

THE REACTIONS OF 2-NITROSO-1-NAPHTHOL-4-SULFONIC ACID WITH NITRATE IN ACIDIC SOLUTIONS

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ABSTRACT. — The reaction of excess nitrate with 2-nitroso-1-naphthol-4-sulfonic acid in hot, aqueous, perchloric acid solutions forming 2,4-dinitro-1-naphthol has been studied to establish if it is possible to adapt the reaction to the determination of nitrate in natural waters. The reaction was found to occur under optimum conditions of heating at 50° C, in 4.9 *M* HClO₄, for 35 minutes. Although 2,4-dinitro-1-naphthol is the product formed when the nitrate ion to 2-nitroso-1-naphthol-4-sulfonic acid molar ratio is 2 or greater, when the ratio is 1 or less, 2-nitro-1-naphthol-4-sulfonic acid is the product. Solutions of 2-nitro-1-naphthol-4-sulfonic acid, prepared under reaction conditions similar to those above, conformed to Beer's law over a nitrate (as nitrogen) concentration range of 0.3—13 ppm (under conditions of absorbance measurements), at both 221 and 260 mμ.

Many trace impurities, such as heavy metals and nitrate ions, in water used for drinking purposes, are toxic. More than 45 parts per million (ppm) of nitrate (as N) is often fatal to infants. Over prolonged periods of time, 15 to 20 ppm nitrate (as N) 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.

Because of the toxic properties of the nitrate ion, it is advantageous to have a rapid, accurate, and simple method for its determination in water. Existing methods are complicated by several factors including the necessity of prior separations for the removal of interfering substances, use of prolonged evaporation steps either for concentrating to attain minimal concentration levels or to obtain a non-aqueous reaction media, and by many other tedious procedures.

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 (Witt and Kaufman, 1891), the development of a simple method for the determination of nitrate was thought to be possible utilizing this reaction. Such a study is reported here.

EXPERIMENTAL

MATERIALS

Reagent grade chemicals meeting American Chemical Society specifications were used whenever they were commercially available. Other reagents were the best available. The 2-nitroso-1-naphthol-4-sulfonic acid was prepared by nitrosolation of 1-naphthol-4-sulfonic

acid (Witt and Kaufman, 1891; Caskey, 1962): neutralization equivalent, 325.6 (aqueous potentiometric titration with standard NaOH); theor. 325.30. The water used was deionized water prepared from distilled water by passing it through a monobed, self-indicating, ion-exchange resin, Rohm and Haas Amberlite MB3 (Mallinckrodt 3326), and stored free from carbonate. The standard sodium hydroxide was prepared and stored free from carbonate.

A Perkin-Elmer Model 137B Infracord was used to determine infrared spectra, utilizing potassium bromide pellets. The constant temperature bath, equipped with a Precision Scientific Co. Portatemp regulator, was adjustable from 5° C above ambient to 95° ± 0.25° C. A Corning Model 12 pH meter, equipped with a general-use, glass electrode and a fiber-type, saturated calomel electrode, was used for potentiometric titrations. The electrode system was calibrated using buffers prepared from commercially available concentrates. Beckman Model DB and DK-1A recording spectrophotometers were used for absorbance measurements, along with matched, silica, 1.00-, 2.00-, or 10.00-cm, absorption cells.

ELEMENTAL ANALYSES

Quantitative elemental analyses were made by Alfred Bernhardt Mikroanalytisches Laboratorium, 433 Mulheim (Ruhr), West Germany.

PREPARATION OF 2,4-DINITRO-1-NAPHTHOL

2-Nitroso-1-naphthol-4-sulfonic acid, 9.09 g, was dissolved in deionized water, 76 ml, and concentrated nitric acid, 24 ml, added. The mixture was heated to 70-80° C and then cooled in an ice bath. The solid formed was removed by filtration, washed with water and air dried; yield, 6.24 g. 95% theor., mp 134-136.5° C, dec. 136.5° C. This crude product was purified by dissolving it in dilute, aqueous sodium hydroxide which was then washed with ether. The aqueous solution was acidified with dilute phosphoric acid, the product extracted into ether, and the latter evaporated to dryness. After recrystallization from three solvents—benzene, chloroform, and absolute ethanol—the solid was sublimed under vacuum at 100° C.

