conditions concerned in studies involving the vitamin B complex. Assay results for one of the known entities of the vitamin B complex, without knowledge of the relative amount of the other entities present under the particular conditions of assay, may be subject to wide variation and of questionable value, because of the influence of the amounts of the other entities present.

Simplification of the assay technique involving a simplified basal ration and the use of pure entities or proved substances as essential supplements will aid in the interpretation of results and extend their practical value.

While the subject of this paper has been presented primarily from the standpoint of the three known entities of the vitamin B complex, it is recognized that still other entities ultimately may be revealed. The data do not presume to present evidence in support of or as argument against the existence of factors other than those discussed. Any deductions of such character, based upon the evidence submitted, would be unwarranted, and in fact immaterial within the scope of these data. If other factors of the vitamin B complex exist and are of significance in influencing rate of growth or other conditions to which reference has been made in this paper, such a factor or factors are contained in the rice polish concentrate and have been operative in a comparable manner throughout the series of comparisons recorded. Invalidating and disconcerting contaminants are eliminated from this basal ration and obviously do not exist in the crystalline lactoflavin and crystalline vitamin B_1 supplements used.

Summary

A single simplified basal ration using sucrose as the carbohydrate may be employed, when properly supplemented, for the biological assay of vitamin B_1, lactoflavin (vitamin B_2 or G) and the vitamin B_6 or antidermatitis factor. Any one of these three factors may be detected, and its relative amount determined, by providing, as additional supplements to the basal ration, the other two factors, preferably at known quantitative levels.

The vitamin B_6 or antidermatitis factor may be assayed comparatively on the basis of the percentage incidence of the typical acrodynia type dermatitis by employing as additional supplements to the basal ration, pure and known amounts of lactoflavin and vitamin B_1.

Each of the three definitely established factors of the vitamin B complex affects growth rate to a readily distinguishable degree and, within limits, in proportion to the amount provided. However, the rate of growth as affected by the quantitative amount of any one of the three factors is significantly influenced by the amount of the other factors present.

BAINBRIDGE, N. Y. RECEIVED APRIL 12, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WELLESLEY COLLEGE]

A Study of the Tautomeric Equilibria of Nitrosonaphthol–Naphthoquinoneoxime Systems[1]

BY H. S. FRENCH AND D. J. PERKINS

A limited amount of work has been done to determine the structure of aromatic nitrosohydroxy compounds by means of both physical and chemical methods. The earlier work[2] led to conflicting conclusions. Within the last eight years a renewed interest is indicated.[3] The improved methods of investigation have been more fruitful of results. It seemed especially worthwhile to extend the method of absorption spectra determinations, as it was used by Anderson[3b,c] and his co-workers on nitrosophenols, to the three isomeric nitrosonaphthols. Similar studies have been done recently on the analogous benzeneazonaphthol–naphthoquinone hydrazone system.[4]

Scheibe and his co-workers have shown that the absorption bands characteristic of negatively polarized groups are shifted in the opposite direction from those of positively polarized groups when the solvent is changed from a polar to a non-polar

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(1) The material in this paper comprises a portion of a thesis presented by D. Jane Perkins to the Graduate Committee of Wellesley College in partial fulfilment of the requirements for the degree of Master of Arts, 1935.

(2) (a) Sluiter, *Rec. trav. chim.*, **25**, 8 (1906); *Ber.*, **44**, 1327 (1911); (b) Ilinski, *ibid.*, **17**, 2581 (1884); (c) Schmidt, *J. prakt. Chem.*, [2] **44**, 513 (1891); (d) Böniger, *Ber.*, **27**, 23, 3050 (1894).

(3) (a) Woroshtzow and Bogdanow, *ibid.*, **62B**, 68 (1929); (b) Anderson and Geiger, THIS JOURNAL, **54**, 3064 (1932); (c) Anderson and Yanke, *ibid.*, **56**, 732 (1934).

(4) (a) Burawoy and Markowitsch, *Ann.*, **503**, 180 (1933); *ibid.*, **504**, 71 (1933); Burawoy, *ibid.*, **509**, 60 (1934); (b) Kuhn and Bär, *ibid.*, **516**, 143 (1935).

liquid.[5] For example, in all compounds which contain the carbonyl group the point of maximum absorption is displaced slightly toward the red, and is lowered, with a change in solvent from alcohol to hexane. The opposite is true for hydroxy compounds. Scheibe's work thus introduces the possibility of classifying certain absorption bands as being caused by definite groups in a compound according to their change in position with change in solvent.

