitrophenolate anion, when recorded on the two Beckman DB spectrophotometers, occurred at 398 mμ and 399 mμ. When recorded on the Beckman DK-IA, it occurred at 406 mμ. A check of the three spectrophotometers was then made for wavelength accuracy, using a Holmium filter, for which an absorption maximum was indicated on the two Beckman DB spectrophotometers at a wavelength of 416.1 mμ and on the Beckman DK-IA at a wavelength of 422.8 mμ, while the correct value was 418.4 mμ ± 1.1 mμ. The wavelength indicated by the two Beckman DB spectrophotometers was 2.3 mμ lower than the correct value while the wavelength indicated by the Beckman DK-IA was 4.4 mμ higher than the correct value. It appeared then, that the correct value of the wavelength of the maximum absorption of the 4-nitrophenolate anion was 401.3 mμ ± 1.1 mμ. This agreed very well with the value of 401 mμ reported by Fickling, Fischer, Mann, Packer and Vaughan (25).

The wavelength maximum of the 4-nitrophenolate anion at 401 mμ was selected for study because it was the maximum with the longest wavelength and it was also the maximum that showed the greatest difference in absorbance between that of the acid and its anion.

Two independant sets of data were collected for the evaluation of the thermodynamic value of the ionization constant of 4-nitrophenol. That data is reported in Table 2, Parts I and II.

Table 2. Data for the Determination of pK_a° Values of 4-Nitrophenol Part. I. First Run.

Solution[b] Number	4-Nitrophenol 1.000×10^{-3} M (ml)	0.1173 N HCl (ml)	0.0900 N NaOH (ml)	Buffer[a] (ml)	A @ 398 mμ
65	0.00	10.00	-----	----	0.000
66	2.00	10.00	-----	----	0.002
67	3.00	10.00	-----	----	0.003
68	4.00	10.00	-----	----	0.004
69	5.00	10.00	-----	----	0.007
70	6.00	10.00	-----	----	0.008
71	0.00	-----	10.00	----	0.000
72	2.00	-----	10.00	----	0.497
73	3.00	-----	10.00	----	0.743
74	4.00	-----	10.00	----	0.989
75	5.00	-----	10.00	----	1.234
76	6.00	-----	10.00	----	1.480
77	0.00	-----	-----	5.00	0.000
78	2.00	-----	-----	5.00	0.218
79	3.00	-----	-----	5.00	0.327
80	4.00	-----	-----	5.00	0.434
81	5.00	-----	-----	5.00	0.542
82	6.00	-----	-----	5.00	0.650
83	0.00	-----	-----	10.00	0.000
84	2.00	-----	-----	10.00	0.200
85	3.00	-----	-----	10.00	0.300
86	4.00	-----	-----	10.00	0.400
87	5.00	-----	-----	10.00	0.500
88	6.00	-----	-----	10.00	0.600
89	0.00	-----	-----	15.00	0.000
90	2.00	-----	-----	15.00	0.188
91	3.00	-----	-----	15.00	0.282
92	4.00	-----	-----	15.00	0.375
93	5.00	-----	-----	15.00	0.469
94	6.00	-----	-----	15.00	0.561

[a] 35.4950 g of Na_2HPO_4 and 34.0225 g of KH_2PO_4 dissolved in 1000.0 g (in vacuum) of water.

[b] All solutions were diluted to 100.0 ml.

Table 2. Data for the Determination of pK_a^o Values of 4-Nitrophenol Part II. Second Run.

Solution[b] Number	4-Nitrophenol 1.000×10^{-3} M (ml)	0.1173 N HCl (ml)	0.0900 N NaOH (ml)	Buffer[a] (ml)	A @ 398 mμ
95	0.00	10.00	-----	----	0.000
96	2.00	10.00	-----	----	0.002
97	3.00	10.00	-----	----	0.003
98	4.00	10.00	-----	----	0.005
99	5.00	10.00	-----	----	0.007
100	6.00	10.00	-----	----	0.008
101	0.00	-----	10.00	----	0.000
102	2.00	-----	10.00	----	0.494
103	3.00	-----	10.00	----	0.736
104	4.00	-----	10.00	----	0.973
105	5.00	-----	10.00	----	1.188
106	6.00	-----	10.00	----	1.394
107	0.00	-----	-----	5.00	0.000
108	2.00	-----	-----	5.00	0.215
109	3.00	-----	-----	5.00	0.322
110	4.00	-----	-----	5.00	0.429
111	5.00	-----	-----	5.00	0.532
112	6.00	-----	-----	5.00	0.637
113	0.00	-----	-----	10.00	0.000
114	2.00	-----	-----	10.00	0.200
115	3.00	-----	-----	10.00	0.296
116	4.00	-----	-----	10.00	0.392
117	5.00	-----	-----	10.00	0.490
118	6.00	-----	-----	10.00	0.588
119	0.00	-----	-----	15.00	0.000
120	2.00	-----	-----	15.00	0.188
121	3.00	-----	-----	15.00	0.279
122	4.00	-----	-----	15.00	0.370
123	5.00	-----	-----	15.00	0.463
124	6.00	-----	-----	15.00	0.554

[a] 35.4950 g of Na_2HPO_4 and 34.0225 g of KH_2PO_4 dissolved in 1000.0 g (in vacuum) of water.

[b] All solutions were diluted to 100.0 ml.

The evaluation of the negative logarithm of the thermodynamic value of the ionization constant, K_a°, was done in two parts. Since the $p(a_{H^+}\gamma_{Cl^-})$ values were reported by Bates and Gary (9) for the buffers used, and the ratio of the molar concentration of the anion to the molar concentration of the undissociated acid was measured experimentally and obtained from the relation $\left[\frac{A-A_1}{A_2-A}\right]$, the sum of these two terms was evaluated and recorded in Table 3 as $p(K_a^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-})$. The validity of the latter term was demonstrated. A rearrangement of equation *1* and a combination of terms yielded

$$p(a_{H^+}\gamma_{Cl^-}) - \log\left[\frac{A-A_1}{A_2-A}\right] = pK_a^\circ - \log\left[\frac{\gamma_{HX}\gamma_{Cl^-}}{\gamma_{X^-}}\right]. \qquad \{15\}$$

Since the activity coefficient of the undissociated acid was taken as unity, this equation reduced to

$$p(a_{H^+}\gamma_{Cl^-}) - \log\left[\frac{A-A_1}{A_2-A}\right] = p(K_a^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-}). \qquad \{16\}$$

Equation *16* was used to evaluate the values of $p(K_a^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-})$ for the data recorded in Table 2 with the correct value of $p(a_{H^+}\gamma_{Cl^-})$ for each ionic sgrength at 25.0 °C as recorded by Bates and Gary (9). An average value of $p(K_a^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-})$ at the ionic strength 0.0500 was calculated to be 7.137 for the first run with a standard deviation of 0.002 and 7.142 for the second run with a standard deviation of 0.001. The average value of $p(K_a^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-})$ at the ionic strength 0.1000 was calculated to be 7.147 for the first run with a standard deviation of 0.002 and 7.143 for the second run with a standard deviation of 0.003. The average value of $p(K_a^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-})$ at the ionic strength of 0.1500 was 7.160 for the first run

with a standard deviation of 0.001 and 7.155 for the second run with a standard deviation of 0.003. Details have been presented in Table 3.

In order to evaluate the thermodynamic value of the ionization constant, the term containing the activity coefficients in equation *1* had to be evaluated. There were essentially three ways by which the activity coefficient term could have been evaluated. One method of evaluating the activity coefficient utilized the extended form of the Debye-Hückel equation, equation *4*, where A has a constant value for a particular ionic strength and temperature given by the slope of the Debye-Hückel-Onsager equation, Ba_i was assigned a value of 1.0 as an approximation of what it should be, and β was assigned a value of usually either 0.1 or 0.2. Than by substituting in the correct ionic strength, the activity coefficient term was evaluated and either added or subtracted to the experimentally determined value of $\rho(K_a^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-})$ to get pK_a°. Another method utilized the simple Debye-Hückel equation , equation 2, where A had the same meaning, and the parameter Ba_i was varied until the best value of the negative logarithm of the thermodynamic value of the ionization constant, pK_a° was obtained for the experimentally determined values of $\rho(K_a^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-})$ at different ionic strengths. The third method of evaluating the activity coefficient term utilized equation *4* also, but instead of assigning a particular value to the parameters Ba_i and β, these parameters were varied over a reasonable range, such as Ba_i from 0.5 to 7.0 and β from -5.0 to 5.0, for each ionic strength used. The resulting term was then either added to or substracted, depending upon its sign, to the experimentally determined values of $\rho(K_a^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-})$ at the corresponding ionic strength to get the pK_a° value for a particular value of Ba_i and β at the corresponding ionic strength. These values were than averaged and the sum of the squares of the difference between each pK_a° value calculated at

Table 3. Calculation of $\rho(K_a^{\circ}\gamma_{Cl^-}/\gamma_{X^-})$ of 4-Nitrophenol for T = 25.0 °C and λ = 401.0 mμ

4-Nitrophenol M x 10^{+5}	Ionic Strength	$A-A_1$	A_2-A	Log $A-A_1/A_2-A$	$\rho(K_a^{\circ}\gamma_{Cl^-}/\gamma_{X^-})$
2.000	0.0500	.216	.279	-0.1112	7.137
3.000	0.0500	.324	.416	-0.1086	7.135
4.000	0.0500	.430	.555	-0.1108	7.137
5.000	0.0500	.535	.692	-0.1118	7.138
6.000	0.0500	.642	.830	-0.1115	7.138
Average					7.137
Std. Dev.					0.002
2.000	0.1000	.198	.297	-0.1761	7.150
3.000	0.1000	.297	.443	-0.1737	7.148
4.000	0.1000	.396	.589	-0.1724	7.146
5.000	0.1000	.493	.734	-0.1728	7.147
6.000	0.1000	.592	.880	-0.1722	7.146
Average					7.147
Std. Dev.					0.002
2.000	0.1500	.186	.309	-0.2205	7.161
3.000	0.1500	.297	.461	-0.2181	7.158
4.000	0.1500	.371	.614	-0.2188	7.159
5.000	0.1500	.462	.765	-0.2190	7.159
6.000	0.1500	.553	.919	-0.2206	7.161
Average					7.160
Std. Dev.					0.001

[a] $\rho(a_{H^+}\ \gamma_{Cl^-})$ = 7.026, 6.974, and 6.970 at ionic strengths of 0.05, 0.10, and 0.15, respectively (5).

Table 3. Calculation of $\rho(K_a^{\circ}\gamma_{Cl^-}/\gamma_{X^-})$ of 4-Nitrophenol for T = 25.0 °C and λ = 401 mμ

4-Nitrophenol M x 10^{+5}	Ionic Strength	$A-A_1$	A_2-A	Log $A-A_1/A_2-A$	$\rho(K_a^{\circ}\gamma_{Cl^-}/\gamma_{X^-})$
2.000	0.0500	.213	.279	-0.1172	7.143
3.000	0.0500	.317	.415	-0.1170	7.143
4.000	0.0500	.420	.548	-0.1156	7.142
5.000	0.0500	.523	.681	-0.1146	7.141
6.000	0.0500	.627	.815	-0.1139	7.140
Average					7.142
Std. Dev.					0.001
2.000	0.1000	.200	.292	-0.1644	7.138
3.000	0.1000	.296	.436	-0.1690	7.142
4.000	0.1000	.391	.577	-0.1710	7.143
5.000	0.1000	.485	.719	-0.1682	7.145
6.000	0.1000	.581	.861	-0.1708	7.145
Average					7.143
Std. Dev.					0.003
2.000	0.1500	.186	.306	-0.2162	7.156
3.000	0.1500	.277	.455	-0.2155	7.156
4.000	0.1500	.366	.602	-0.2160	7.156
5.000	0.1500	.457	.747	-0.2134	7.153
6.000	0.1500	.547	.895	-0.2138	7.154
Average					7.155
Std. Dev.					0.003

[a] $\rho(a_{H^+}\gamma_{Cl^-})$ = 7.026, 6.974, and 6.940 at ionic strengths of 0.05, 0.10, and 0.15, respectively (5).

each ionic strength, for the same parameters Ba_i and β, and the average values of all the pK_a^o values for the same parameters, Ba_i and β, were determined. The parameters of Ba_i and β which gave the smallest sum were considered the "best parameters" and the corresponding value of the average pK_a^o was considered the best value of the negative logarithm of the thermodynamic value of the ionization constant.