PREPARATION OF 2-NITRO-1-NAPHTHOL-4-SULFONIC ACID

2-Nitroso-1-naphthol-4-sulfonic acid, 10.78 g, was placed in a round-bottom flask and treated with trifluoroacetic acid, 200 ml, and 30% hydrogen peroxide, 4.6 ml, forming a slurry which was stirred for 2½ hours. The solvents were volatilized from the slurry keeping the temperature below 46° C: yield, 10.30 g, 96% theor., mp 159-160° C, dec. 155° C. The solid 2-nitro-1-naphthol-4-sulfonic acid was dissolved in water, potassium chloride, 5.45 g, added, and the monopotassium salt recrystallized from water.

PROCEDURES

The nitration reaction 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. In general, solutions were prepared (three or more trials were run) by pipetting volumes of perchloric acid into volumetric flasks and similarly adding water (and/or sodium nitrate solution). The flasks were placed in the constant temperature bath for 15 minutes. Measured volumes of 2-nitroso-1-naphthol-4-sulfonic acid solution were added; the flasks were stoppered, shaken, and the observation of time started. Concentrations reported pertain to the resulting solutions. At the end of the measured time intervals, ice-cold water was added, the solutions diluted to volume, and the spectra obtained.

The neutralization equivalent of 2,4-dinitro-1-naphthol was obtained using 70 v/v% ethanol as the sample solvent. The solution was maintained at 50° C by using a stirring-hot plate. Other neutralization equivalents were also obtained potentiometrically, but in aqueous solutions at room temperature.

RESULTS AND DISCUSSION

2,4-Dinitro-1-naphthol was isolated as a canary yellow, crystalline solid, which, after sublimation, melted sharply: mp 138-139° C, dec. 139° C, lit. mp 138° C (Davis, 1922). Mixed melting points with

commercially available material (Eastman Kodak P5168) occurred at 138 - 139° C. A potentiometric titration of sublimed 2,4-dinitro-1-naphthol with aqueous sodium hydroxide (0.1182 *N* with rel. std. dev. 0.055%, 6 trials), yielded a typical titration curve of a weak acid indicating only one acidic group in the molecule: neut. equiv. 236.5; theor. 234.2. Anal. calcd. for $C_{10}H_6N_2O_5$: C, 51.29; H, 2.58; N, 11.96; O, 34.16. Found: C, 51.36; H, 2.70; N, 12.11; O (difference), 33.83.

The characteristics of the ultraviolet spectra of 2-nitroso-1-naphthol-4-sulfonic acid and 2,4-dinitro-1-naphthol are presented in Table 1. The progress of a reaction, where 2,4-dinitro-1-naphthol is formed from 2-nitroso-1-naphthol-4-sulfonic acid, can be followed by a decrease in absorbance at 249 and 261 $m\mu$, and by an increase in absorbance at 299 $m\mu$.

In order to determine the conditions under which this system could be adapted to the determination of nitrate, it was necessary to study the effects of acid concentration, temperature, and time on the chemical system. The conditions for the prepara-

tion of 2-nitroso-1-naphthol-4-sulfonic acid indicated the compound was stable in hot, acidic, aqueous solutions for a considerable period of time. However, it was soon observed that the acid concentrations necessary for a reaction between low concentrations of nitrate and 2-nitroso-1-naphthol-4-sulfonic acid caused partial decomposition of the latter. The exact conditions of stability were made the focus of attention.

The effect of temperature on the stability of 2-nitroso-1-naphthol-4-sulfonic acid (2.50×10^{-4} *M*) in 2.90 *M* perchloric acid and heated for 35 minutes, is presented in Figure 1.

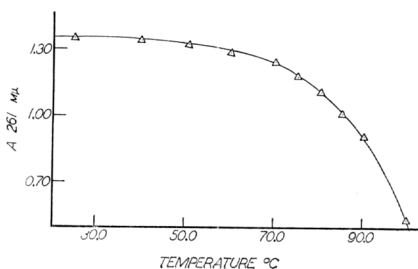


FIGURE 1. — The stability of 2-nitroso-1-naphthol-4-sulfonic acid (2.50×10^{-4} *M*) as a function of temperature when heated in 2.90 *M* perchloric acid for 35 minutes.

