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

by

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2-Nitroso-1-naphthol-4-sulfonic acid reacts quantitatively in a few minutes with excess nitrate in a dilute, acidic, aqueous medium to form 2,4-dinitro-1-naphthol. The work reported here concerns the determination of conditions under which nitrate reacts quantitatively with an excess of standard 2-nitroso-1-naphthol-4-sulfonic acid. The establishment of such a set of conditions indicates the feasibility of developing a spectrophotometric method for the determination of nitrate based on its reaction with 2-nitroso-1-naphthol-4-sulfonic acid.

In the presence of considerable perchloric acid, nitrate and 2-nitroso-1-naphthol-4-sulfonic acid mixed in a 2:1 mole ratio reacted at 50° C. in 45 minutes to form 2,4-dinitro-1-naphthol. When they were mixed in a 1:1 mole ratio and treated under stronger conditions they reacted to form a mono-nitrated naphthol. When they were mixed in a mole ratio less than 1:1 and treated in an appropriate manner, absorbance data on the reaction mixture indicated the system obeyed Beer's law at both a wavelength maximum of the product and a wavelength maximum of 2-nitroso-1-naphthol-4-sulfonic acid. Beer's law was obeyed between 0.3 and 3 p. p. nitrate under the conditions of measurement of the absorbance.

## EXPERIMENTAL

### Reagents

Reagent grade chemicals meeting American Chemical Society specifications were used whenever they were commercially available. All other chemicals were of the highest grade available.

The 2-nitroso-1-naphthol-4-sulfonic acid was prepared by nitrosolation of 1-naphthol-4-sulfonic acid. The product was purified by absorption of

impurities on activated charcoal and by recrystallization from dilute hydrochloric acid.

Standard solutions of nitrate were prepared by weight from sodium nitrate.

#### Equipment

A Corning Model 12 pH meter, equipped with a general use glass electrode and a fiber type, saturated calomel electrode, was used. The electrode system was calibrated using National Bureau of Standards standard buffers (1).

Beckman Model DB and DK-IA recording spectrophotometers and a Cary Recording Spectrophotometer, Model 11, were used for the absorbance measurements, along with matched, silica absorption cells.

A Perkin Elmer Infracord was used to determine infrared spectra. Both nujol mulls and potassium bromide pellets were used.

A constant temperature bath equipped with a Precision Scientific Co. Porta-temp regulator was used. It was adjustable from room temperature to 95° C. and could be controlled  $\pm 0.5^\circ$  C.

#### Procedures

The procedure used for the reaction of 2-nitroso-1-naphthol-4-sulfonic acid with nitrate under quantitative conditions was quite simple. A volume of a standard solution of 2-nitroso-1-naphthol-4-sulfonic acid was transferred to a 100 ml. volumetric flask to which was then added an appropriate volume of concentrated (about 71%) perchloric acid. The flask was placed in the temperature bath for about 15 minutes and then an appropriate volume of standard sodium nitrate was added to the flask. After a period of heating, the flask was removed from the bath and the reaction mixture treated with ice cold deionized water and diluted to volume. Absorbance measurements were made against deionized water blanks. The length of time of the reaction was measured over the period between the addition of the

nitrate and the quenching of the reaction by the addition of ice water. Some times the order of addition of the nitrate solution and the perchloric acid was reversed.

#### 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% theoretical; m.p. 134-136.5°C., dec. 136.5°C.

This crude product was purified by dissolving it in dilute sodium hydroxide solution which was washed with ether. The aqueous solution was acidified with  $H_3PO_4$  and the product extracted into ether and the latter then evaporated to dryness. After recrystallization from three solvents, benzene, chloroform, and absolute ethanol, the solid was sublimed under vacuum at 100°C.

#### RESULTS AND DISCUSSION

2,4-Dinitro-1-naphthol was isolated as a canary yellow, crystalline solid, which after sublimation melted sharply: m.p. 138-139° C., dec. at 139° C.; lit. m.p. 138° C. (2). It was found that a portion from a given preparation would melt with decomposition while another portion, treated identically would melt without decomposition. This effect was not correlatable to solvent, crystal form or melting technique. Mixed melting points with commercially available material occurred at 138-139° C.