Robinson and Biggs (4) utilized the first method to evaluate the activity coefficient. They determined the pH of the solutions experimentally. The working equation they used to calculate the pK_a^o value of 4-nitrophenol was

$$pK_a^o = pH - \log \left[\frac{\alpha}{1-\alpha}\right] - \log \gamma_{X^-}$$

where α was the fraction of 4-nitrophenol present as the anion and the other terms have already been defined. Since the pH, measured experimentally, was actually the $-\log a_{H^+}$, the activity coefficient of chloride did not have to be evaluated separately. Only the activity coefficient of the 4-nitrophenolate anion needed to be evaluated. Robinson and Biggs (4) used the extended form of the Debye-Hückel equation or the Guggenheim equation, equation *4*, to evaluate the activity coefficient of the 4-nitrophenolate anion in solution, where Ba_i was set equal to 1.0 and β was set equal to 0.2. They assumed that the value of the closest distance of approach of the ions was $a = 3.04$ °A, but stated that this was probably too low for 4-nitrophenolate anion and compensated for this with an increase in the coefficient of the linear term, β. The Guggenhein equation was developed for activity coefficients of charged species, in solutions with ionic strengths greater than 0.10, which did not obey the simple Debye-Hückel equation. In order to directly compare the results of

this work with the results obtained by Robinson and Biggs, the data obtained in this experiment was evaluated by the equation

$$pK_a^\circ = \rho(a_{H^+}\gamma_{Cl^-}) - \log\left[\frac{A-A_1}{A_2-A}\right] + \frac{Az_i^2\sqrt{\mu}}{1+Ba_i\sqrt{\mu}} - \beta\mu + \log\gamma_{Cl^-} \qquad \{17\}$$

where $Ba_i = 1.0$ and $\beta = 0.2$, and the fourth and fifth terms of the equation were thus used to calculate the activity coefficient of the 4-nitrophenolate anion. The simple Debye-Hückel equation,

$$-\log\gamma_{Cl^-} = \frac{A\sqrt{\mu}}{1 + Ba_i\sqrt{\mu}}, \qquad \{18\}$$

was used to calculate the activity coefficient of the chloride ion, with $A = 0.5108$ and $Ba_i = 1.5$, which are the standard values used to evaluate $\log\gamma_{Cl^-}$, following the convention used by G. Scatchard and L. G. Epstein (29), and by Bates and Guggenheim (10). The average values of the negative logrithm of the thermodynamic value of the ionization constant, calculated for each value of $\rho(K_a^\circ\cdot\gamma_{Cl^-}/\gamma_{X^-})$ at each ionic strength, μ_i, listed in Table 3 was 7.136, 7.138, 7.145 at ionic strengths of 0.0500, 0.1000, and 0.1500, respectively, at 25.0 °C. Details are presented in Table 4. Equation *18* was similar to the equation used by Robinson and Biggs (4) except that they used pH instead of the terms $\rho(a_{H^+}\gamma_{Cl^-}) + \log\gamma_{Cl^-}$. This work gave an average value at all ionic strengths for the pK_a° of 4-nitrophenol of 7.140. The average value of pK_a° of 4-nitrophenol obtained by Robinson ang Biggs (4) was 7.149, the difference between their value and the value obtained in the present study being 0.009 pK_a units, which was a fairly good agreement. For all practical purposes, the value obtained by Robinson and Biggs was duplicated by this method of evaluation of the activity coefficients.

Table 4. Calculation of pK_a^o Values of 4-Nitrophenol

4-Nitrophenol M x 10^{+5}	Ionic Strength	$pK_a^{o\,a}$	$pK_a^{o\,b}$
2.000	0.0500	7.119	7.134
3.000	0.0500	7.117	7.132
4.000	0.0500	7.119	7.134
5.000	0.0500	7.120	7.135
6.000	0.0500	7.120	7.135
2.000	0.0500	7.125	7.140
3.000	0.0500	7.125	7.140
4.000	0.0500	7.125	7.140
5.000	0.0500	7.123	7.138
6.000	0.0500	7.122	7.137
Average		7.122	7.136
Std. Dev.		0.003	0.003
2.000	0.1000	7.122	7.143
3.000	0.1000	7.120	7.141
4.000	0.1000	7.118	7.139
5.000	0.1000	7.117	7.140
6.000	0.1000	7.116	7.139
2.000	0.1000	7.110	7.131
3.000	0.1000	7.114	7.135
4.000	0.1000	7.115	7.136
5.000	0.1000	7.117	7.138
6.000	0.1000	7.117	7.138
Average		7.117	7.138
Std. Dev.		0.003	0.003
2.000	0.1500	7.126	7.149
3.000	0.1500	7.123	7.146
4.000	0.1500	7.124	7.147
5.000	0.1500	7.124	7.147
6.000	0.1500	7.126	7.149
2.000	0.1500	7.121	7.144
3.000	0.1500	7.121	7.144
4.000	0.1500	7.121	7.144
5.000	0.1500	7.118	7.144
6.000	0.1500	7.119	7.142
Average		7.122	7.145
Std. Dev.		0.003	0.003

[a]Using equation *21*.

[b]Using equation *19*.

After carefully examining the paper by Robinson and Biggs, it was found that they did not report observing any absorbance for the undissociated 4-nitrophenol, while in this laboratory, a small absorbance was found for the completely undissociated 4-nitrophenol at the wavelength maximum of the dissociated 4-nitrophenolate anion. A small absorbance for the undissociated 4-nitrophenol at 401 mμ was also observed by Fickling, Fischer, Mann, Packer, and Vaughan (25), who reported a molar absorptivity of 38. Robinson and Biggs (4) evaluated the fraction, α, of 4-nitrophenol present as the anion. When a small compensation was made for the undissociated 4-nitrophenol, using the data presented by Robinson and Biggs, a new value for pK_a° was obtained. The equation used by Robinson and Biggs to calculate pK_a° was

$$pK_a^\circ = pH - \log \left[\frac{\alpha}{1-\alpha}\right] - \log \gamma_{X^-},$$

where the pH was 6.818, to which they applied a pH correction of 0.001, α was 0.374, and $-\log \gamma_{X^-}$ was 0.105, giving a value for pK_a° of 7.146. The correction to α was made in this laboratory by using the molar absorptivity of 38 given by Fickling (25) for the undissociated 4-nitrophenol and the concentration of 4-nitrophenol given by Robinson and Biggs of 7.154×10^{-5} M and then calculating the absorbance of the solution. This gave an absorbance value of 0.003 for the undissociated 4-nitrohpenol. This absorbance value was then substracted from the absorbance value of 0.490 listed for a pH = 6.818 and molar concentration of 4-nitrophenol of 7.154×10^{-5} M. A new molar absorptivity value was then calculated for this solution of 4-nitrophenol and the value obtained divided by the molar absorptivity value of 18,330 for the 4-nitrophenol when it was completely dissociated. The value for α was found to be 0.371, and with the same values for pH,

- log γ_{X^-}, and pH correction as given before, a value of 7.153 was calculated for the pK_a° of 4-nitrophenol. This indicated that a different value for the pK_a° of 4-nitrophenol might of been obtained by Robinson and Biggs if they would of observed the small absorbance from the completely undissociated 4-nitrophenol.

In the second method the values of pK_a° of 4-nitrophenol were calculated by the equation

$$pK_a^\circ = p(a_{H^+}\gamma_{Cl^-}) - \log\left[\frac{A-A_1}{A_2-A}\right] + \frac{A\sqrt{\mu}}{1+3.1\sqrt{\mu}} - \frac{A\sqrt{\mu}}{1+1.5\sqrt{\mu}} \qquad \{19\}$$

where A was 0.5108. Thus, equation *2*, was utilized to evaluate the activity coefficient of the 4-nitrophenolate anion, and equation *18* to evaluate the activity coefficient of the chloride ion. Details have been presented in Table 4. The parameter Ba_i was determined by successive approximations to be 3.1. This was done by substituting different values into equation *19* in place of the Ba_i and calculating a value of pK_a° at each ionic strength. The same value, that was used in place of Ba_i, was used to calculate a value of pK_a° at each ionic strength. This value was varied from 0.5 to 4.0. After calculating all the results, the value 3.1 gave a miminum value for the sum of the squares of the differences between the value of the pK_a° at each ionic strength and the average value of the pK_a° for all the ionic strengths. The calculations gave average pK_a° values of 7.122, 7.117, 7.122 at ionic strengths of 0.0500, 0.1000, and 0.1500, respectively, at 25.0 °C. The average of all three values, representing the best pK_a° values, was 7.120 with a standard deviation of 0.003.

The data in Table 4, in which has been listed the pK_a° values of 4-nitrophenol obtained when the activity coefficient term was evaluated by both the extended Debye-Hückel equation utilizing fixed parameters of Ba_i and

β, the first method, and the simple Debye-Hückel equation, the second method, has shown that the manner in which the activity coefficient term was evaluated drastically affected the calculated negative logarithm of the thermodynamic value of the ionization constant.

The third method of evaluating the activity coefficient term involved numerous calculations so a computer program was written to evaluate equation *4* with variable parameters Ba_i and β and calculate the negative logarithm of the thermodynamic value of the ionization constant. This program which has been reported elsewhere by Cox (15) was written to calculate a value for pK_a° in the equation

$$pK_a^\circ = \rho(a_{H^+}\gamma_{Cl^-}) - \log\left[\frac{A-A_1}{A_2-A}\right] + \frac{Az_i^2\sqrt{\mu}}{1 + Ba_i\sqrt{\mu}} - \beta\mu - \frac{A\sqrt{\mu}}{1 + 1.5\sqrt{\mu}} \qquad \{20\}$$

where $\rho(a_{H^+}\gamma_{Cl^-}) - \log\left[\frac{A-A_1}{A_2-A}\right]$ was the average value for $\rho(Ka\gamma_{Cl^-}/\gamma_{X^-})$ at each ionic strength, Table 3, Ba_i was a parameter varied from 0.5 to 7.0 in increments of 0.1, β was a parameter varied from -5.0 to +7.0 in increments of 0.05, and A was the value of the slope in the Debye-Hückel Onsager equation. The same value of Ba_i and β was used to calculate the pK_a° at each ionic strength, these values of the pK_a° were than averaged and the average was printed out with the corresponding values of Ba_i and β. The sum of the squares of the difference between each pK_a° value calculated at each ionic strength, for the same parameter values Ba_i and β, and the average value of all the pK_a° values for the same parameter values, Ba_i and β, was than calculated and printed out. Also printed out was the sum of the term

$$\frac{Az_i^2\sqrt{\mu}}{1 + Ba_i\sqrt{\mu}} - \beta\mu - \frac{A\sqrt{\mu}}{1 + 1.5\sqrt{\mu}} = -\log\gamma_{X^-} + \log\gamma_{Cl^-} \qquad \{21\}$$

that was added or substrated from the average value of the term $p(K_a^o \cdot \gamma_{Cl^-}/\gamma_{X^-})$ at each ionic strength. Then by looking at the print out of the sum of the squares of the differences between the pK_a^o values calculated at each ionic strength and the average value of all the pK_a^o values, the minimum value was found for the sum of this differences squared corresponding to a particular value of the parameters Ba_i and β, and the best average value for the thermodynamic value of the ionization constant was obtained. The magnitude of the correction for the activity coefficients at each ionic strength can also be obtained by finding the corresponding correction in the print out of equation *21*.