TABLE 1. — Ultraviolet absorption spectra

2-Nitroso-1-naphthol 4-sulfonic Acid				2,4-Dinitro-1-naphthol		2-Nitro-1-naphthol 4-sulfonic Acid	
Exp.		Lit. ¹		Exp.		Exp.	
λ_{max} (mμ)	ϵ	λ_{max} (mμ)	ϵ^2	λ_{max} (mμ)	ϵ^3	λ_{max} (mμ)	ϵ^3
261	27,000	261	26,385	210	22,400	221	38,700
347	5,000	347	4,451	249	16,800	270	21,300
				299	12,300	295	9,610
				375	8,450	387	5,280

¹ (Caskey, 1962).

² From slopes of Beer's law plots.

³ From slopes of Beer's law plots, calculated via IBM 1620 computer from the original data.

The absorbance decrease at 261 $m\mu$ became significant at 60° C, indicating significant decomposition of 2-nitroso-1-naphthol-4-sulfonic acid occurred. In 2.90 M perchloric acid the temperature must be no higher than 50° C, to insure stability of 2-nitroso-1-naphthol-4-sulfonic acid.

The stability of 2-nitroso-1-naphthol-4-sulfonic acid ($[1.72 \text{ to } 2.50] \times 10^{-4} M$) as a function of perchloric acid concentration at 50.5° C, and heated for 35 minutes, is presented in Figure 2. The slight negative slope indicated that the increasing concen-

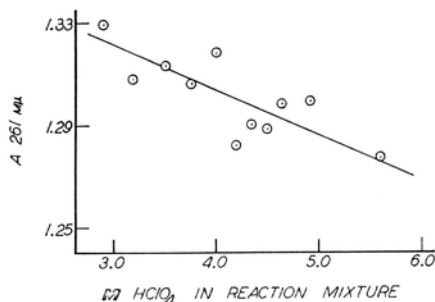


FIGURE 2. — The stability of 2-nitroso-1-naphthol-4-sulfonic acid ($[1.72 \text{ to } 2.50] \times 10^{-4} M$) as a function of perchloric acid concentration at 50.5° C when heated for 35 minutes.

tration of perchloric acid caused only a slight increase in decomposition of 2-nitroso-1-naphthol-4-sulfonic acid. A concentration of 5.0 - 6.0 M perchloric acid caused less than a 3% decrease in absorbance. In a similar study conducted at 90° C, in which the solutions were heated for 1 hr, $1.537 \times 10^{-3} M$ 2-nitroso-1-naphthol-4-sulfonic acid was shown to decompose significantly in 0.5 M or more concentrated perchloric acid solutions; very little decomposition was observed when the acid concentration was less than 0.1 M .

The stability of 2-nitroso-1-naphthol-4-sulfonic acid ($1.92 \times 10^{-4} M$) as a function of time of heating in 4.91 M perchloric acid at 50.5° C is presented in Figure 3. Little or no

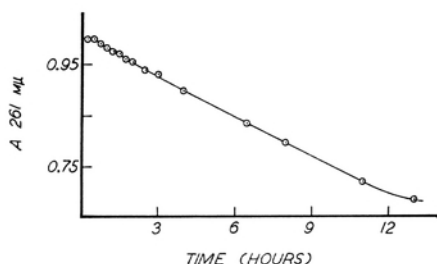


FIGURE 3. — The stability of 2-nitroso-1-naphthol-4-sulfonic acid ($1.92 \times 10^{-4} M$) as a function of time of heating at 50.5° C, in 4.91 M perchloric acid.

decomposition occurred during the first 30 minutes, but during the first hour it was about 2% and during the first two hours it was 5%. Longer heating periods led to further decomposition. In a similar study conducted with $1.537 \times 10^{-3} M$ 2-nitroso-1-naphthol-4-sulfonic acid in 2.49 M perchloric acid at 94° C, significant decomposition occurred rapidly and amounted to more than 50% after a five minute period of heating.