A potentiometric titration with aqueous NaOH of the sublimed crystals of 2,4-dinitro-1-naphthol in about 70% v/v ethanol yielded a typical titration curve of a weak acid and indicated only one acidic group in the molecule: neutralization equivalent, 235.3; theor. 234.2.

The infrared spectra of 2,4-dinitro-1-naphthol differed from that of 2-nitroso-1-naphthol-4-sulfonic acid. In the spectrum of the former but not in the spectrum of the latter, there were two pairs of sharp, strong peaks in the 6-7  $\mu$  region often credited to nitro absorption. The peaks in the 8-10  $\mu$  region often credited to the sulfonic acid functional group were present in the spectrum of the latter but were absent in the spectrum of the former.

The characteristics of the ultraviolet-visible spectra of 2-nitroso-1-naphthol-4-sulfonic acid, 2,4-dinitro-1-naphthol and the mono-nitro product obtained are shown in Table I. The spectrum of 2-nitroso-1-naphthol-4-

Table I. Ultraviolet-visible Absorption Spectra

2-Nitroso-1-naphthol-4-sulfonic acid		2,4-Dinitro-1-naphthol		Mononitroproduct-Unknown structure	
max. (m )		max. (m )		max. (m )	
261	26,385	211.5	19,200	220.5	36,000
347	4,451	252	14,500	270	19,000
		300	9,900	297	8,800
		375	6,980	384	5,800

sulfonic acid is the simplest one. The ultraviolet absorption by 2,4-dinitro-1-naphthol is less intense, while that of the mononitro product is more intense, than that of 2-nitroso-1-naphthol-4-sulfonic acid. It is to be noted that both of the nitro compounds have an absorption maximum near 300 m. It is also to be noted that 2-nitro-1-naphthol has been reported (3) to have an absorption at 270 m with a molar absorptivity of 16700.

Although it was known from the conditions under which it was prepared that 2-nitroso-1-naphthol-4-sulfonic acid was stable in a hot, acidic, aqueous solution for a considerable period of time, the conditions of the stability had not been delimited, which therefore were made the focus of attention. The effect of acid concentration was studied first and is shown in Table II. 2-Nitroso-1-naphthol-4-sulfonic acid was shown to decompose in 0.1 M  $\text{HClO}_4$  at 90°C., but was shown to be stable in concentrations of at least 5.72 M  $\text{HClO}_4$ , the upper limit of the study, at 50°C.

The effect of the temperature of heating on the stability of 2-nitroso-1-naphthol-4-sulfonic acid is shown in Table III. The solutions were prepared from 10.00 ml.  $5.00 \times 10^{-4}$  M 2-nitroso-1-naphthol-4-sulfonic acid, 5.00 ml. deionized water and 5.00 ml. concentrated  $\text{HClO}_4$  and were heated for 35 minutes. The solutions were 3.34 M in  $\text{HClO}_4$  during the heating process. The decrease of the absorbance values taken at the wavelength maximum using 1,000 cm. cells showed that at temperatures of 70° C. or greater a significant decomposition of 2-nitroso-1-naphthol-4-sulfonic acid occurred. The system seems stable up to and including temperatures of 50° C.

The effect of the length of time of heating 2-nitroso-1-naphthol-4-sulfonic acid in 5.00 M  $\text{HClO}_4$  at 50°C. is shown in Table IV. The absorbance at 261  $\text{m}\mu$ , measured in 1,000 cm. cells, on solutions prepared from 10.00 ml. aliquots of a solution prepared from 100.0 ml.  $5.00 \times 10^{-4}$  M 2-nitroso-1-naphthol-4-sulfonic acid, 50.0 ml. deionized water and 110.0 ml. concentrated  $\text{HClO}_4$ , and then diluted to 50.0 ml., decreased only about 2% during the first hour of heating and only 5% during the first two hours of heating. Longer periods of heating lead to considerable decomposition.