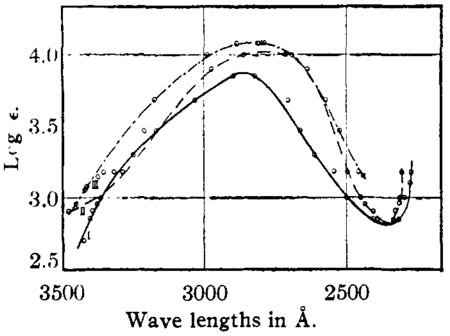

Fig. 1.—Nitrosobenzene: I in alcohol; II in cyclohexane; III in ether.

The following paper therefore falls into two parts. First, we extend the work of Scheibe, which was concerned chiefly with aliphatic compounds, to a similar study of the effect of solvent upon certain simple cyclic compounds. And, second, we apply the data from this preliminary study, together with data analogous to those used for nitrosophenols of the benzene series, to the study of the tautomerism of the nitrosonaphthols.

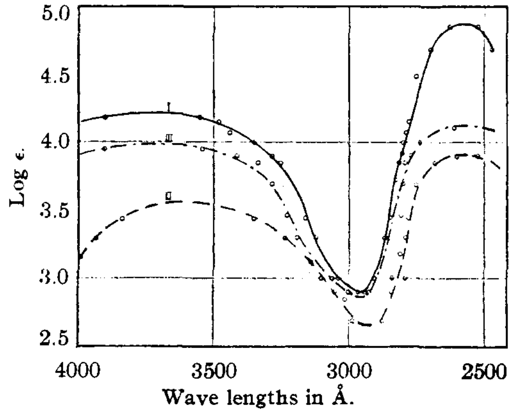

Fig. 2.—1-Nitrosonaphthalene: I in alcohol; II in cyclohexane; III in ether.

Effect of Solvent.—No work has been reported previously from which the effect of solvent on the absorption spectra of nitrosobenzene and 1-nitrosonaphthalene can be determined. Curves for these compounds in alcohol, ether, and cyclohexane are shown in Figs. 1 and 2. The effect of the change of solvent in this order is a shift of the longer wave length band (characteristic of the nitroso group) toward the blue.

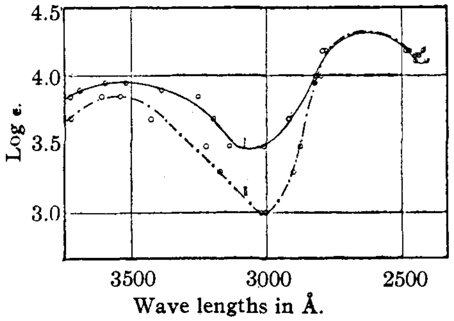

Fig. 3.—1,2-Naphthoquinone-dioxime: I in alcohol; II in ether.

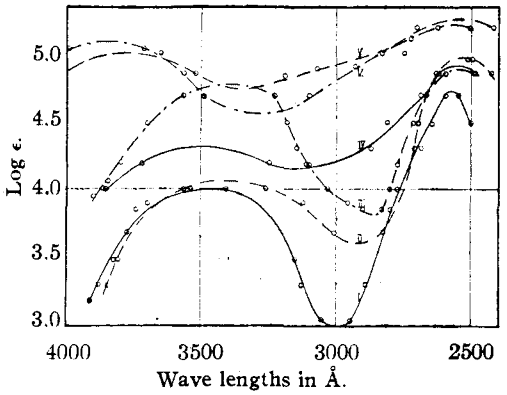

Fig. 4.—Methyl ether of 1-nitroso-2-naphthol, I in alcohol; II in cyclohexane, III in ether; methyl ether of 2-nitroso-1-naphthol; IV in alcohol; V in cyclohexane; VI in ether.

Our results with phenol and the two naphthols are not given here, since they agree with work previously published.[6] This previously published work concerns itself with only one solvent at a time. When the results are combined, it can be seen that the effect of the solvent on the band characteristic of the hydroxyl group is similar to that for the nitroso group, namely, a shift toward the blue. The bands of nitrosonaphthol, then, would be expected to be shifted toward the blue with a change of solvent from polar to non-polar, if the compound exists mainly in the benzenoid

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(5) Scheibe and others, (a) *Ber.*, **58**, 586 (1925); (b) **59**, 1321, (c) 2617 (1926).