Paabo, Bates, and Robinson (18) gave the number 0.5108 representing Az_i^2 for a 1:1 electrolyte at 25 °C as being the correct value for the parameter A in the Debye-Hückel-Onsager equation. However, according to Robinson and Stokes (20), the value that should have been used was 0.5115. The program was separately executed with each value of Az_i^2; the best thermodynamic value of the ionization constant of 4-nitrophenol for Az_i^2 = 0.5108 was 7.120 with parameter values of Ba_i = 3.1 and β = 0.00 and for Az_i^2 = 0.5115 was 7.120 with parameter values of Ba_i = 3.1 and β = 0.00. The two values for this pK_a^o were different in the $4^{\underline{th}}$ place after the decimal point which was not significantly different. The values listed by Robinson and Stokes for the parameter A will be used in calculating all the activity coefficients for the determination of the value of the thermodynamic ionization constant whenever an activity coefficient must be calculated.

A nonlinear-least-squares program written by D. W. Marquardt and programmed by T. Baumeister III, J. Ann Sheldon and Ruby M. Stanley was borrowed from J. Tyrrell (24), who helped alter the program to handle the data of the present study for evaluating the best thermodynamic value of

the ionization constant from the experimentally determined $\rho(K_a^\circ \cdot \gamma_{Cl^-}/\gamma_{X^-})$ at each ionic strength. An average value of pK_a° of 7.120 ± 0.003 pK units, using a value for the parameter Ba_i of 3.12 ± 0.24, was calculated for the thermodynamic value of the ionization constant of 4-nitrophenol by this program. This value agreed well with the pK_a° value of 7.120 calculated by the other program. The results obtained from the use of this computer program indicated that the data obtained in the present study was very precise, precision being a fair indication of accuracy.

Fickling, Fischer, Mann, Packer and Vaughan (25) evaluated the thermodynamic value of the pK_a° of 4-nitrophenol spectrophotometrically. Values of pK_a° of 7.155, 7.153, 7.146, 7.153, and 7.150, for the ionic strengths of 0.01, 0.015, 0.02, 0.02, and 0.04, respectively were obtained by them. A colorimetric determination of the thermodynamic value of the ionization constant of 4-nitrophenol was done by Judson and Kilpatric (26), with a value of 7.14 being obtained. Luden (17) determined a pK_a° value of 6.91 potentiometrically, and Michaelis and Gyemant (27) obtained a pK_a° value of 7.09 potentiometrically.

The best value of pK_a° of 4-nitrophenol at 25.0 °C determined by the present study was 7.120 ± 0.003. On the basis of the calculated values, the use of the extended Debye-Hückel equation with variable parameters Ba_i and β was not warrented since the pK_a° of 4-nitrophenol evaluated with this equation gave the same answer as determined by using the simple Debye-Hückel equation with a variable parameter Ba_i, although this might not be true in every case. Using the computer program to evaluate the activity coefficients by the extended Debye-Hückel equation with the variable parameters Ba_i and β, the simple Debye-Hückel equation is also tested since the parameter β is varied through zero so that it can be easily seen whether the extended

Debye-Hückel equation is needed or if the simple Debye-Hückel equation will suffice. On the other hand using the extended Debye-Hückel equation with variable parameters Ba_i and β and determining the best pK_a^o value by finding the smallest sum of the squares of the difference between each pK_a^o value calculated at each ionic strength, for the same parameter values Ba_i and β, and the average value of all the pK_a^o values for the same parameter values Ba_i and β, gives a better statistical evaluation of pK_a^o than assigning a particular value of Ba_i and β. It would appear that the best method of evaluating the activity coefficient term to determine the thermodynamic value of the ionization constant is by the third method.

The spectrophotometric determination of the thermodynamic value of the ionization constant for an acid using a buffer with an accurately known thermodynamic acidity function, $p(a_{H^+}\gamma_{Cl^-})$, given by Bates and Gary (9), instead of measuring the pH of the buffer solution, was suitable for determining accurate and reproducable values of the thermodynamic value of the ionization constant. This simplified method gave results that were in the same range as values recorded in the literature.

Thus the negative logarithm of the thermodynamic value for the ionization constant of 4-nitrophenol was determined to be 7.120 ± 0.003 at 25.0 °C using the spectrophotometric method advanced by Bates and Gary (9).

V. CONCLUSION

The negative logarthm of the thermodynamic value for the ionization constant of 4-nitrophenol was determined to be 7.120 ± 0.003 at 25.0 °C using the spectrophotometric method advanced by Bates and Gary (9).

It was shown that the spectrophotometric method for determining the negative logarithm for the thermodynamic value of the ionization constant using the $\rho(a_{H^+}\gamma_{Cl^-})$ values given by Bates and Gary (9) gave values of pK_a° nearly identical to those obtained from the spectrophotometric method used by Robinson and Biggs, where the pH of the solution was measured, so long as the activity coefficient terms were handled in the same manner.

The best values of the parameters in the Debye-Hückel equation were the values that gave the smallest sum of the squares of the differences between each pK_a° value calculated at each ionic strength and the average value of all the pK_a° values calculated from the same parameters at all the ionic strengths.

Now that the use of this method has been clearly demonstrated in this laboratory, it will be possible to proceed with the study of substituent effects, and thereby with the design, preparation and study of more specific reagents for determinations of trace impurities in water. Such studies are currently in progress.

VI. LITERATURE CITED

(1) A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis," 3rd ed, John Wiley and Sons, Inc., New York, N.Y., 1961, p 738.

(2) H. V. Halban, and L. Ebert, Z. *Physik. Chem., 112,* 359 (1904).

(3) R. G. Bates and G. Schwarzenbach, *Helv. Chim. Acta, 37,* 1069 (1954).

(4) R. A. Robinson and A. I. Biggs, *Trans. Faraday Soc., 51,* 901 (1943).

(5) R. G. Bates and J. F. Acree, *J. Res. Nat. Bur. Std., 30,* 129 (1943).

(6) A. Hantzsch, *Chem. Ber., 32,* 3066 (1899).

(7) H. Lunden, *J. Chim. Phys., 5,* 574 (1907).

(8) A. F. Hollemann and G. Wilhelmy, *Rec. Trav. Chim., 21,* 432 (1902).

(9) R. G. Bates and R. Gary, *J. Res. Nat. Bur. Std., A 65,* 495 (1961).

(10) R. G. Bates and E. A. Guggenheim, *Pure Appl. Chem., 1,* 163 (1960).

(11) R. A. Robinson, *J. Res. Nat. Bur. Std., A 68,* 159 (1964).

(12) K. C. Srivastave, *Bull. Acad. Polon. Sci., Ser. Sci. Chim., 14* (2) 96 (1966).

(13) Harold F. Walton, "Principles and Methods of Chemical Analysis," 2nd ed, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1964, p 101.

(14) J. M. Wilson, N. E. Gore, J. E. Sawbridge, and F. Cardenas-Cruz, *J. Chem. Soc., B,* 852 (1967).

(15) R. A. Cox, *Master's Thesis* Southern Illinois University, Carbondale, Illinois (1971).

(16) N. A. Lange, "Handbook of Chemistry," 10th ed, McGraw-Hill Book Company, Inc., New York, N.Y., 1967, p 655.

(17) R. G. Bates, *J. Res. Nat. Bur. Std., A 66,* 179 (1962).

(18) M. Paabo, R. G. Bates, R. A. Robinson, *J. Res. Nat. Bur. Std., A 67,* 573 (1963).

(19) H. A. Laitinen, "Chemical Analysis," McGraw-Hill Book Company, Inc., New York, N.Y., 1960, p 7.

(20) R. A. Robinson and R. H. Stokes, "Electrolytic Solutions", Butterworths Scientific Publications, London, 1959, p 468.

(21) R. G. Bates, "Determination of pH; Theory and Practice," John Wiley and Sons, Inc., New York, N.Y., 1964, p 52.

(22) R. G. Bates, G. L. Siegel, and S. F. Acree, *J. Res. Nat. Bur. Std.*, *31*, 205 (1943).

(23) A. I. Biggs, *Trans. Faraday Soc.*, *50*, 800 (1954).

(24) J. Tyrrell, Southern Illinois University, Carbondale, Illinois, 62901, personal communication, 1970.

(25) M. M. Fickling, A. Fischer, B. R. Mann, J. Packer and J. Vaughan, *J. Amer. Chem. Soc.*, *81*, 4226 (1959).

(26) C. M. Judson and M. Kilpatrick, *J. Amer. Chem. Soc.*, *71*, 3110 (1949).

(27) L. Michaelis and A. Byemant, *J. Chem. Phys.*, *109*, 165 (1920).

(28) G. Seatchard and L. F. Epstein, *Chem. Rev.*, *30*, 211 (1942).

Chapter 5

FEASIBILITY OF GAS-CHROMTOGRAPHIC SEPARATION AND DETERMINATION OF DERIVATIVES OF NAPHTHOLSULFONIC ACIDS

Peter C. Lindahl and Albert L. Caskey

I. INTRODUCTION

The separation and isolation of pure compounds from a reaction mixture may be a tedious process, especially in reaction systems where several isomeric compounds are produced. The monosulfonated, monohydroxy-naphthalene isomers, the naphtholsulfonic acids, constitute one such system. A total of 14 isomeric naphtholsulfonic acids are possible.

Naphtholsulfonic acids, which are the starting materials from which nitrosonaphtholsulfonic acids are prepared, are usually prepared by sulfonation of hydroxynaphthalenes, naphthols, or by sulfonation of aminonaphthalenes, naphthylamines, which are subsequently transformed into naphtholsulfonic acids by the classical Bucherer reaction. During the sulfonation reaction several sulfonated isomers are usually formed, and the conditions of the sulfonation reaction determine which isomers are formed.

It is very difficult to separate the various, isomeric naphtholsulfonic acids from each other and from the materials from which they are synthesized. Similarly, the corresponding nitrosonaphtholsulfonic acids most likely contain isomeric sulfonic acids. Careful study of nitrosonaphtholsulfonic acids necessitates pure compounds; obtaining pure nitrosonaphtholsulfonic acids is perhaps most easily accomplished by obtaining pure naphtholsulfonic acids.

Gas chromatography has been used for the analysis of a wide range of volatile mixtures containing close-boiling homologs and isomers. Nonvolatile or low-volatile compounds have also been analyzed after they are converted to more volatile derivatives. By evaluating the gas chromatographic characteristics of various volatile derivatives of naphtholsulfonic acids and salts, information may be obtained for the qualitative and quantitative determination of the corresponding naphtholsulfonic acids and salts.

The preparation of the isomeric naphtholsulfonic acids, or salts, that are not commercially available must be accomplished, as must the synthesis of volatile derivatives of the corresponding naphtholsulfonic acids and salts that are gas chromatographically stable. The optimum conditions for the gas-chromatographic separation of these volatile derivatives, such as column temperature, injection-port temperature, column material, solid support, liquid phase, and sample size must be investigated. The use of preparative gas chromatography to obtain pure naphtholsulfonic acids necessitates the degradation of these volatile derivatives back to the parent acid or salt. Preliminary studies have shown that the acetoxynaphthalenesulfonyl chlorides and the methoxynaphthalenesulfonyl chlorides are promising volatile derivatives for full investigation.

Thus, the ultimate goal of this project is to gas chromatographically purify naphtholsulfonic acids and salts so they may be used to design, prepare, and study possible reagents useful in determinations of trace constituents in water analysis.

II. HISTORICAL

All of the various chromatographic methods except for gas-liquid chromatography have been employed as techniques for the separation of the isomeric naphtholsulfonic acids. Paper chromatography has been the most frequently applied method for the analysis of these acids. The results and conditions for the paper chromatography of 1-naphthol-2-sulfonic acid (1, 2, 3, 4), 1-naphthol-3-sulfonic acid (1, 2, 3, 4), 1-naphthol-4-sulfonic acid (1, 2, 3, 4, 5), 1-naphthol-5-sulfonic acid (1, 2, 3, 4, 5, 6), 1-naphthol-6-sulfonic acid (2, 3), 1-naphthol-7-sulfonic acid (3), 1-naphthol-8-sulfonic acid (1, 2, 3), 2-naphthol-1-sulfonic acid (1, 2, 3, 7, 8, 9, 10), 2-naphthol-3-sulfonic acid (7), 2-naphthol-4-sulfonic acid (3, 7, 10), 2-naphthol-5-sulfonic acid (3, 7, 10), 2-naphthol-6-sulfonic acid (1, 2, 3, 4, 5, 7, 10, 11, 12, 13, 14), 2-naphthol-7-sulfonic acid (1, 2, 3, 4, 7, 10, 11), and 2-naphthol-8-sulfonic acid (1, 2, 3, 4, 7, 10) have been described in the literature.