Table II. Effect of acid concentration on 2-nitroso-1-naphthol-4-sulfonic acid

$\underline{M}$ $\text{HClO}_4$	Study at 90°C. <sup>a</sup> A at 261 m	Study at 50°C. <sup>b</sup> A at 261 m $\mu$
0.00025	1.636	
0.00050	1.636	
0.0025	1.636	
0.0050	1.630	
0.025	1.592	
0.050	1.542	
0.25	1.578	
0.50	1.404	
2.5	0.575	
2.90		1.329
3.10		1.308
3.57		1.313
4.07		1.318
4.27		1.282
4.43		1.290
4.58		1.288
4.72		1.298
4.99		1.299
5.00	0.501	
5.72		1.277

<sup>a</sup>Prepared from 10.00 ml.  $3.07 \times 10^{-4}$   $\underline{M}$  2-nitroso-1-naphthol-4-sulfonic acid, deionized water as needed, and concentrated  $\text{HClO}_4$ , and heated 60 minutes. 2.000 cells.

<sup>b</sup>Prepared from 10.00 ml.  $5.00 \times 10^{-4}$   $\underline{M}$  2-nitroso-1-naphthol-4-sulfonic acid, 5.00 ml. deionized water, and concentrated  $\text{HClO}_4$ , and heated 35 minutes. Absorbance 1.328 without heating. 1.000 cells.

Table III. The effect of temperature on heating acidic solutions of 2-nitroso-1-naphthol-4-sulfonic acid

Temperature °C.	A at 261 m $\mu$
25	1.345
40	1.333
50	1.330
60	1.290
70	1.250
75	1.183
80	1.054
85	0.949
90	0.913
95	0.527

Inasmuch as the ability to chelate cobalt (II) is lost during the acid hydrolysis of 2-nitroso-1-naphthol-4-sulfonic acid, it is reasonable to believe that the nitroso functional group has been hydrolyzed from the molecule. The product of the hydrolysis might be 1,2-naphthoquinone-4-sulfonic acid, but the identification of the product has not been attained.

It was now possible to adjust the conditions for a quantitative reaction between nitrate and 2-nitroso-1-naphthol-4-sulfonic acid such that there was a negligible amount of decomposition of the latter. A change in the amount of 2-nitroso-1-naphthol-4-sulfonic acid was therefore related to its reaction with nitrate. A nitrate concentration one hundred fold larger than the concentration of 2-nitroso-1-naphthol-4-sulfonic acid was selected for use as



Table IV. Effect of time on the acid decomposition of 2-nitroso-1-naphthol-4-sulfonic acid

A at 261 m $\mu$	Time (hours)
1.000	0.25
1.000	0.50
0.990	0.75
0.987	1.00
0.975	1.25
0.970	1.50
0.960	1.75
0.954	2.00
0.939	2.50
0.927	3.00
0.898	4.00
0.835	6.50
0.796	8.00
0.719	11.00
0.683	13.00

were a time interval of 35 minutes and a temperature of 50°C., which were considered as at least the initial optimum values for these variables. It seems most prudent to determine initially the effect of the  $\text{HClO}_4$  concentration on the nitration reaction, since this variable of the three variables had the least effect on the stability of 2-nitroso-1-naphthol-4-sulfonic acid.

The effect of the concentration of  $\text{HClO}_4$  on the reaction between excess nitrate and 2-nitroso-1-naphthol-4-sulfonic acid is shown in Figure 1. The solutions were prepared from 10.00 ml.  $5.00 \times 10^{-4}$  M 2-nitroso-1-naphthol-4-sulfonic acid, 5.00 ml. 0.100 M  $\text{NaNO}_3$ , and amounts of concentrated  $\text{HClO}_4$  ranging between 5.00 ml. and 14.00 ml., and were heated for 35 minutes at 50° C. The decrease in the absorbance values taken at the wavelength maximum, 261 m $\mu$ , using 1.000 cm. cells showed that an acid concentration less than 4.0 M will not cause a reaction to occur. An acid concentration of 5.0 M is clearly in the range of concentrations which consistently cause the nitration reaction to occur.