(6) (a) Klingstedt, *Compt. rend.*, **174**, 812 (1922); *ibid.*, **175**, 365 (1922); *ibid.*, **176**, 674 (1923); (b) de László, *Proc. Roy. Soc.* (London), **A111**, 355 (1926); (c) Marchlewski and Moroz, *Bull. soc. chim.*, **35**, 473 (1924).

form and contains therefore the nitroso and hydroxyl groups.

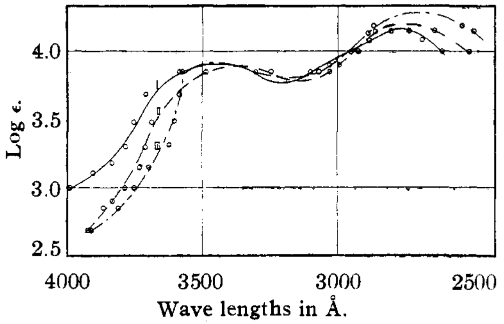

Fig. 5.—4-Nitroso-1-naphthol: I, in alcohol; II, in chloroform; III, in ether.

By comparison of previous work on benzoquinone[5c,6c,7] and on both 1,2-naphthoquinone and 1,4-naphthoquinone[8] it may be seen that a change of solvent from polar to non-polar causes a slight shift in the absorption bands to the red. The same is true for a cyclic ketone like cyclohexanone.[9] This agrees with Scheibe's results[6] and others[10] on open-chain ketones.

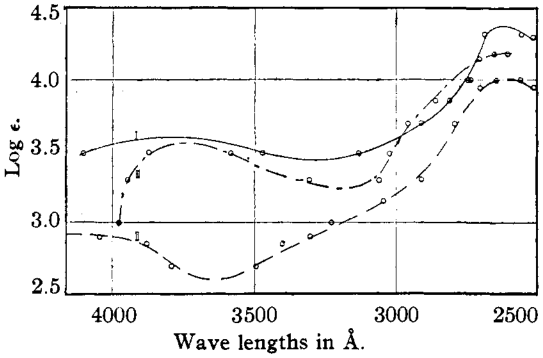

Fig. 6.—2-Nitroso-1-naphthol: I, in alcohol; II, in cyclohexane; III, in ether.

An attempt to find the effect of solvent on the absorption spectra of oximes is shown in Figs. 3 and 4, on 1,2-naphthoquinone dioxime, and the methyl ethers of the naphthoquinone monoximes (which are known to be of the oxime type).[2b] A displacement to the red, or else almost no displacement at all, is the only effect. The bands of nitrosonaphthol, then, would be expected to be unchanged or slightly displaced toward the red with a change of solvent from polar to non-polar, if the compound exists mainly in the quinonoid form, as naphthoquinone monoxime.

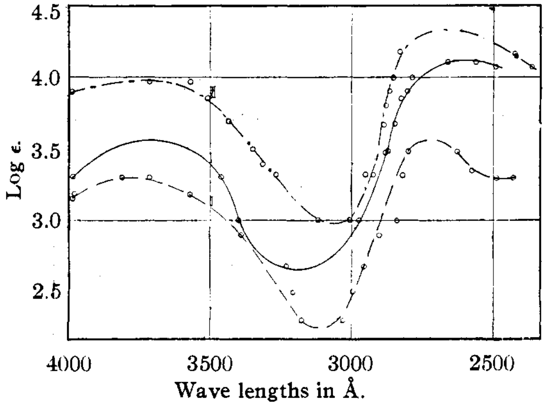

Fig. 7.—1-Nitroso-2-naphthol: I, in alcohol; II, in cyclohexane; III, in ether.

Figures 5, 6 and 7 show the absorption spectra of the three isomeric nitrosonaphthols in different solvents. The longer wave length band of the 2-nitroso-1-naphthol is displaced to the red, while the corresponding bands for the other two isomers remain practically unchanged. Merely from this study of solvent effect, therefore, it might appear that all three isomers exist largely in the quinonoid form, although the case is clearer for the 2-nitroso-1-naphthol than for the others. We realize also (1) the probability of a change in the sensitive, tautomeric mixtures with a change of solvent, and (2) the possibility of association of solute molecules in certain solvents, and (3) the possibility of chelation, or the formation of a so-