Column chromatography (15) has been used to separate 1-naphthol-4-sulfonic and 2-naphthol-4-sulfonic acids.

Electrophoresis has been utilized to investigate 1-naphthol-4-sulfonic acid (16), 1-naphthol-5-sulfonic acid (16, 17), 2-naphthol-1-sulfonic acid (18), 2-naphthol-6-sulfonic acid (18, 19), and 2-naphthol-8-sulfonic acid (18). High voltage electrophoresis has also been used. The following named naphtholsulfonic acid isomers have been investigated: 1-4 (20), 1-5 (20), 2-6 (20, 21), and 2-8 (20).

The technique of salting-out chromatography has been used to separate 1-naphthol-2- and 1-naphthol-4-sulfonic acids (22), and 2-naphthol-6- and 2-naphthol-8-sulfonic acids (23).

The separation and identification of the isomeric 1-naphtholsulfonic acids by ascending thin-layer chromatography has been reported (24).

The separations of 1-naphthol-4-sulfonic acid, 1-naphthol-5-sulfonic acid, 2-naphthol-6-sulfonic acid, and 2-naphthol-8-sulfonic acid from sulfuric acid using a liquid-anion-exchange resin have been studied (25).

High-speed liquid chromatography has been used for the separations of 2-naphthol-6-sulfonic acid from a higher molecular weight impurity (26) and from 2-naphthol-3,6-, and 2-naphthol-6,8-disulfonic acids (27).

To our knowledge no one has reported using gas-liquid chromatography to analyze the naphtholsulfonic acids, although gas chromatography has been used to investigate volatile derivatives of naphthalenesulfonic acids. 1-Naphthalenesulfonic acid has been chromatographed as 1-naphthalenesulfonyl chloride (28), and the 2-isomer as the 2-naphthalenesulfonyl chloride (29) and the 2-naphthalenesulfonyl fluoride (30). The 1- and 2-naphthalenesulfonic acids have also been converted to their corresponding methyl esters and chromatographed (28).

There are several comprehensive reviews of the naphtholsulfonic acids (31, 32). The most extensive literature survey on the methods of synthesis and the reactions of the naphtholsulfonic acids has been presented in Elsevier's *Encyclopedia of Organic Chemistry* (31). The preparative methods of the technically important naphtholsulfonic acids have been summarized in two other technical chemical encyclopedias (33, 34).

1-Acetoxynaphthalene-2-sulfonic acid (35) and 1-acetoxynaphthalene-5-sulfonic acid (36) have been described in the literature along with the corresponding acetoxynaphthalenesulfonyl chlorides.

The methoxynaphthalenesulfonic acids prepared by the reaction of the naphtholsulfonic acid with dimethyl sulfate have been described for the

following named isomers: 1-methoxynaphthalene-3-sulfonic acid (37), 1-methoxynaphthalene-4-sulfonic acid (37, 38, 39), 1-methoxynaphthalene-5-sulfonic acid (37, 38), 1-methoxynaphthalene-8-sulfonic acid (38), 2-methoxynaphthalene-1-sulfonic acid (37, 40), 2-methoxynaphthalene-5-sulfonic acid (37), 2-methoxynaphthalene-6-sulfonic acid (37), 2-methoxynaphthalene-7-sulfonic acid (37), and 2-methoxynaphthalene-8-sulfonic acid (37). The methoxynaphthalenesulfonyl chlorides of the corresponding methoxynaphthalenesulfonic acids have been synthesized. The following named methoxynaphthalenesulfonyl chlorides have been reported in the literature: 1-methoxynaphthalene-3-sulfonyl chloride (37), 1-methoxynaphthalene-4-sulfonyl chloride (37, 38, 41), 1-methoxynaphthalene-5-sulfonyl chloride (37, 38), 1-methoxynaphthalene-8-sulfonyl chloride (38), 2-methoxynaphthalene-1-sulfonyl chloride (37), 2-methoxynaphthalene-5-sulfonyl chloride (37), 2-methoxynaphthalene-6-sulfonyl chloride (37), 2-methoxynaphthalene-6-sulfonyl chloride (37), 2-methoxynaphthalene-7-sulfonyl chloride (37), and 2-methoxynaphthalene-8-sulfonyl chloride (37).

2-Naphthalenediazonium-5-sulfonate has been prepared by the reaction of sodium 2-aminonaphthalene-5-sulfonate with sodium nitrite in hydrochloric acid (42). [*See page 241 of this Report for comments on nomenclature of diazonium inner salt compounds.]

2-Hydroxy-1-naphthalenediazonium-4-sulfonate has been synthesized from 1-amino-2-naphthol-4-sulfonic acid by reaction with sodium nitrite in neutral medium (43). Reduction of the 2-hydroxy-1-naphthalenediazonium-4-sulfonate using absolute ethanol yielded 2-naphthol-4-sulfonic acid (44).

2-Naphthol-1-sulfonic acid can be produced by the reaction of 2-naphthol with chlorosulfonic acid (45) or concentrated sulfuric acid (46).

III. EXPERIMENTAL

A. Equipment

An F and M Scientific Corporation, Research Chromatograph Model #810, gas chromatograph was used for the isothermal investigations. Helium was used as the carrier gas in all operations. Helium flow rates were measured with a soap-film meter. Various-length, six-millimeter, glass columns were used. Two, column-packing materials were used: 20 % silicone high-vacuum grease on Chromosorb W-AW-DMCS and 5 % silicone-gum rubber SE-30 on Chromosorb W-AW-DMCS. Samples were injected with a Hamilton micro-syringe, Model #702, 25-µl capacity.

Infrared spectra were recorded on a Beckman, Model IR-10, Spectrophotometer. Potassium bromide pellets were prepared in a Perkin-Elmer KBr die.

Melting points were taken on a Thomas Hoover Capillary Melting Point Apparatus.

A Buchler Instruments, Model PTFE-IGN, Portable Flash-Evaporator was used to remove volatile solvents.

Vacuum sublimations were performed in an Ace Glass Incorporated, #8020, Vacuum Sublimation Apparatus.

B. Reagents

Reagent-grade chemicals meeting American Chemical Society specifications were used whenever they were commercially available. When they were not available, the best commercially-available reagents were used including potassium 1-hydroxynaphthalene-2-sulfonate (Eastman P 7451), sodium 1-hydroxynaphthalene-3-sulfonate (J. T. Baker N 697), sodium

1-hydroxynaphthalene-4-sulfonate (Eastman P 232), sodium 1-hydroxynaphthalene-5-sulfonate (Eastman T 2807), sodium 1-hydroxynaphthalene-8-sulfonate (Eastman P 6954), sodium 2-hydroxynaphthalene-6-sulfonate (Eastman T 399), sodium 2-hydroxynaphthalene-7-sulfonate (Eastman T 920), sodium 2-hydroxynaphthalene-8-sulfonate (Eastman T 4069), 1-amino-2-hydroxynaphthalene-4-sulfonic acid (Eastman T 360), 2-naphthol(Matheson Coleman and Bell NX 120), and 2-aminonaphthalene-5-sulfonic acid (Pfaltz and Bauer).

C. Elemental Analyses

Quantitative elemental analyses were made by Galbaith Laboratories, Inc., Knoxville, Tennessee.

D. Preparation of Samples for Gas Chromatography

The acetoxynaphthalenesulfonyl chlorides and the methoxynaphthalenesulfonyl chlorides were dissolved in chloroform. The chloroform solutions were injected onto the column.

E. Synthesis

1. General Synthesis of Methoxynaphthalenesulfonic Acids

The alkali methoxynaphthalenesulfonates were prepared according to the following described procedure. The alkali naphtholsulfonate was dissolved in a minimum amount of deionized water, treated with more than an equivalent amount of strong base, and placed in a three-necked, round-bottomed flask fitted with a stirring motor, dropping funnel and thermometer. An excess amount of dimethyl sulfate was added dropwise to the solution. The alkali methoxynaphthalenesulfonate precipitated during the reaction.

The reaction mixture was cooled and the precipitate was collected on a sintered-glass funnel. The solid was first air dried and then dried in a vacuum oven at 45 °C.

2. General Synthesis of Methoxynaphthalenesulfonyl Chlorides

The methoxynaphthalenesulfonyl chlorides were prepared according to the following described synthesis. The alkali methoxynaphthalenesulfonate was placed in a round-bottomed flask and reacted with phosphorus pentachloride in phosphorus oxychloride or triturated with phosphorus pentachloride. In most cases the resulting liquid was heated to 95 °C for several hours; then the phosphorus oxychloride and phosphorus pentachloride were removed by vacuum evaporation. The residue was treated with cold, deionized water and chloroform. The water and chloroform layers were filtered and separated. The chloroform solution was washed several times with deionized water and then the chloroform was evaporated under vacuum at room temperature. The resulting residue was treated with several portions of hot ligroine. The ligroine solution was decanted from the residue and then the ligroine was vacuum evaporated at room temperature leaving the crude product.

The crude product was purified by sublimation under vacuum at an elevated temperature.

3. General Synthesis of Acetoxynaphthalenesulfonic Acids

The alkali acetoxynaphthalenesulfonates were prepared according to the following described synthesis. The alkali naphtholsulfonate was placed in a three-necked, round-bottomed flask fitted with stirring motor, condenser, and thermometer. The sample was dissolved or suspended in

glacial acetic acid and reacted with acetic anhydride. The reaction solution was heated for several hours, cooled to room temperature, and then filtered through a medium-porosity, sintered-glass funnel. The glacial acetic acid and excess acetic anhydride were removed by evaporation in a rotating, vacuum evaporator. The residue was taken up in a minimum amount of deionized water, treated with degassed, decolorizing carbon, Darco G-60, and filtered through glass-filter paper. The water was evaporated on the rotating, vacuum evaporator. The residue was collected as the alkali acetoxynaphthalenesulfonate.

4. General Synthesis of Acetoxynaphthalenesulfonyl Chlorides

The acetoxynaphthalenesulfonyl chlorides were prepared according to the following described procedure. The alkali acetoxynaphthalenesulfonate was placed in a round-bottomed flask and triturated with phosphorus pentachloride. The reaction mixture was refluxed in chloroform for two hours, followed by refluxing with a water-chloroform mixture. The reaction mixture was filtered and separated. The chloroform solution was washed several times with deionized water, and decolorized with Darco G-60, decolorizing carbon, and then the chloroform was evaporated. The resulting residue was treated with ligroine and heated on a steam cone to remove the ligroine leaving the crude product. The crude product was purified by sublimation under vacuum at an elevated temperature.