The effect of the length of time of heating the nitration reaction mixture in 5.0 M  $\text{HClO}_4$  at 50° C. is shown in Figure 2. The solutions were prepared from 10.00 ml.  $5.00 \times 10^{-4}$  M 2-nitroso-1-naphthol-4-sulfonic acid, 5.00 ml. 0.100 M  $\text{NaNO}_3$ , and 11.00 ml. concentrated  $\text{HClO}_4$  and were heated for various time intervals. The increase in absorbance at 300 m $\mu$ , and the decrease in the absorbance at 261 m $\mu$  showed that the time interval of 45 minutes was sufficient for a complete reaction to occur in the system. The absorbance values reported were taken in 1.000 cm. cells.

The product of the nitration reaction was readily shown to be stable. The effect of the length of time of heating 2,4-dinitro-1-naphthol in 2.50 M  $\text{HClO}_4$  is shown in Table V. The solutions were prepared from 10.00 ml.

Table V. Effect of time on the stability of 2,4-dinitro-1-naphthol in hot aqueous acid

A at 300 $\text{m}\mu$	Time (Minutes)
0.361	7
0.378	10
0.366	15
0.357	20
0.348	25
0.351	31
0.349	35
0.349	40
0.350	45
0.354	50

$3.703 \times 10^{-4}$  M 2-nitroso-1-naphthol-4-sulfonic acid, 5.00 ml. 0.100 M  $\text{NaNO}_3$ , and 5.00 ml. 10.0 M  $\text{HClO}_4$ , and were heated at  $94^\circ\text{C}$ . for the indicated time intervals. The absorbance values taken at the wavelength maximum at 300  $\text{m}\mu$  using 1.000 cm. cells showed that no significant decomposition of 2,4-dinitro-1-naphthol occurred in 50 minutes. This evidence is also supported by the linear regions in Figures 1 and 2.

Attempts were made to obtain Beer's law data by varying the nitrate concentration while maintaining an excess of 2-nitroso-1-naphthol-4-sulfonic acid in the systems, and utilizing 5.00 M  $\text{HClO}_4$  with a heating time of 45

minutes at 50°C. All of these attempts failed to cause any nitration to occur.

It was then decided to use more rigorous conditions. The solutions were prepared from 1.00 ml.  $5.00 \times 10^{-3}$  M 2-nitroso-1-naphthol-4-sulfonic acid, 1.00 ml.  $\text{NaNO}_3$  solution, and 5.00 ml. concentrated  $\text{HClO}_4$  and were heated for 45 minutes at 50°C. The concentration of the nitrate solutions ranged from  $5.00 \times 10^{-4}$  M  $\text{NaNO}_3$  to  $3.00 \times 10^{-3}$  M  $\text{NaNO}_3$ . The solutions were 8.44 M in  $\text{HClO}_4$  during the heating process. The decrease and increase of the absorbance values taken 261 and 220.5 m $\mu$  using 1.000 cm. cells showed that the system obeyed Beer's law and that the absorbance of any individual solution could be related to the concentration of nitrate in the original 1.00 ml. sample taken. These results were reproduced. Plots of the data are shown in Figure 3.

The product obtained in the nitration reactions run in the presence of excess 2-nitroso-1-naphthol-4-sulfonic acid does not have the ability to chelate with cobalt(II) ions. This evidence, along with the similarity of its spectrum to that of 2-nitro-1-naphthol, tends to indicate that it is 2-nitro-1-naphthol-4-sulfonic acid. The latter compound is mentioned and then briefly in only one reference in the chemical literature, which indicates no obvious way of characterizing the observed product.

The data in Figures 1 and 2 exhibits considerable scattering in the regions that lie between no reaction and complete reaction. Perhaps this scattering of the data is due to catalysis of the nitration reaction in certain instances. Some evidence was obtained that the reaction forming 2,4-dinitro-1-naphthol might be autocatalytic.

It can be concluded that it is feasible to develop a method for the spectrophotometric determination of nitrate utilizing 2-nitroso-1-naphthol-4-sulfonic acid.

This project has been completed as outlined in the proposal of research.