The nitration reaction was studied using concentrations of sodium nitrate in a one-hundred fold, or greater, mole excess in respect to the concentration of 2-nitroso-1-naphthol-4-sulfonic acid. The conditions of the other variables were similar to those previously employed in the stability studies. No significant formation of 2,4-dinitro-1-naphthol was observed in 2.90 M perchloric acid when $2.50 \times 10^{-4} M$ 2-nitroso-1-naphthol-4-sulfonic acid and $2.50 \times 10^{-2} M$ NaNO_3 were heated for 35 minutes at temperatures as high as 90° C; the

data, when plotted, yielded a curve almost identical to that of Figure 1. Hence a higher acid concentration or a higher temperature was needed.

The effect of the perchloric acid concentration on the formation of 2,4-dinitro-1-naphthol at 50.5° C is presented in Figure 4, and was studied using solutions containing (1.72

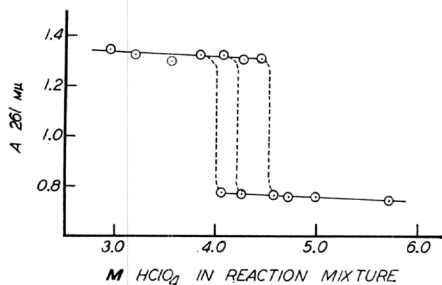


FIGURE 4.—The stability and formation of 2,4-dinitro-1-naphthol, as a function of perchloric acid concentration. The solutions contained $(1.72 \text{ to } 2.50) \times 10^{-4} \text{ M}$ 2-nitroso-1-naphthol-4-sulfonic acid and exactly a 100 fold greater concentration of sodium nitrate, respectively, and were heated for 35 minutes at 50.5° C.

to 2.50) $\times 10^{-4} \text{ M}$ 2-nitroso-1-naphthol-4-sulfonic acid with exactly a one-hundred fold greater concentration of sodium nitrate, respectively, and heated for 35 minutes. It can be seen that although nitration sometimes occurred in 4.0 - 4.5 M perchloric acid, concentrations greater than 4.5 M were required to insure nitration. The slight decrease in slope of the solid lines was perhaps due to a slight decomposition of 2-nitroso-1-naphthol-4-sulfonic acid.

The effect of time on the formation and stability of 2,4-dinitro-1-naphthol in 4.91 M perchloric acid at 50.5° C is presented in Figure 5. Inasmuch as the absorbance at 261 $\text{m}\mu$ reached a minimum value (the concentration

of 2-nitroso-1-naphthol-4-sulfonic acid had reached a minimum value) and the absorbance at 299 $\text{m}\mu$ had reached a maximum value (the concentration of 2,4-dinitro-1-naphthol had reached a maximum value), the nitration was complete within 35 minutes. It was evident that once the maximum concentration of 2,4-dinitro-1-naphthol was formed, it was essentially independent of time. In a similar experiment using $1.537 \times 10^{-4} \text{ M}$ 2-nitroso-1-naphthol-4-sulfonic acid and $2.50 \times 10^{-2} \text{ M}$ sodium nitrate in 2.49 M perchloric acid at 94° C, the absorbance at 249 $\text{m}\mu$ reached a minimum, constant value after 25 minutes, indicating the nitration was complete within 25 minutes, and the product, 2,4-dinitro-1-naphthol was stable in the hot perchloric acid.

The system was studied as a function of nitrate concentration. The pertinent data is presented in Figure 6. When a reaction was observed not to occur in 4.91 M perchloric acid, a higher concentration of perchloric acid, 8.44 M , at 50.5° C was found, by trial and error, to cause a reaction to occur between 2-nitroso-1-naphthol-4-sulfonic acid and sodium nitrate in a series of solutions containing $7.14 \times 10^{-4} \text{ M}$ 2-nitroso-1-naphthol-4-sulfonic acid and varying concentrations of nitrate (less than $7.14 \times 10^{-4} \text{ M}$ sodium nitrate) during the heating period of 45 minutes. A higher concentration of perchloric acid was examined since it had been shown (see Figure 2) to have a smaller effect on the stability of 2-nitroso-1-naphthol-4-sulfonic acid than did longer heating periods or higher temperatures. The absorbance values at 261 and 221 $\text{m}\mu$ for the