5. 1-Naphthol-2-Sulfonic Acid

Potassium 1-naphthol-2-sulfonate, obtained as a practical grade reagent, was used without further purification.

a. Potassium 1-Methoxynaphthalene-2-Sulfonate

Potassium 1-naphthol-2-sulfonate, 10.0 g (0.38 mole), was dissolved in deionized water, 50 ml, containing potassium hydroxide, 3.0 g (0.054 mole). Dimethyl sulfate, 14 g (0.11 mole), was added. The precipitate, a light-tan solid, was collected as potassium 1-methoxynaphthalene-2-sulfonate: yield, 4.7 g, 45 % theoretical.

b. 1-Methoxynaphthalene-2-Sulfonyl Chloride

Potassium 1-methoxynaphthalene-2-sulfonate, 25.1 g (0.091 mole), was refluxed with phosphorus pentachloride, 19.0 g (0.91 mole), in phosphorus oxychloride, 335 g (2.19 moles), for two hours. The crude product was sublimed three times at 50 °C. The sublimate, 1-methoxynaphthalene-2-sulfonyl chloride, was a white solid: yield, 6.4 g, 27 % theoretical; mp 64 - 65.5 °C. Anal. Calcd. for $C_{11}H_9ClO_3S$: C, 51.47; H, 3.53; Cl, 13.81; S, 12.49. Found: C, 51.50; H, 3.58; Cl, 13.79; S, 12.25.

c. Potassium 1-Acetoxynaphthalene-2-Sulfonate

Potassium 1-naphthol-2-sulfonate, 12.0 g (0.046 mole), was dissolved in glacial acetic acid, 525 g (8.75 moles), containing fused sodium acetate, 1.0 g (0.012 mole). Acetic anhydride, 32.4 g (0.32 mole), was added slowly to the solution and then the reaction solution was heated on a steam cone for six hours. The residue, a light-brown solid, was collected as potassium 1-acetoxynaphthalene-2-sulfonate: yield, 13.6 g, 98 % theoretical.

d. 1-Acetoxynaphthalene-2-Sulfonyl Chloride

Potassium 1-acetoxynaphthalene-2-sulfonate, 13.6 g (0.045 mole), was triturated with phosphorus pentachloride, 13.0 g (0.062 mole), and then

heated on a steam cone for one hour. Ligroine was added and an off-white solid precipitated from the solution: yield, 2.1 g, 16 % theoretical; mp 93.5 - 95 °C [lit. mp 87.5 °C (35)]. Anal. Calcd. for $C_{12}H_9ClO_4S$: C, 50.62; H, 3.19; Cl, 12.45; S, 11.26. Found: C, 50.40; H, 3.01; Cl, 12.60; S, 11.07.

6. 1-Naphthol-3-Sulfonic Acid

Sodium 1-naphthol-3-sulfonate, obtained as a practical-grade reagent, was used without further purification.

a. Sodium 1-Methoxynaphthalene-3-Sulfonate

Sodium 1-naphthol-3-sulfonate, 10.0 g (0.04 mole), was dissolved in deionized water, 50 ml, containing sodium hydroxide, 4.0 g (0.1 mole); then dimethyl sulfate, 12.0 g (0.10 mole), was added. The reaction was kept at 25 °C for one hour. The precipitate, a chocolate-brown solid, was collected as sodium 1-methoxynaphthalene-3-sulfonate: yield, 6.5 g, 61 % theoretical.

b. 1-Methoxynaphthalene-3-Sulfonyl Chloride

Sodium 1-methoxynaphthalene-3-sulfonate, 5.0 g (0.019 mole), was refluxed with phosphorus pentachloride, 7.5 g (0.036 mole), and phosphorus oxychloride, 7.5 g (0.049 mole), for 3.5 hours. The crude product was sublimed three times at 65 °C. The sublimate, 1-methoxynaphthalene-3-sulfonyl chloride, was a light-yellow solid: yield, 2.6 g, 53 % theoretical; mp 75.5 - 77 °C [lit. mp 75.5 °C cor. (37)]. Anal. Calcd. for $C_{11}H_9ClO_3S$: C, 51.47; H, 3.53; Cl, 13.81; S, 12.49. Found: C, 51.34; H, 3.43; Cl, 14.02; S, 12.58.

7. 1-Naphthol-4-Sulfonic Acid

Sodium 1-naphthol-4-sulfonate, obtained as a practical-grade reagent, was used without further purification.

a. Sodium 1-Methoxynaphthalene-4-Sulfonate

Sodium 1-naphthol-4-sulfonate, 49.2 g (0.20 mole), was dissolved in sodium hydroxide, 90 ml of 10 %; then dimethyl sulfate, 33.4 g (0.27 mole), was added. The reaction mixture was heated at reflux temperature for two hours. The precipitate, a light-brown solid, was collected as sodium 1-methoxynaphthalene-4-sulfonate: yield, 33.4 g, 64 % theoretical.

b. 1-Methoxynaphthalene-4-Sulfonyl Chloride

Sodium 1-methoxynaphthalene-4-sulfonate, 9.3 g (0.036 mole), was triturated with phosphorus pentachloride, 7.5 g (0.036 mole). The crude solid was sublimed, twice, at 83 °C. The sublimate, 1-methoxynaphthalene-4-sulfonyl chloride, was a white solid: yield, 4.7 g, 51 % theoretical; mp 97 - 99 °C [lit. mp 98.5 °C cor. (37), 96 - 97 °C (38), 98 - 99 °C (41)]. Anal. Calcd. for $C_{11}H_9ClO_3S$: C, 51.47; H, 3.53; Cl, 13.81; S, 12.49. Found: C, 51.54; H, 3.41; Cl, 13.65; S, 12.56.

c. Sodium 1-Acetoxynaphthalene-4-Sulfonate

Sodium 1-naphthol-4-sulfonate, 12.2 g (0.049 mole), was reacted with acetic anhydride, 162 g (1.59 moles). 4-Toluenesulfonic acid, 0.5 g (0.0026 mole), was added as a catalyst. The reaction mixture was heated via an oil bath, at reflux temperature for 55 hours. The residue, a tan solid, was collected as sodium 1-acetoxynaphthalene-4-sulfonate: yield, 13.9 g, 97 % theoretical.

8. 1-Naphthol-5-Sulfonic Acid

Sodium 1-naphthol-5-sulfonate, obtained as a technical-grade reagent, was used without further purification.

a. Sodium 1-Methoxynaphthalene-5-Sulfonate

Sodium 1-naphthol-5-sulfonate, 49.2 g (0.20 mole), was dissolved in sodium hydroxide, 150 ml of 6.7 %; then dimethyl sulfate, 26.7 g (0.21 mole), was added. The reaction mixture was heated at reflux temperature for two hours. The precipitate, a chocolate-brown solid, was collected as sodium 1-methoxynaphthalene-5-sulfonate: yield, 19.9 g, 38 % theoretical.

b. 1-Methoxynaphthalene-5-Sulfonyl Chloride

Sodium 1-methoxynaphthalene-5-sulfonate, 37.7 g (0.15 mole), was triturated with phosphorus pentachloride, 40.0 g (0.19 mole). The crude solid was sublimed four times at 90 °C. The sublimate, 1-methoxynaphthalene-5-sulfonyl chloride, was a yellow solid: yield, 10.6 g, 27 % theoretical; mp 117 - 119 °C [lit, mp 119.5 °C, cor. (37)]. Anal. Calcd. for $C_{11}H_9ClO_3S$: C, 51.47; H, 3.53; Cl, 13.81; S, 12.49. Found: C, 51.74; H, 3.70; Cl, 13.91; S, 12.70.

c. Sodium 1-Acetoxynaphthalene-5-Sulfonate

Sodium 1-naphthol-5-sulfonate, 25.0 g (0.11 mole), was suspended in glacial acetic acid, 157 g (2.61 moles), and acetic anhydride, 108 g (1.06 moles) added. The reaction mixture was heated in an oil bath, at reflux temperatures for 7.5 hours. The residue, a gray-tan solid, was collected as sodium 1-acetoxynaphthalene-5-sulfonate: yield, 23.8 g, 81 % theoretical.

d. 1-Acetoxynaphthalene-5-Sulfonyl Chloride

Sodium 1-acetoxynaphthalene-5-sulfonate, 11.6 g (0.040 mole), was triturated with phosphorus pentachloride, 12.0 g (0.058 mole), and then refluxed in chloroform, 45 g (0.38 mole), for thirty minutes. The crude product was sublimed, twice, at 90 °C. The sublimate, 1-acetoxynaphthalene-5-sulfonyl chloride, was a yellow solid: yield, 3.0 g, 26 % theoretical; mp 119 - 121 °C [lit. mp 129 °C (36)]. Anal. Calcd. for $C_{12}H_9ClO_4S$: C, 50.62; H, 3.19; Cl, 12.45; S, 11.26. Found: C, 50.32; H, 3.14; Cl, 12.73; S, 11.32.

9. 1-Naphthol-6-Sulfonic Acid

The technical-grade 1-aminonaphthalene-6-sulfonic acid to be used to synthesize 1-naphthol-6-sulfonic had a purple color. 1-Aminonaphthalene-6-sulfonic acid, 44.6 g (0.2 mole), was dissolved in water, 300 ml, containing sodium bicarbonate, 16.8 g (0.2 mole). The resulting solution was heated to boiling, treated with Darco G-60, and filtered. This latter process was performed three times. The solution was cooled and a dilute solution of hydrochloric acid was added until a precipitate was obtained. The precipitate was collected on a sintered-glass funnel. Further acidification of the filtrate yielded a purple colored precipitate which was recycled. 1-Aminonaphthalene-6-sulfonic acid, an off-white solid, was collected: total collected, 14.7 g, 33 % theoretical.

10. 1-Naphthol-8-Sulfonic Acid

Sodium 1-naphthol-8-sulfonate, obtained as a practical-grade reagent, was used without further purification.

a. Sodium 1-Methoxynaphthalene-8-Sulfonate

Sodium 1-naphthol-8-sulfonate, 24.6 g (0.10 mole), was dissolved in sodium hydroxide, 100 ml of 5 %; then dimethyl sulfate, 13.4 g (0.11 mole), was added to the sodium hydroxide solution. The precipitate, a chocolate-brown solid, was collected as sodium 1-methoxynaphthalene-8-sulfonate: yield, 15.1 g, 58 % theoretical.

b. 1-Methoxynaphthalene-8-Sulfonyl Chloride

Sodium 1-methoxynaphthalene-8-sulfonate, 15.1 g (0.059 mole), was triturated with phosphorus pentachloride, 15.0 g (0.072 mole). The crude solid was sublimed at 60 °C. The sublimate, 1-methoxynaphthalene-8-sulfonyl chloride, was a yellow solid: yield, 1.9 g, 13 % theoretical; mp 96 - 97 °C. Anal. Calcd. for $C_{11}H_9ClO_3S$: C, 51.47; H, 3.53; Cl, 13.81; S, 12.49. Found: C, 51.46; H, 3.46; Cl, 14.02; S, 12.29.

11. 2-Naphthol-1-Sulfonic Acid

Sodium 2-naphthol-1-sulfonate was synthesized from commerically available 2-naphthol.

a. Sodium 2-Naphthol-1-Sulfonate

Sodium 2-naphthol-1-sulfonate was prepared by the reaction of 2-naphthol with chlorosulfonic acid. 2-Naphthol, 72.0 g (0.5 mole), was dissolved in anhydrous nitrobenzene, 280 g (2.3 moles). Chlorosulfonic acid, 61.5 g (0.53 mole), was added dropwise. The precipitate was collected as sodium 2-naphthol-1-sulfonate: yield, 15.3 g, 12 % theoretical.

Sodium 2-naphthol-1-sulfonate was also prepared by the reaction of 2-naphthol with concentrated sulfuric acid. 2-Naphthol, 28.8 g (0.20 mole),

was added to a solution of metaboric acid, 3.0 g (0.068 mole), dissolved in concentrated sulfuric acid, 50 g of 94 - 96 %. The resulting solid was heated at 27 °C for 23 hours. After neutralization of the sulfuric acid, sodium 2-naphthol-1-sulfonate was obtained by evaporation of the solvent: yield, 8.8 g, 18 % theoretical

b. Sodium 2-Methoxynaphthalene-1-Sulfonate

Sodium 2-naphthol-1-sulfonate, 8.8 g (0.036 mole), was dissolved in deionized water, 45 ml, and a solution of concentrated sodium hydroxide, 5.4 ml. Dimethyl sulfate, 18 g (0.14 mole), was added slowly keeping the temperature of the reaction mixture at 25 °C. The precipitate, a white solid, was collected as sodium 2-methoxynaphthalene-1-sulfonate: yield, 1.5 g, 16 % theoretical.