LITERATURE CITED

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- (2) Davis, T. L., J. Am. Chem. Soc. 44, 1588 (1922).
- (3) Edwards, W. R. Jr., and Tate, C. W., Anal. Chem. 23, 826 (1951).

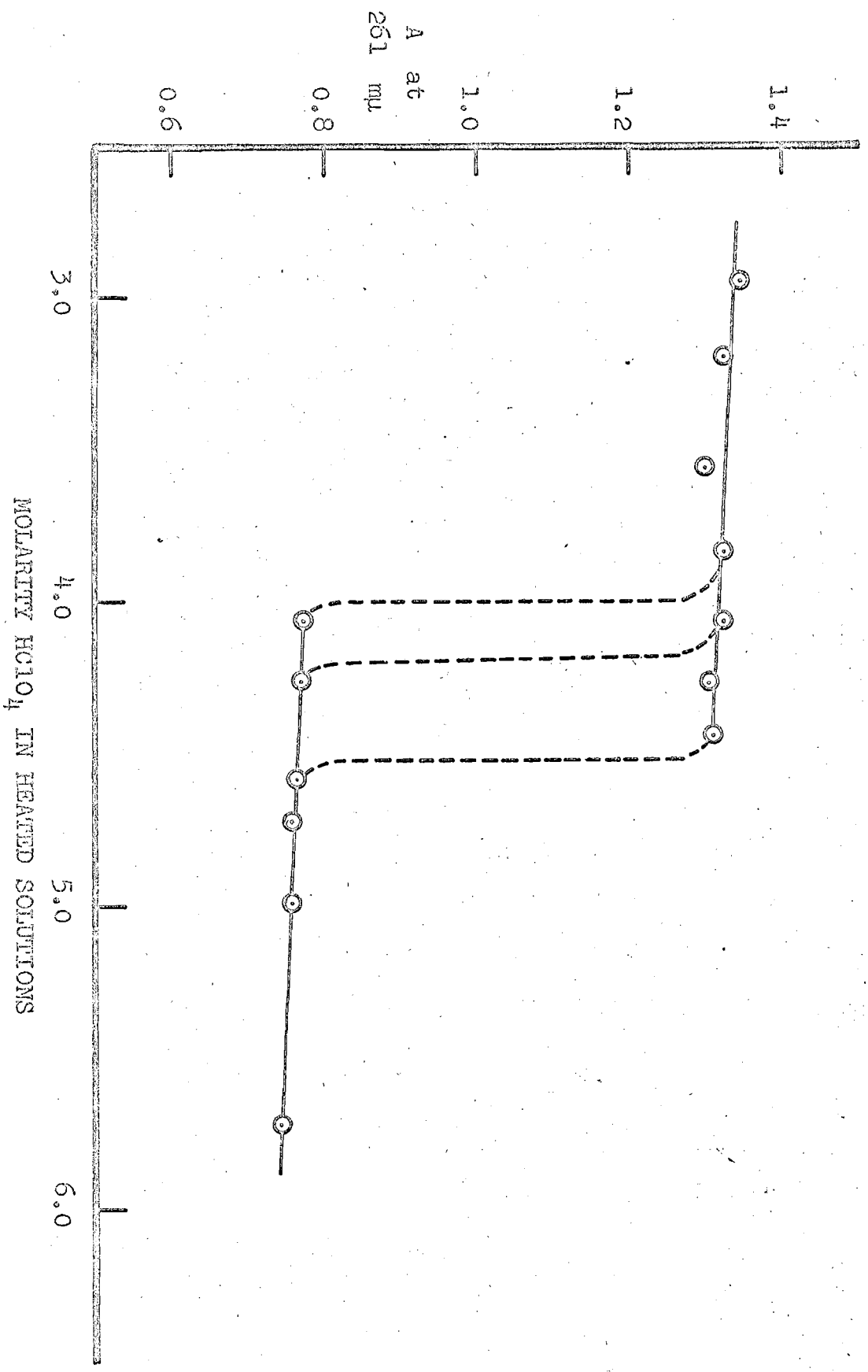


FIGURE 1. THE EFFECT OF THE CONCENTRATION OF  $\text{HClO}_4$  ON THE REACTION BETWEEN EXCESS NITRATE AND 2-NITROSO-1-NAPHTHOL-4-SULFONIC ACID