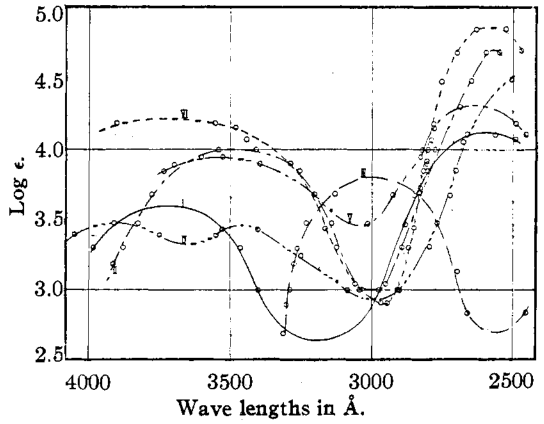

Fig. 8.—I, 1-nitroso-2-naphthol in alcohol; II, methyl ether of 1-nitroso-2-naphthol in alcohol; III, 2-naphthol in alcohol; IV, 1,2-naphthoquinone in alcohol, V, 1,2-naphthoquinone dioxime in alcohol; VI, nitrosonaphthalene in alcohol.

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(7) Klingstedt, *Compt. rend.*, **176**, 1550 (1923); Lifschitz, *Rec. trav. chim.*, **43**, 269 (1924); Light, *Z. physik. Chem.*, **122**, 422 (1926).

(8) Goldschmidt and Graef, *Ber.*, **61**, 1862 (1928); Macbeth, Price and Winzor, *J. Chem. Soc.*, 327 (1935).

(9) Henderson, Henderson and Heilbron, *Ber.*, **47**, 876 (1914); Bielecki and Henri, *ibid.*, **47**, 1690 (1914); Wolf, *Z. physik. Chem.*, **B3**, 137 (1929); Lowry and Lishmund, *J. Chem. Soc.*, 1315 (1935).

(10) Rice, This Journal, **42**, 727 (1920).

called hydrogen bond. Thus far the case remains open.

Comparison of Curves of Quinonoid and Benzenoid Compounds.—In Fig. 8 are shown absorption spectra for solutions in alcohol of the tautomeric 1-nitroso-2-naphthol, its methyl ether, the dioxime of 1,2-naphthoquinone and 1,2-naphthoquinone itself (all definitely of the quinonoid type), and of β-naphthol and 1-nitrosonaphthalene (both definitely of the benzenoid type). Figures 9 and 10 show corresponding groups of curves for the other two isomers.

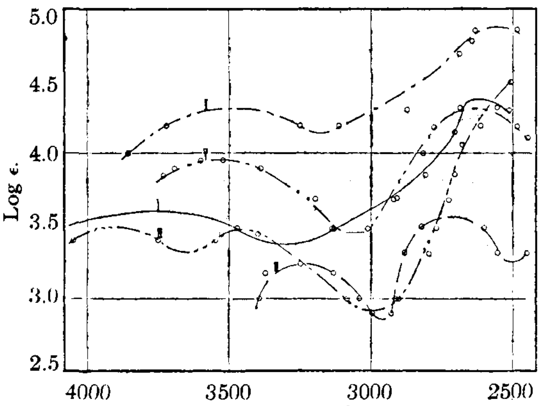

Fig. 9.—I, 2-nitroso-1-naphthol in alcohol; II, methyl ether of 2-nitroso-1-naphthol in alcohol; III, 1-naphthol in alcohol; IV, 1,2-naphthoquinone in alcohol; V, 1,2-naphthoquinone dioxime in alcohol.

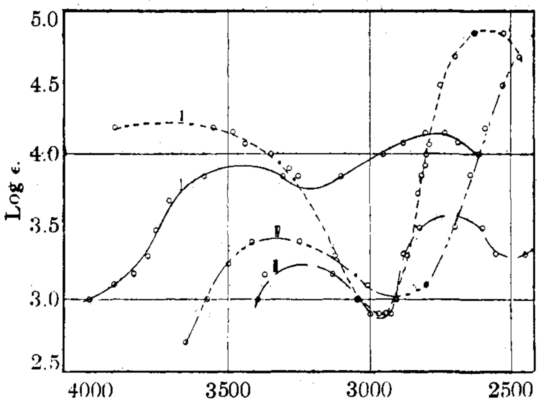

Fig. 10.—I, 4-nitroso-1-naphthol in alcohol; II, 1-nitrosonaphthalene in alcohol; III, 1-naphthol in alcohol; IV, 1,4-naphthoquinone in alcohol.