12. 2-Naphthol-4-Sulfonic Acid

Barium 2-naphthol-4-sulfonate was synthesized from commerically available 1-amino-2-naphthol-4-sulfonic acid.

a. 2-Hydroxy-1-Naphthalenediazonium-4-Sulfonate

2-Hydroxy-1-naphthalenediazonium-4-sulfonate was prepared from commercially available 1-amino-2-naphthol-4-sulfonic acid. 1-Amino-2-naphthol-4-sulfonic acid, 48.0 g (0.20 mole), was dissolved in distilled water, 200 ml, and then a concentrated solution of copper sulfate, 4.0 g (0.016 mole), was added. The solution was cooled to below 5 °C and then sodium nitrite, 40 ml of 5 M, was added slowly. The resulting solution was filtered. The diazonium compound was precipitated with concentrated hydrochloric acid, 60 ml, collected, and air dried. The precipitate, a

yellow solid, was collected as 2-hydroxy-1-naphthalenediazonium-4-sulfonate; yield, 50.6 g, 94.5 % theoretical.

b. Barium 2-Naphthol-4-Sulfonate

Barium 2-naphthol-4-sulfonate was prepared by the reduction of 2-hydroxy-1-naphthalenediazonium-4-sulfonate. 2-Hydroxy-1-naphthalenediazonium-4-sulfonate, 30 g (0.11 mole), was refluxed with absolute ethanol, 450 ml, for 30 hours. The ethanolic solution was neutralized with a barium hydroxide solution, and the solvent was removed under vacuum on a rotary evaporator. The residue, a dark-red, hard, friable mass, was collected as barium 2-naphthol-4-sulfonate: yield, 27.9 g, 96 % theoretical.

13. 2-Naphthol-5-Sulfonic Acid

The sodium 2-naphthol-5-sulfonate derivatives were prepared from commercially available 2-aminonaphthalene-5-sulfonic acid.

a. 2-Naphthalenediazonium-5-Sulfonate

(1) Procedure I

2-Aminonaphthalene-5-sulfonic acid, 23.0 g (0.1 mole), was dissolved in water, 100 ml, containing sodium bicarbonate, 8.0 g (0.095 mole). The solution was filtered and cooled; then sodium nitrite, 7.0 g (0.1 mole) was added. This solution was added slowly to concentrated hydrochloric acid, 65 ml. The reaction temperature was kept below 5 °C. Cold, absolute ethanol, 75 ml, was added to the reaction flask and a red-brown solid precipitated from solution. The precipitate was collected on a sintered-glass funnel, washed with absolute ethanol, followed by ethyl

ether, and air dried. The precipitate, a red-brown solid, was collected as 2-naphthalenediazonium-5-sulfonate and dried in a vacuum oven at 60 °C: yield, 10.9 g, 47 % theoretical.

(2) Procedure II

2-Aminonaphthalene-5-sulfonic acid, 22.3 g (0.1 mole), was dissolved in water, 200 ml, containing sodium bicarbonate, 8.4 g (0.1 mole). The solution was filtered and cooled; then sodium nitrite, 7.0 g (0.1 mole) was added. This solution was added slowly to a solution of hydrochloric acid, 290 ml of 12 %. The temperature of the reaction mixture was kept below 4 °C. The reaction mixture was stirred for an hour after the addition was completed. The cold, reaction mixture was poured through a sintered-glass funnel and a dark-red, finely-crystalline solid was collected and washed with ethyl ether. The precipitate, a dark-red solid, was collected as 2-naphthalenediazonium-5-sulfonate and dried in a vacuum oven at 60 °C: yield, 16.4 g, 70 % theoretical.

(3) Procedure III

2-Aminonaphthalene-5-sulfonic acid, 22.3 g (0.1 mole), was dissolved in water, 100 ml, containing sodium bicarbonate, 8.4 g (0.1 mole). The solution was filtered and cooled to 2 °C, concentrated hydrochloric acid, 65 ml, added and a thick precipitate formed. This mixture was cooled to 0 °C and a solution of sodium nitrite, 7.0 g (0.1 mole), in water, 20 ml, was added. A thick, yellow precipitate was collected, washed with absolute ethanol and ethyl ether, and air dried. The air-dried solid had a red coating after being exposed to the atmosphere overnight. The infrared spectrum of this compound was not identical to the spectra of the compounds obtained in Procedures I and II.

b. Sodium 2-Methoxynaphthalene-5-Sulfonate

2-Naphthalenediazonium-5-sulfonate, 27.3 g (0.12 mole), was treated with absolute methanol, 500 ml. The mixture was heated to reflux for 24 hours. The excess methanol was removed by rotary evaporation leaving a dark-red residue. The residue was treated with water, 300 ml, and the solution was filtered. The filtrate was decolorized with Darco G-60, after it had been neutralized with sodium carbonate. The water was removed by rotary evaporation leaving a light-tan solid. The residue, a tan solid, was collected as sodium 2-methoxynaphthalene-5-sulfonate and dried in a vacuum oven at 50 °C: yield, 7.7 g, 25 % theoretical.

c. 2-Methoxynaphthalene-5-Sulfonyl Chloride

Sodium 2-methoxynaphthalene-5-sulfonate, 7.7 g (0.03 mole), was triturated with phosphorus pentachloride, 7.0 g (0.034 mole), and allowed to stand at room temperature for one hour. The reaction product was treated with ice and chloroform. The water and chloroform layers were separated and then the chloroform was evaporated. A viscous yellow oil remained after the chloroform was evaporated. The oil was treated with hot ligroine, 150 ml, three times. The ligroine was evaporated at room temperature, leaving a dirty-white, semi-crystalline solid and a viscous, colorless oil.

14. 2-Naphthol-6-Sulfonic Acid

Sodium 2-naphthol-6-sulfonate, obtained as a technical-grade reagent, was used without further purification.

a. Sodium 2-Methoxynaphthalene-6-Sulfonate

Sodium 2-naphthol-6-sulfonate, 24.6 g (0.10 mole), was extracted with sodium hydroxide, three, 100-ml portions of 5 %. Each extraction solution was treated with dimethyl sulfate, 20.0 g (0.16 mole). The precipitate, a light-tan solid, was collected as sodium 2-methoxynaphthalene-6-sulfonate: yield, 7.6 g, 29 % theoretical.

b. 2-Methoxynaphthalene-6-Sulfonyl Chloride

Sodium 2-methoxynaphthalene-6-sulfonate, 10.0 g (0.038 mole), was triturated with phosphorus pentachloride, 16.0 g (0.077 mole). The crude product was sublimed at 80 °C. The sublimate, 2-methoxynaphthalene-6-sulfonyl chloride,was a yellow solid: yield, 0.5 g, 5 % theoretical; mp 96 - 98 °C [lit. mp 93 °C cor. (37)]. Anal. Calcd. for $C_{11}H_9ClO_3S$: C, 51.47; H, 3.53; Cl, 13.81; S, 12.49. Found: C, 51.57; H, 3.54; Cl, 13.91; S, 12.65.

15. 2-Naphthol-7-Sulfonic Acid

Sodium 2-naphthol-7-sulfonate, obtained as a technical-grade reagent, was used without further purification.

a. Sodium 2-Methoxynaphthalene-7-Sulfonate

Sodium 2-naphthol-7-sulfonate, 49.2 g (0.20 mole), was dissolved in sodium hydroxide, 90 ml of 10 %; then dimethyl sulfate, 33.4 g (0.27 mole), was added. The precipitate, a brown solid, was collected as sodium 2-methoxynaphthalene-7-sulfonate: yield, 26.2 g, 50 % theoretical.

b. 2-Methoxynaphthalene-7-Sulfonyl Chloride

Sodium 2-methoxynaphthalene-7-sulfonate, 26.2 g (0.10 mole), was refluxed with phosphorus oxychloride, 335 g (2.19 moles), and phosphorus pentachloride, 19.0 g (0.092 mole), for two hours. The crude product was sublimed, twice, at 70 °C. The sublimate, 2-methoxynaphthalene-7-sulfonyl chloride, was a light-yellow solid: yield, 8.1 g, 31 % theoretical; mp 83 - 84.5 °C [lit. mp 83 °C cor. (37)]. Anal. Calcd. for $C_{11}H_9ClO_3S$: C, 51.47; H, 3.53; Cl, 13.81; S, 12.49. Found: C, 51.28; H, 3.54; Cl, 14.06; S, 12.66.

16. 2-Naphthol-8-Sulfonic Acid

Sodium 2-naphthol-8-sulfonate, obtained as a technical-grade reagent, was used without further purification.

a. Sodium 2-Methoxynaphthalene-8-Sulfonate

Sodium 2-naphthol-8-sulfonate, 49.2 g (0.2 mole), was dissolved in sodium hydroxide, 90 ml of 10 %; then dimethyl sulfate, 33.4 g (0.27 mole), was added. The reaction mixture was heated at reflux for two hours. The precipitate, a tan solid, was collected as sodium 2-methoxynaphthalene-8-sulfonate: yield, 29.6 g, 57 % theoretical.

b. 2-Methoxynaphthalene-8-Sulfonyl Chloride

Sodium 2-methoxynaphthalene-8-sulfonate, 29.6 g (0.11 mole), was refluxed with phosphorus oxychloride, 335 g (2.19 moles), for two hours. The crude product was sublimed four times at 50 °C. The sublimate, 2-methoxynaphthalene-8-sulfonyl chloride, was a light-yellow solid: yield, 3.0 g, 10 % theoretical; mp 76 - 77 °C [lit. mp 77.5 °C cor. (37)]. Anal.

Calcd. for $C_{11}H_9ClO_3S$: C, 51.47; H, 3.53; Cl, 13.81; S, 12.49. Found: C, 51.68; H, 3.48; Cl, 13.92; S, 12.58.

17. Column Packings

a. 20 % High Vacuum Silicone Grease on Chromosorb W-AW-DMCS

The column-packing material was prepared by dissolving high-vacuum, silicone grease (Dow Corning Corp., Midland, Mich.), 5.0 g, in methylene chloride, 800 ml, and then adding 60 to 80-mesh Chromosorb W-AW-DMCS (Hewlett-Packard), 20.0 g. The solvent was removed by heating the mixture on a hot plate. The resulting material was placed in a vacuum oven held at 100 °C for 12 hours. The dry mixture was used to pack the chromatographic columns.

b. 5 % Silicone Gum Rubber SE-30 on Chromosorb W-AW-DMCS

The column-packing material was prepared by dissolving silicone-gum rubber, SE-30 (Hewlett-Packard), 1.0 g, in methylene chloride, 600 ml, and then adding 60 to 80-mesh Chromosorb W-AW-DMCS (Hewlett-Packard), 19.0 g. The solvent was removed by heating the mixture on a hot plate. The resulting material was placed in a vacuum oven held at 100 °C for four hours. The dry mixture was used to pack the chromatographic columns.

18. Columns

The gas-chromatographic columns used were made from six-millimeter-diameter, borosilicate-glass tubing, Pyrex or Kimax, of various lengths. The columns were coiled or bent to fit the oven compartment and then filled with the appropriate packing material.

IV. RESULTS AND DISCUSSION

The preparation of 1-acetoxynaphthalene-2-sulfonyl chloride and 1-acetoxynaphthalene-5-sulfonyl chloride from their corresponding naphtholsulfonic acids was accomplished quite readily, but the preparation of 1-acetoxynaphthalene-4-sulfonyl chloride, a compound not found in the literature from the acetylated derivative of 1-naphthol-4-sulfonic acid was not accomplished. Although the melting points of the 1-acetoxynaphthalene-2-and -5-sulfonyl chlorides did not agree with the literature melting points, infrared spectra data and elemental analyses together with the fact that isomeric structures of the starting materials were known indicated that compounds synthesized were 1-acetoxynaphthalene-2-sulfonyl chloride and 1-acetoxynaphthalene-5-sulfonyl chloride. The acetoxynaphthalenesulfonyl chlorides prepared are quite stable when stored cold, but hydrolyze when stored at room temperature. The smell of acetic acid can be detected from the compounds after they are stored at room conditions for several days in a screw-capped bottle.