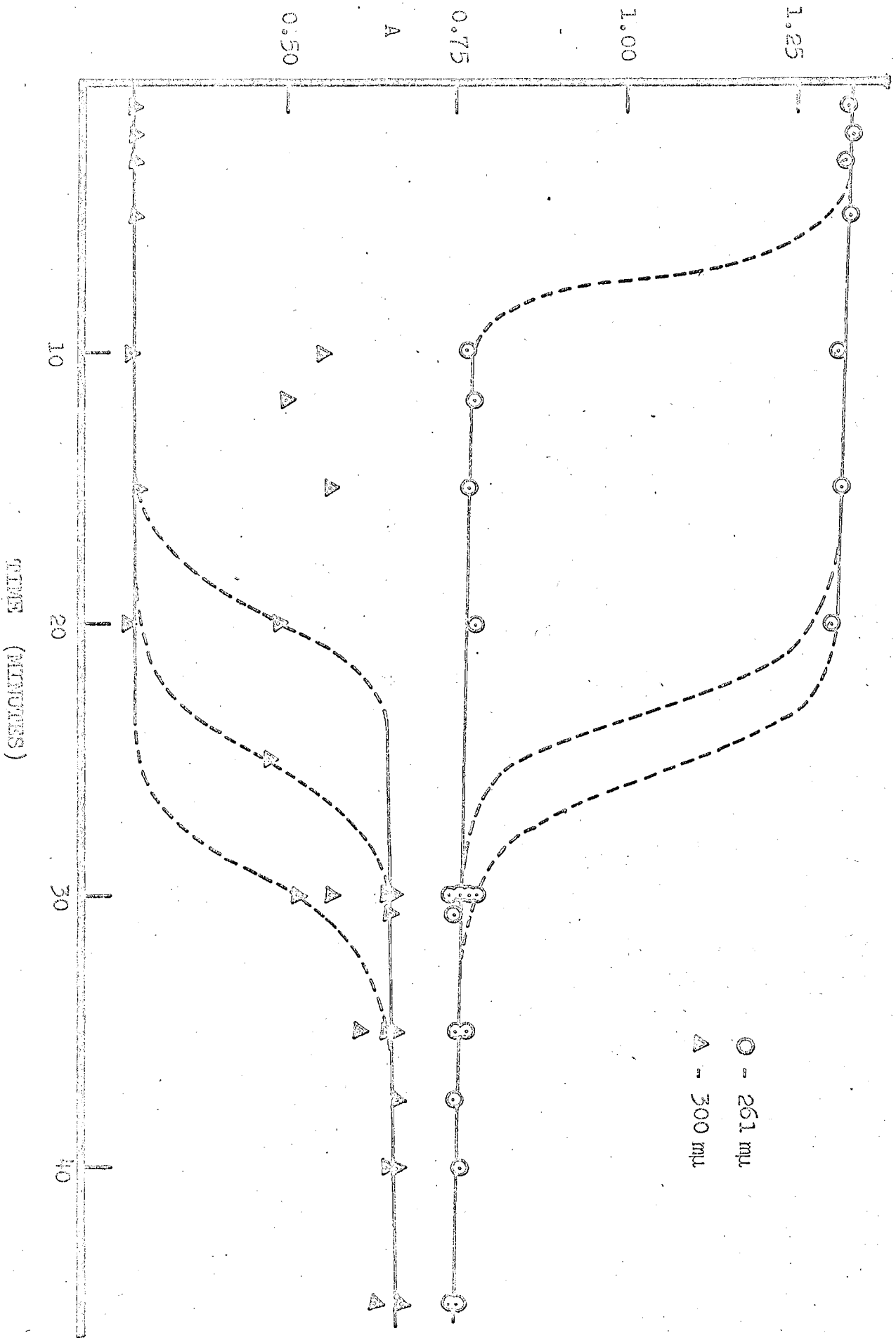


FIGURE 2. THE EFFECT OF THE LENGTH OF TIME OF HEATING THE NITRATION MIXTURE