A number of things could be noted with respect to wave lengths and intensities, similarities and dissimilarities, or the general effect on absorption of introducing nitroso groups or hydroxyl groups into an aromatic molecule. We prefer to leave the

TABLE I

LOG ε AT 100 Å. INTERVALS (SUMMARY OF CURVES)

	4000	3900	3800	3700	3600	3500	3400	3300	3200	3100	3000	2900	2800	2700	2600	2500	Maximum at
1 Nitrosobenzene in																	
Alcohol							2.86	3.19	3.40	3.58	3.73	3.85	3.82	3.58	3.28	3.01	2860
Cyclohexane							2.91	3.13	3.36	3.63	3.85	3.98	4.01	4.00	3.76	3.21	2780
Ether							3.11	3.30	3.63	3.81	3.96	4.06	4.07	4.01	3.76	3.36	2840
2 Nitrosonaphthalene in																	
Alcohol	4.15	4.19	4.21	4.22	4.20	4.15	4.06	3.91	3.66	3.17	2.94	3.08	3.96	4.65	4.86	4.79	3725
Cyclohexane	3.15	3.37	3.49	3.55	3.56	3.54	3.49	3.40	3.26	3.01	2.75	2.67	3.20	3.81	3.91	3.87	3590
Ether	3.90	3.95	3.98	3.99	3.98	3.94	3.86	3.71	3.36	3.06	2.90	3.00	3.80	4.05	4.62	4.10	3725
3 1,2-Naphthoquinonedioxime in																	
Alcohol				3.89	3.95	3.95	3.91	3.83	3.68	3.47	3.50	3.72	4.08	4.27	4.30	4.21	3550
Ether				3.74	3.84	3.86	3.72	3.56	3.34	3.12	2.99	3.34	4.06	4.30	4.31	4.23	3575
4 Methyl ether of																	
1-Nitroso-2-napthol in																	
Alcohol		3.21	3.60	3.85	3.95	3.99	3.98	3.80	3.66	3.20	3.00	3.26	3.83	4.31	4.68	4.46	3475
Cyclohexane		..	3.51	3.81	3.96	4.04	4.06	4.03	3.96	3.83	3.66	3.61	3.78	4.46	4.91	4.96	3420
Ether		3.91	4.20	4.46	4.65	4.74	4.76	4.74	4.56	4.16	3.95	3.83	4.03	4.59	4.85	4.85	3400
2-Nitroso-1-naphthol in																	
Alcohol			4.08	4.22	4.29	4.31	4.29	4.22	4.15	4.16	4.21	4.30	4.45	4.65	4.88	4.88	3490
Cyclohexane		4.96	4.99	4.98	4.92	4.82	4.74	4.74	4.80	4.86	4.91	4.97	5.04	5.16	5.24	5.24	3760
Ether		5.06	5.06	5.01	4.89	4.70	4.59	4.55	4.57	4.66	4.80	4.92	5.04	5.13	5.20	5.17	3830
5 4-Nitroso-1-naphthol in																	
Alcohol		3.10	3.30	3.62	3.82	3.90	3.90	3.83	3.77	3.85	3.95	4.05	4.15	4.13	3.96		3450
Chloroform		2.73	2.99	3.36	3.68	3.83	3.89	3.87	3.80	3.79	3.89	4.07	4.19	4.19	4.10		3360
Ether		2.70	2.86	3.12	3.55	3.91	3.90	3.84	3.81	3.83	3.93	4.11	4.25	4.28	4.25	4.15	3430
6 2-Nitroso-1-naphthol in																	
Alcohol	3.55	3.58	3.59	3.58	3.55	3.50	3.46	3.44	3.45	3.50	3.58	3.70	3.88	4.21	4.37		3790
Cyclohexane	2.90	2.85	2.73	2.62	2.61	2.70	2.80	2.90	2.99	3.08	3.20	3.36	3.63	3.93	4.01		4210
Ether		3.42	3.54	3.55	3.49	3.40	3.32	3.27	3.24	3.29	3.54	3.80	4.00	4.15	4.19		3730
7 1-Nitroso-2-naphthol in																	
Alcohol	3.28	3.44	3.53	3.56	3.51	3.38	3.00	2.72	2.66	2.71	2.90	3.35	3.91	4.06	4.11	4.08	3710
Cyclohexane	3.15	3.25	3.30	3.27	3.20	3.09	2.91	2.64	2.35	2.25	2.46	3.00	3.49	3.55	3.40	3.30	3760
Ether	3.88	3.94	3.97	3.98	3.96	3.82	3.61	3.37	3.15	2.99	3.02	3.60	4.22	4.32	4.31	4.24	3700

curves as they stand, with few comments, pending further work on the preparation and study of the much needed nitroso derivatives of the methyl naphthyl ethers. It does seem in each case, however, that the curve of the tautomeric mixture resembles the curves of the quinonoid types more closely than those of the benzenoid types.