The syntheses were accomplished of the methoxynaphthalenesulfonyl chlorides from the eight, commerically available naphtholsulfonic acids, which include the: 1-2, 1-3, 1-4, 1-5, 1-8, 2-6, 2-7, and 2-8 isomers. One new methoxynaphthalenesulfonyl chloride was among the above compounds synthesized, this was 1-methoxynaphthalene-2-sulfonyl chloride. Although 1-methoxynaphthalene-8-sulfonyl chloride was previously reported to have been prepared no physical data was reported. The melting points, elemental analyses and infrared-spectral data all indicated that the compounds prepared were the methoxynaphthalenesulfonyl chlorides. The methoxynaphthalenesulfonyl chlorides are stable to room conditions for several months but cold storage was used to increase their shelf life.

The synthetic route for the preparation of methoxy compounds from the corresponding amino compounds by diazotization followed by treatment with methanol is not described in the literature except as an afterthought. Alcohols have been used extensively to reduce the diazonium group of an aryl diazonium compound to the hydrogen substitutent, although it has been noted that the reaction yielded a greater proportion of the alkyl-aryl ethers as the molecular weight of the alcohol decreased. The 2-naphthalene-diazonium-5-sulfonate was isolated as a dark-red crystalline solid. Literature sources describe the material as a green, microcrystalline powder (46), or as golden yellow needles or prisms (47), or as the hydrochloride which is a yellow paste (41). The compound was identified as a naphthalenediazoniumsulfonate from the infrared spectrum because of the sharp, strong band at 2280 cm^{-1} often credited to the diazonium group absorption and the multiple bands in the 1300-1000 cm^{-1} region often credited to the sulfonate functional group. The sodium 2-methoxynaphthalene-5-sulfonate isolated from the reaction of the diazonium compound with methanol was characterized as a sulfonic acid salt by the multiple bands in the 1300-1000 cm^{-1} infrared region and as a methoxy compound by a single peak in the NMR region attributed to aliphatic protons.

The 2-naphthol-1-sulfonic acid was isolated as the sodium salt. This product was identified by preparation of three arylamine-salt derivatives. The derivatives were the aniline salt: mp 166-167 °C [lit. mp 167 - 168 °C (48), 182 °C, cor. (49)], the o-toluidine salt: mp 181.5-183 °C [lit. mp 178-179 °C, cor. (48)], and the p-toluidine salt: mp 161-162.5 °C [lit, mp 162 °C, cor. (48)].

The acetoxynaphthalenesulfonyl chlorides could not be gas chromatographed inasmuch as they decomposed in the injection port, which was quite evident since glass columns were used.

On the other hand the methoxynaphthalenesulfonyl chlorides were readily gas chromatographed by injecting a chloroform dissolved sample. A column temperature of 195 °C with a helium-flow rate of about 100 cc/min worked very satisfactorily for these compounds. The gas chromatography of the methoxynaphthalenesulfonyl chlorides studied required no special techniques or handling. The compounds are apparently thermally stable during the vaporization and separation processes. Good separations of the methoxynaphthalenesulfonyl chlorides from impurities present in the starting material were observed using either 20 % high-vacuum, silicone grease or 5 % silicone-gum rubber, SE-30, on Chromosorb W-AW-DMCS. The results are shown in Table 1, Parts I and II.

Thus the feasibility has been demonstrated of the purification and isolation of volatile derivatives of positional isomers of certain naphtholsulfonic acids. Qualitative identification of several of the isomers is also possible using the retention-time data obtained. Expansion of the work reported here will allow quantitative determination of the volatile derivatives. Lindahl and Caskey (50), previously presented orally the work reported here.

The degradation of the methoxynaphthalenesulfonyl chlorides to the respective naphtholsulfonic acids needs careful scrutiny. Although it may not be possible to synthetically obtain all of the geometrical isomers, it is reasonable to expect that several can be obtained.

The work reported here is currently being extended in this laboratory.

Table I. Retention Times of Methoxynaphthalenesulfonyl Chlorides
Part I. Column Packing of 20 % High-Vacuum, Silicone Grease on Chromosorb-W-AW-DMCS

Substituted Naphthalenes	Rentention Time (min)	
	3.5-Foot Column at 195 °C	5-Foot Column at 200 °C
1-OCH_3-2-SO_2Cl	9.6	12.9
1-OCH_3-4-SO_2Cl	14.0	19.2
1-OCH_3-5-SO_2Cl	11.8	17.0
2-OCH_3-7-SO_2Cl	13.9	19.2
2-OCH_3-8-SO_2Cl	9.3	12.9

Table I. Retention Times of Methoxynaphthalenesulfonyl Chlorides Part II. Column Packing of 5 % Silicone-Gum Rubber, SE-30, on Chromosorb-W-AW-DMCS

Substituted Naphthalenes	Retention Time (min)	
	2-Foot Column at 190 °C	4-Foot Column at 195 °C
1-OCH_3-2-SO_2Cl	2.3	9.6
1-OCH_3-4-SO_2Cl	3.1	14.6
1-OCH_3-5-SO_2Cl	2.6	12.1
1-OCH_3-8-SO_2Cl	2.7	12.3
2-OCH_3-6-SO_2Cl	3.4	14.5
2-OCH_3-7-SO_2Cl	3.2	13.8
2-OCH_3-8-SO_2Cl	2.2	10.0

V. CONCLUSION

It can be concluded that it is feasible to develop a gas chromatographic method for the analysis of the isomeric naphtholmonosulfonic acids that will use the methoxynaphthalenesulfonyl chlorides as the chromatographable derivatives.

It also appears that the synthesis of methoxynaphthalenesulfonic acids from the corresponding aminonaphthalenesulfonic acids via the reaction of the diazonium compound with methanol may be an important pathway by which the entire isomeric series of methoxynaphthelenesulfonyl chlorides can be prepared so that a more complete gas chromatographic method can be developed.

The feasibility of determining the purity of naphtholsulfonic acids, has led not only to their preparative gas chromatography, but opens wide the door to the preparation of new, pure nitrosonaphtholsulfonic acids which will be sensitive, specific, ideal, water-soluble reagents for the determination of trace impurities in water.

VI. LITERATURE CITED

(1) J. Latinak, *Chem. Listy, 48,* 1354 (1954).

(2) J. Latinak and L. Skalicky, *Chem. Listy, 50,* 1598 (1956).

(3) V. J. Kolsek and M. Perpar, *Chemiker - Ztg, 83,* 712 (1959).

(4) A. Gruene, *Lab. Sci.* (Milan), *12,* 97 (1964).

(5) D. Dimitrov, B. N. Panaiotova, and A. Draganov, *Godishnik Khim. - Technol. Inst., 10,* 145 (1963).

(6) F. Brodman and L. Teodorescu, *Rev. Chem.* (Bucharest), *14,* 346 (1963).

(7) J. Latinak, *Collect. Czech. Chem. Commun. 26,* 403 (1961).

(8) V. K. M. Rao, *J. Sci. Ind. Res., 14B,* 161 (1955).

(9) R. Aragones - Apodaca, *Inform. Quim. Anal.* (Madrid), *17,* 53 (1963).

(10) K. Yano, O. Manabe, and H. Hiyama, *Kagaku to Kogyo* (Osaka), *31,* 11 (1957).

(11) J. Latinak, *Collect. Czech. Chem. Commun., 25,* 1649 (1960).

(12) I. Ranogajec and S. Sarcevic, *Bull. Sci., Cons. Acad.* RSF Yougoslavie, *11,* 242 (1966).

(13) R. Aragones - Apodaca, *Chim. Anal.* (Paris), *45,* 399 (1963).

(14) R. Aragones - Apodaca, *Chim. Anal.* (Paris), *44,* 482 (1962).

(15) P. Ruggli and P. Jensen, *Helv. Chim. Acta., 19,* 64 (1936).

(16) V. Jokl, *J. Chromatogr., 13,* 451 (1964).

(17) G. Pastuska and H. Trinks, *Chemiker - Ztg., 86,* 135 (1962).

(18) M. Wurst and E. Wurstova, *Chem. Prum., 11,* 398 (1961).

(19) J. B. Lloyd and F. Beck, *Stain Technol., 39,* 7 (1964).

(20) T. Terashima, *Shokuhin Eiseigaku Zasshi, 5,* 309 (1964).

(21) T. Terashima and S. Fujita, *Shokuhin Eiseigaku Zasshi, 5,* 313 (1964).

(22) W. Funasaka, T. Kojima, K. Fujimura, and T. Minami, *Bunseki Kagaku, 12,* 466 (1963).

(23) W. Funasaka, T. Kojima, and K. Fujimura, *Bunseki Kagaku, 10,* 374 (1961).

(24) V. J. R. DeDeyne, *J. Chromatogr., 31,* 260 (1967).

(25) V. S. Fritz and R. K. Gillette, *Anal. Chem.*, *40*, 1777 (1968).

(26) J. A. Schmit and R. C. Williams, *DuPont Co. Liquid Chromatography Laboratory Report LC # 156 and 163*, 1971.

(27) J. A. Schmit and R. A. Henry, *Chromatographia*, *3*, 497 (1970).

(28) W. Funasaka, T. Kojima, and T. Toyota, *Bunseki Kagaku*, *14*, 815 (1965).

(29) J. J. Kirkland, *Anal. Chem.*, *32*, 1388 (1960).

(30) J. S. Parsons, *J. Gas Chromatogr.*, *5*, 254 (1967).

(31) F. Radt, Ed., "Elsevier's Encyclopedia of Organic Compounds," Vol. 12B, Elsevier Publishing Co., New York, N. Y., 1955, pp 5261-5325.

(32) J. F. Thorpe and M. A. Whitney, "Thorpe's Dictionary of Applied Chemistry," 4th ed., Vol. 8, Longmans, Green and Co., New York, N. Y., 1947, pp 332-335 and 342-345.

(33) A. Standen, Ed., "Kirk-Othmer Encyclopedia of Chemical Technology," 2nd ed., Vol. 13, Interscience, New York, N. Y., 1967, pp 719-721.

(34) W. Foerst, Ed., "Ullmanns Encyklopadie der technischen Chemie," Band 12, Urban and Schwarzenberg, Munchen, 1960, pp 609-612.

(35) R. Anschutz, *Justus Liebigs Ann. Chem.*, *415*, 64 (1918).

(36) K. Heller, *J. Prakt. Chem.*, *121*, 193 (1929).

(37) R. Knusli, *Ph.D. Thesis*, Eidgenossischen Techischen Hochschule, Zurich, Switzerland, 1948.

(38) G. M. Oksengendler and E. P. Gendrikov, *Zh. Obshch. Khim.*, *29*, 3898 (1959); *J. Gen. Chem.* USSR, *29*, 3857 (1959).

(39) J. Percival, *Chem. News*, *59*, 226 (1889).

(40) M. Janczewski and T. Bartnik, *Roczniki Chem.*, *37*, 1105 (1963).

(41) C. Butler and F. A. Royle, *J. Chem. Soc.*, *123*, 1649 (1923).

(42) F. Radt, Ed., "Elsevier's Encyclopedia of Organic Compounds," Vol. 12B, Elsevier Publishing Co., New York, N. Y. 1955, p 5397.

(43) G. T. Morgan and E. Jones, *J. Soc. Chem. Ind.* (London), *42*, 97T (1923).

(44) H. E. Fierz-David and L. Blangey, "Fundamental Processes of Dye Chemistry," Interscience, New York, N. Y., 1949, p 199.

(45) K. H. Engel, *J. Amer. Chem. Soc.*, *52*, 2835 (1930).

(46) S. Forsling, *Chem. Ber.*, *20*, 2099 (1887).

(47) H. Erdmann, *Justus Liebigs Ann. Chem.*, *275*, 262 (1893).

(48) R. B. Forster and C. M. Keyworth, *J. Soc. Chem. Ind.* (London), *46*, 25T (1927).

(49) S. V. Bogdanov and V. A. Ivanova, *Zh. Obsch. Khim.*, *7*, 2884 (1937).

(50) P. C. Lindahl and A. L. Caskey, "Study of Naphtholsulfonic Acids by Gas Chromatography," Abstracts 6th Regional Meeting, Amer. Chem. Soc., Lincoln, Nebraska, 107 (1970).