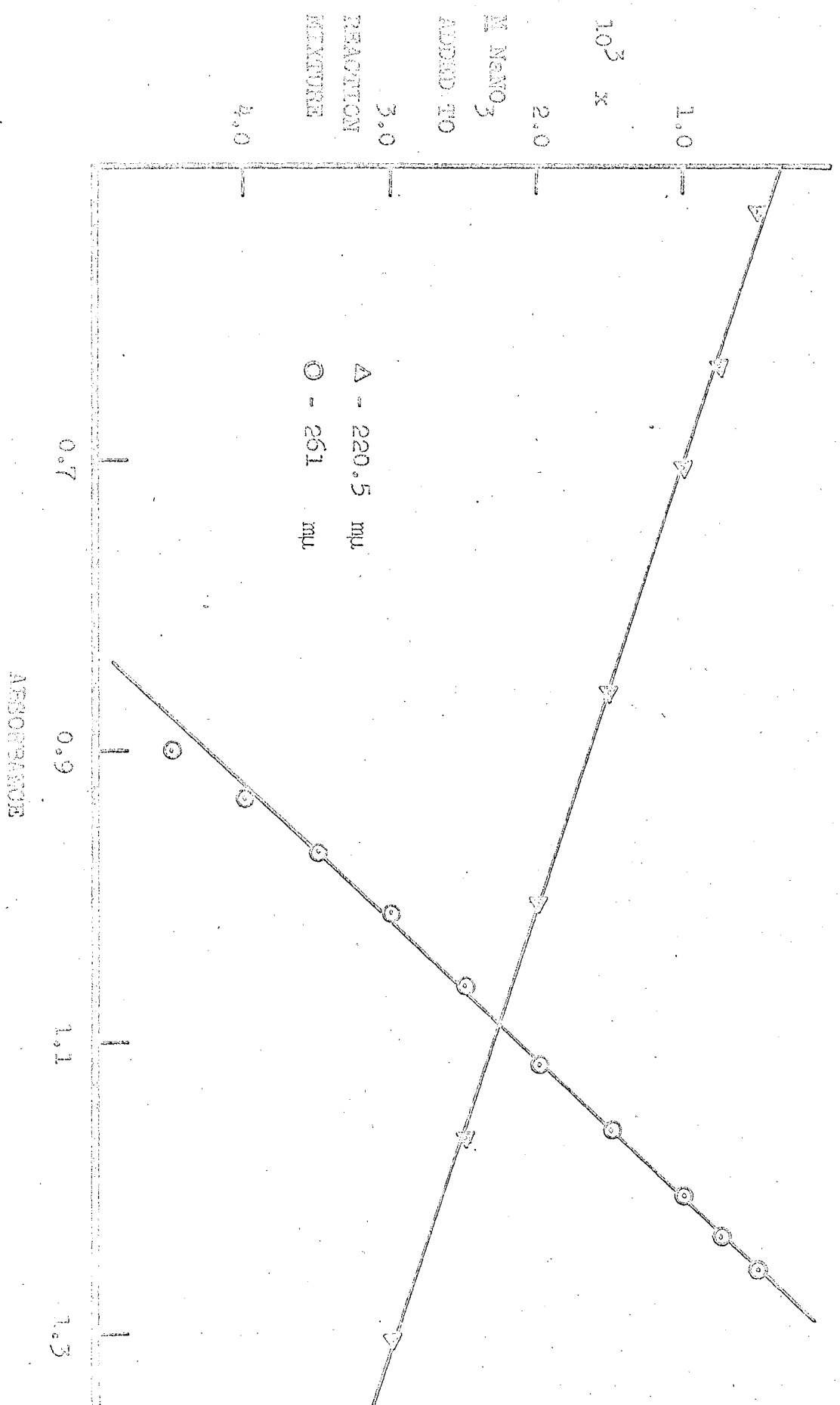


FIGURE 3. DERRIS TAM PLOT. NITRATE CONCENTRATION