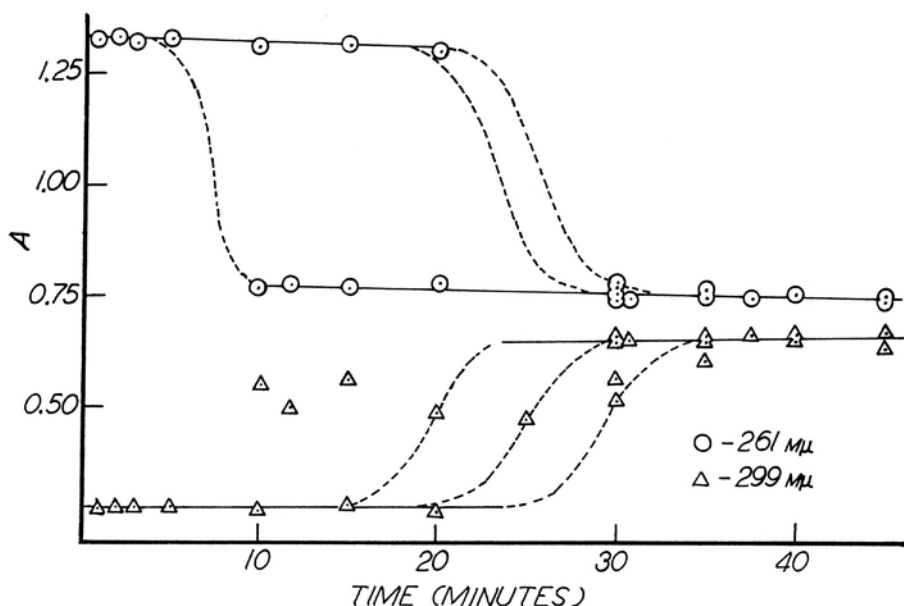


FIGURE 5.—The stability and formation of 2,4-dinitro-1-naphthol as a function of time at 50° C in 4.91 *M* perchloric acid. The solutions contained 1.92×10^{-4} *M* 2-nitroso-1-naphthol-4-sulfonic acid and 1.92×10^{-2} *M* sodium nitrate.

diluted solutions (plotted as a function of the nitrate concentration in them) gave a linear relationship between 0.3 and 13 ppm nitrate (as N). This study was reproduced in a second similar study.

The spectra of the solutions used to obtain the information presented

in Figure 6 indicated that the product of the nitration reaction was not the expected product, 2,4-dinitro-1-naphthol. The new product did not form a complex with cobalt, indicating that the 2-nitroso-1-naphthol functional groups had been affected in some manner. It was noted that both the new nitration product and 2,4-dinitro-1-naphthol had an absorption maximum near 300 $m\mu$. It was also noted that 2-nitro-1-naphthol had been reported by Edwards and Tate (1951) to have an absorption at 270 $m\mu$ with a molar absorptivity of 16,700 in ethanol. The new product had an absorption at 270 $m\mu$ with a molar absorptivity of 21,300. It seemed reasonable to expect that the new product was an isolable intermediate for the formation of 2,4-dinitro-1-naphthol containing only one

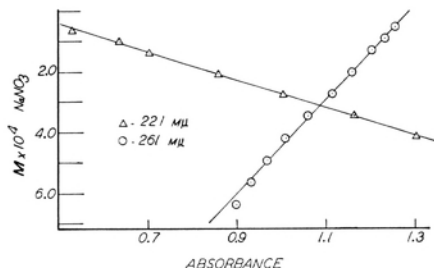


FIGURE 6.—The absorbance of 2-nitro-1-naphthol-4-sulfonic acid as a function of nitrate concentration in 8.44 *M* perchloric acid after heating at 50.5° C for 45 minutes.

nitro group, and the product might be 2-nitro-1-naphthol-4-sulfonic acid.

Using a procedure similar to that described by Emmons and Ferris (1953), 2-nitro-1-naphthol-4-sulfonic acid was successfully prepared from 2-nitroso-1-naphthol-4-sulfonic acid using hydrogen peroxide dissolved in trifluoroacetic acid. Although characterization of 2-nitro-1-naphthol-4-sulfonic acid has not been reported, Witt and Schneider (1901) have reported the partial characterization of several monovalent and bivalent metal salts of 2-nitro-1-naphthol-4-sulfonic acid. The crude product was successfully recrystallized from water as the monopotassium salt. The characteristics of the ultraviolet spectrum are presented in Table 1 and the infrared spectrum in Figure 7. The recrystallized potassium 2-nitro-1-naphthol-4-sulfonate was titrated with aqueous sodium hydroxide (0.1176 N, with rel. std. dev. 0.063%, 5 trials) yielding a typical titration curve of a weak acid indicating only one weak acidic group in the molecule: neut. equiv. 328.8; theor., 325.3; pKa, 4.8; Anal. calcd. for