Experimental

No new or unpublished methods were used in the preparation of the compounds studied. Each was purified carefully. The solvents were also purified so that they were optically clear throughout the range of the spectrum for which they were used. The methods for obtaining the absorption spectra data have been described already from this Laboratory.[11] For the sake of simplicity not all the experimental points are shown in the curves. Table I summarizes the values of log ϵ at intervals of 100 Å. wave lengths, as well as the positions of the significant absorption maxima.

Summary

1. Absorption spectra curves are shown for the effect of solvent on nitrosobenzene, 1-nitrosonaphthalene, 1,2-naphthoquinone dioxime, and the three nitrosonaphthols.

2. From solvent effects, and from comparison of curves of compounds of fixed quinonoid and of fixed benzenoid structure, evidence is given for the state of the quinonoid–benzenoid equilibrium in the three nitrosonaphthols.

3. No very definite conclusions are possible without further work, but the quinonoid modification seems to predominate in the equilibria studied.

WELLESLEY, MASS. RECEIVED JANUARY 14, 1937

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[11] Acly and French, THIS JOURNAL, **49**, 853 (1927).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND RADCLIFFE COLLEGE]

The Solubility of Barium Nitrate in Concentrated Nitric Acid

BY CHARLES H. GREENE

The determinations of the solubility of barium nitrate in nitric acid described in this paper were undertaken because of the value of this system for analytical purposes. The use of concentrated nitric acid to separate barium and strontium from calcium was first suggested by Rawson.[1] It is very convenient for the qualitative analysis of the alkaline earth group.[2] Willard and Goodspeed[3] have recently introduced a new technique for the precipitation of lead, barium, and strontium with 100% nitric acid and have shown that these metals may be separated quantitatively from calcium and most other metals by means of this reagent.

A number of investigators[4–8] have measured the solubility of barium nitrate in dilute nitric acid but no quantitative data appear to be available for concentrations of nitric acid above 50%, the range which is of interest for analytical purposes.

Experimental

Barium nitrate of reagent grade was purified by four recrystallizations with rinsing and centrifugal drainage. C. P. nitric acid, either fuming or concentrated as required, was purified by two or more distillations in an all glass still evacuated by a glass aspirator. Conductivity water, analytical reagent sodium carbonate and C. P. sulfuric acid were used.

Preliminary results upon the solubility of strontium nitrate in concentrated nitric acid indicated a slightly greater solubility in acid which had been exposed to full daylight for sixteen hours with consequent decomposition. For this reason, the acid for these experiments was distilled in a dark room and exposed only to red light. The solubility flasks were protected from white light at all times. All of the solutions containing more than 50% nitric acid were analyzed for nitrous acid by the following method.

Samples of 25.00 ml. taken from the flasks after the filtration of the saturated solution, were diluted with 100 ml. of water and oxidized for twenty minutes with 10.00 ml. of 0.1 *N* potassium permanganate. The excess permanganate was reduced with 10.00 ml. of 0.1 *N* oxalic acid and the oxalic acid back titrated with 0.1 *N* permanganate. The oxalic acid and permanganate solutions were compared each time by blank runs with 25 ml. of 18 *N* sulfuric acid in place of the nitric acid solution.

The largest amount of nitrous acid found in any sample was 0.003% while most of the samples contained less than 0.001%. It was thought that this small amount of decomposition would be without appreciable influence on the solubilities measured.

Sealed Pyrex Erlenmeyer flasks containing the acid with a liberal excess of solid barium nitrate were rotated about an inclined axis for twenty-four hours or more in a

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[1] Rawson, *J. Soc. Chem. Ind.*, **16**, 113 (1897).

[2] Greene, *Ind. Eng. Chem., Anal. Ed.*, **8**, 346 (1936).

[3] Willard and Goodspeed, *ibid.*, **8**, 414 (1936).

[4] Chlopin, *Z. anorg. allgem. Chem.*, **143**, 108 (1925).

[5] Fricke and Brummer, *ibid.*, **213**, 319 (1933).

[6] Friend and Wheat, *J. Chem. Soc.*, 501–2 (1933).

[7] Masson, *ibid.*, **99**, 1132 (1911).

[8] Tolmachev, *Compt. rend. acad. sci. U. R. S. S.*, 689 (1930A).