NOTE

* The chemical literature names the diazotized aminonaphthalene-sulfonic acid inner salts in several different ways. The compound obtained from the diazotization of 2-aminonaphthalene-5-sulfonic acid, which we have called 2-naphthalenediazonium-5-sulfonate throughout this Chapter, can also be found to be named as follows: 2-diazonaphthalene-5-sulfonic acid; 2-diazonaphthalene-5-sulfonate; and 5-sulfonaphthalene-2-diazonium hydroxide, inner salt, which is currently the preferred *Chemical Abstracts* nomenclature.

The diazonium compound obtained from the diazotization of 1-amino-2-naphthol-4-sulfonic acid, which we have called 2-hydroxy-1-naphthalene-diazonium-4-sulfonate, can be found listed under any of the following names 1-diazo-2-naphthol-4-sulfonic acid; 1,2-naphtholquinone-4-sulfonic acid-1-diazide; 1,2-diazo-oxide naphthalene-4-sulfonic acid; or 2-hydroxy-4-sulfo-1-naphthalenediazonium hydroxide, inner salt, which is currently the preferred *Chemical Abstracts* nomenclature.

* See page 215 for related material.

Chapter 6

HIGHLIGHTS OF THE RESEARCH -- A SUMMARY

Albert L. Caskey

The results of much research remains hidden in the dusty, bound volumes of sophisticated scientific journals on out-of-the-way shelves in libraries. The results of much other research are lost in the scientific jargon of authors who write only at the level of their professional colleagues. Personnel in other disciplines and the practicing engineer and laymen often never come in contact with such research results, and if they do, the words that are used leave the readers with little enlightenment. In this Chapter is recorded an attempt to report in laymen's terms the significant accomplishments of the research reported in detail in Chapters 1 through 5. It is hoped that this summary will aid those who read it.

In manufacturing, in the chemical industry, in hospitals, in environmental laboratories, in pollution control, in evaluation of natural resources, in water resources, in the food industry, and in many other areas of modern life, the control chemist serves to evaluate natural resources, starting materials, intermediate products, and the final product. The control chemist is essential to modern society. Without

the control chemist quality goods and services that we take for granted would not exist.

Ideally, the control chemist desires some kind of "probe" which can be inserted into the sample, such that the concentration of the constituent of interest can then be read on a dial or recorded by a recorder. In an environmental situation, the probe would measure the concentration of a possible pollutant. In a natural-resource situation, perhaps the probe would measure the amount of a valuable mineral present.

The probe can take many shapes and forms. Perhaps one of the simplest probes is a chemical reagent which can be added to a solution of the sample with the formation of a color. The amount of color formed depends upon the amount of the constituent to be determined. A high concentration of constituent results in an intense color. A low concentration of the constituent results in a faint color. By measuring the intensity of the color, or the amount of the color, the amount of the constituent to be determined is directly measured.

In water-resource situations, the ideal probe is a water-soluble, specific, cheap, readily available reagent that can be added to a sample with little prior treatment and with simple techniques, using simple instruments, and the amount of pollutant of interest measured. The main direction of this research was to design, prepare, study, and evaluate such ideal reagents.

The search for new reagents involved several interrelated and yet independent projects. Perhaps the most essential line of endeavor focused on the preparation, or synthesis, or new reagents. Although many of the starting materials were available from commercial sources, the chemicals available were not pure and in general had unknown compositions. It was

essential, then, to find a method of preparing the reagents that yielded pure materials and that also yielded a means of identifying each reagent. The work reported in Chapter 5 was directed to the solution of this problem. A method of purification and preparation of all of the naphthol-sulfonic acids has been developed. The method uses both analytical and preparative gas chromatography, a technique that is about twenty years old. The information obtained here allows future workers to prepare and identify any of more than a dozen reagents in this series of compounds.

Perhaps the next most important aspect of the overall project was to study in a quantitative way the properties of each of several reagents. By carefully assigning numbers, measured in the laboratory, to the compounds it is possible to accurately describe their properties. This work, the foundation for which is described in Chapter 4 of this report, has already been extended in this laboratory. By evaluating these physical properties very accurately, it is much easier to make predictions concerning the design of new reagents.

In research, as in any endeavor, a real measure of the practical value is direct application to immediate problems that need solving. Hence, effort was directed toward solving specific problems involving pollution in natural-water systems such as rivers, lakes, and other streams. These efforts focus on methods for determining nitrate, a common chemical found in fertilizer and sewage, and cobalt, one of the trace elements essential for life.

The work reported in Chapter 1 describes a new method for the determination of nitrate in natural waters. The proposed reagent is 2-nitrosol-1-naphthol-4-sulfonic acid which reacts with nitrate to form a colored compound, 2-nitro-1-naphthol-4-sulfonic acid. A water sample is taken and simply treated to remove any solid particles that are

present in it and also any interfering substances, and then treated with the reagent. An acid is added and the reaction mixture heated at 60 °C for about thirty minutes. The reaction is stopped, the solution diluted to volume, and the intensity of the color measured.

The method can be run using very simple instrumentation, or very complex instrumentation available only in very sophisticated chemical laboratories. Thus it is readily adaptable to simple techniques used in water treatment plants.

Other than "Dreft," a commercially available, common, household detergent, and chloride, the only interferences encountered with the method were oxidizing and reducing agents which are commonly not found in natural-water systems. Removal of interfering substances is readily accomplished.

The accuracy of the method, determined by the recovery of a known added amounts of nitrate, was found to be better than the Brucine method, which is one of the standard methods commonly used today. The prolonged evaporations necessary for use with the Phenoldisulfonic acid method are not necessary with this method. Hence, this method is much more rapid than the standard Phenoldisulfonic acid method in common use.

Methods for the determination of impurities in many substances are proposed by all kinds of persons working in many laboratories and many nations. Many of the proposed methods are studied only briefly, and therefore contain major flaws. While working on the method for nitrate described in Chapter 1, and briefly summarized above, a report was found which indicated 1-naphthol-4-sulfonic acid was a satisfactory reagent for nitrate. This substance is very similiar in structure to phenoldisulfonic acid and 2-nitroso-1-naphthol-4-sulfonic acid, the reagent described

Chapter 1. Hence, its use might be expected to become common. However, as the work in Chapter 2 clearly shows, the report in the literature did not tell the whole story on the use of 1-naphthol-4-sulfonic acid as a reagent for nitrate. Studies in our laboratory show that the reported conditions of the reaction were not correct. Several other questions were also raised. The background studies reported in Chapter 2 have been expanded in our laboratory so that the complete conditions necessary for the use of 1-naphthol-4-sulfonic acid as a reagent for nitrate have been determined. We have been able to show that the conditions for the use of the reagent must be very carefully controlled. Its use in ordinary control laboratories, such as in water treatment plants or sewage treatment plants, probably is not really practical. It is believed that this work will save many other persons in other laboratories many headaches while trying to use this method of determination.

The element cobalt occurs in the midwestern United States in the lead and zinc deposits in the Ozark Mountains in central and eastern Missouri. It is an essential element in vitamine B_{12}. One needs to be concerned with significant concentrations of any of the heavy metals in water systems. This series of reagents is ideally suited to the determination of cobalt. As described in Chapter 3, cobalt reacts with sodium 2-nitroso-1-naphthol-5-sulfonate to form a beautifully colored, red, very stable complex. It has been shown that the reagent reacts specifically with cobalt, and the other, common, heavy metals do not interfere.

One merely needs to take a sample of water, add the reagent, adjust the pH of the solution to neutral, and pour the mixture into a flask containing excess acid. After the solution is diluted to a known volume

the color is measured. The method can be used in any laboratory. The method is specific enough to work on complicated samples such as steels, which shows the specificity of the reagent.

The communication of results of research efforts to the public is of prime importance, as is rapid presentation of laboratory findings to professional colleagues. The findings of much of the research done on this project have been presented at various scientific meetings. The titles and other pertinent information for the papers presented at scientific meetings have been summarized in Table 1.

The public records show the support for this project from funds provided by the Office of Water Resources Research of the United States Department of Interior through the Water Resources Center, Urbana, Illinois as authorized under the Water Resources Research Act of 1964, P. L. 88-379. However, these public records do not show the direct support by Southern Illinois University. The University funds expended directly for the research involved with this project are summarized in Table 2. The full commitment of Southern Illinois University to the solution of environmental problems is evidenced by the contribution, which is sincerely appreciated and acknowledged, as is the support of the United States Department of Interior.

The patience and encouragement of Nancy J. Caskey are gratefully acknowleged, as is her handiwork in the preparation of many of the drawings in this report. Many thanks are also due the ladies, Kimberlee Burdick and particularly Sandra Day, who typed the manuscript, including the many preliminary drafts.

Table 1. Papers Presented

R. J. Antepenko, F. N. Abercrombie, and A. L. Caskey. "Some Aspects of the Determination of Nitrate in Water Using 1-Naphthol-4-Sulfonic Acid." *Abstracts 3rd Midwest Regional Meeting American Chemical Society*, Columbia, Missouri, 22 (1967).

J. A. Rigdon, G. D. Carlson, and A. L. Caskey. "Spectrophotometric Determination of Cobalt in Natural Waters Using Sodium 2-Nitroso-1-Naphthol-5-Sulfonate." *Abstracts 4th Midwest Regional Meeting American Chemical Society*, Manhattan, Kansas, 20 (1968).

W. A. Gifford, C. E. Williams, G. D. Carlson, and A. L. Caskey. "Sodium 2-Nitroso-1-Naphthol-5-Sulfonate, a Reagent for the Rapid and Accurate Spectophotometric Determination of Available Cobalt in Soils." *Abstracts Annual Meeting Missouri Academy of Science*, St. Louis (1969).

G. D. Carlson and A. L. Caskey. "Cobalt in Steels: Sodium 2-Nitroso-1-Naphthol-5-Sulfonate as an Accurate, Convenient Spectrophotometric Reagent." *Abstracts 5th Midwest Regional Meeting American Chemical Society*, Kansas City, Missouri, 116 (1969).

F. N. Abercrombie and A. L. Caskey. "Use of 2-Nitroso-1-Naphthol-4-Sulfonic Acid as a Spectrophotometric Reagent for Nitrate in Natural Waters." *61st Annual Conference, Illinois Section, American Water Works Association*, Chicago, Illinois (1970).

G. D. Carlson and A. L. Caskey. "The Application of Sodium 2-Nitroso-1-Naphthol-5-Sulfonate to the Spectrophotometric Determination of Cobalt in Natural Waters." *61st Annual Conference, Illinois Section, American Water Works Association*, Chicago, Illinois (1970).

F. N. Abercrombie and A. L. Caskey. "Reactions of 2-Nitroso-1-Naphthol-4-Sulfonic Acid with Nitrate in Aqueous Perchloric Acid." *Abstracts 160th National Meeting American Chemical Society*, Chicago, Illinois, Anal 69 (1970).

S. L. Anderson, D. P. Poe, T. Liu and A. L. Caskey. "Reduction of Sodium 2-Nitroso-1-Naphthol-5-Sulfonate by Cobalt(II)." *Abstracts 6th Midwest Regional Meeting American Chemical Society*, Lincoln, Nebraska, 106 (1970).

P. C. Lindahl and A. L. Caskey. "Study of Naphthol Sulfonic Acids by Gas Chromatography." *Abstracts 6th Midwest Regional Meeting American Chemical Society*, Lincoln, Nebraska, 107 (1970).

A. L. Caskey. "Effect of Trace Impurities on the Evaluation of Thermodynamic Values of Dissociation Constants of Weak Acids." *1970 Midwest Universities Analytical Chemistry Conference*, Madison, Wisconsin, November (1970).

Table 2. Direct Expenditures by Southern Illinois University

Fiscal Year	Salaries	Wages	Travel	Total
1967-68	900.00	500.00		1400.00
1968-69	2170.00	503.99		2673.99
1969-70	2850.00	828.96		3678.96
1970-71			47.18	47.18
All	5920.00	1832.95	47.18	7800.13