$C_{10}H_6NO_6SK$: C, 39.08; H, 1.97; N, 4.56; S, 10.43; K, 12.72; O, 31.24. Found: C, 39.43; H, 2.10; N, 4.54, 4.71; S, 10.21; K, 12.52; O, (difference), 31.11. Anal. calcd. for $C_{10}H_6NO_6SK \cdot H_2O \cdot H_2O$, 5.53. Found: H_2O , 5.96, 6.02.

The ultraviolet spectrum of potassium 2-nitro-1-naphthol-4-sulfonate was identical with the spectra obtained from nitration systems where the molar ratio of sodium nitrate to 2-nitroso-1-naphthol-4-sulfonic acid was 1:1. This evidence indicated that the product formed in hot aqueous perchloric acid by the reaction of sodium nitrate with an equivalent, or greater, concentration of 2-nitroso-1-naphthol-4-sulfonic acid was 2-nitro-1-naphthol-4-sulfonic acid. The evidence also indicated that the latter compound was an intermediate in the formation of 2,4-dinitro-1-naphthol from 2-nitroso-1-naphthol-4-sulfonic acid. The apparent random location of some data points in Figures 4 and 5 can also be accounted for in terms of the intermediate formation of 2-nitro-1-naphthol-4-sulfonic acid.

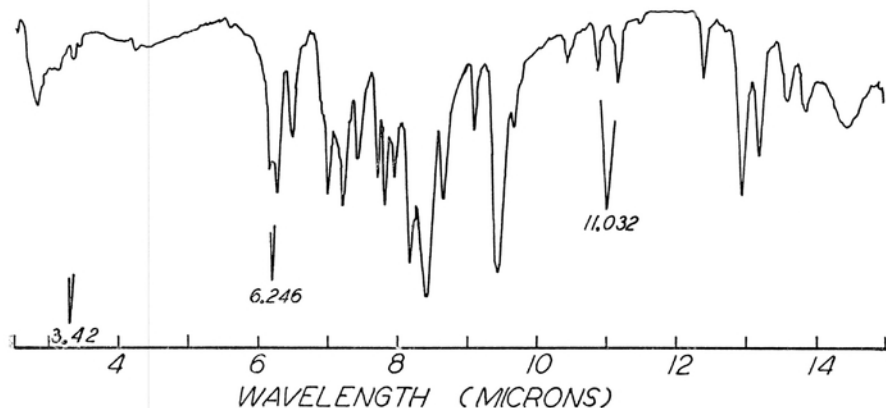


FIGURE 7.—Infrared spectrum of potassium 2-nitro-1-naphthol-4-sulfonate (potassium bromide pellet).

SUMMARY

The stability of the analytical chemical reagent, 2-nitroso-1-naphthol-4-sulfonic acid, has been studied as a function of temperature, length of time of heating, and perchloric acid concentration. It does not significantly decompose when heated for less than 2 hours, in concentrations of perchloric acid less than 4.9 *M*, and temperatures less than 50° C.

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 has been 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 has been isolated, characterized, and clearly reaffirmed to exist as a monohydrate.

Excess 2-nitroso-1-naphthol-4-sulfonic acid reacts with nitrate ion in 8.44 *M* 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 of 2-nitro-1-naphthol-4-sulfonic acid have been shown to be linearly dependent upon the amount of nitrate present. Beer's law is obeyed over a range of 0.3 - 13 ppm nitrate (as N) under the conditions of absorbance measurement.

Preliminary information has been presented which will serve as the basis for the development of a method for the determination of nitrate.

The development of a new method for nitrate determinations can be accomplished by delimiting the ideal conditions for the formation of 2-nitro-1-naphthol-4-sulfonic acid. Kirkbright (1966) has outlined and discussed extensively the additional factors which need consideration in the development of new spectrophotometric methods. These factors are under examination in this laboratory and attempts are being made to extend the concentration limits for the determination of nitrate in water.

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