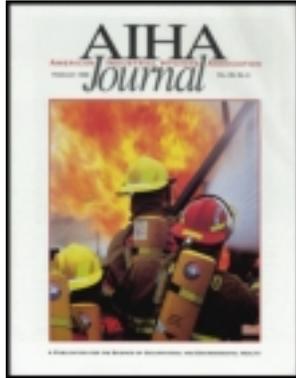


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# Kinetic Evaluation of the Factor Used in the Saltzman Analysis of Oxides of Nitrogen

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⊗ The Saltzman reaction, a modification of the Griess-Isovoy diazotization-coupling, is commonly used for analysis of oxides of nitrogen at air pollution levels. A factor is generally applied to the results to compensate for partial conversion to non-reactive nitrogen (V). A modification of the method used at the Bureau of Mines for the higher levels of oxides of nitrogen found in diesel exhaust yields quantitative results. An explanation for this is offered, based on rate studies of the gas-phase oxidation of nitric oxide to nitrogen dioxide.

## Introduction

### *Background and Objectives*

THE SALTZMAN<sup>1</sup> METHOD, employing the Griess-Isovoy reaction, has had wide acceptance for the analysis of oxides of nitrogen at atmospheric levels. This reaction involves the diazotization of sulfanilic acid by nitrous acid (from oxides of nitrogen) followed by coupling with N(1-naphthyl)-ethylenediamine to yield an azo dye. The raw results are generally divided by a factor of about 0.7 to compensate for the formation of nitric acid. Only the nitrous acid formed takes part in diazotization and coupling. Controversy as to the value of the factor persists.<sup>2</sup>

A modification<sup>3</sup> of the Saltzman reaction has long been used at the Bureau of Mines for the analysis of diesel exhaust gas. Concentrations of nitrogen oxides are higher (500 to 2000 ppm) than ambient levels, by a factor of at least 100. The exhaust gases are collected directly from the engine, mainly in the form of nitric oxide, in vacuum bottles<sup>4</sup> containing reagent. This permits rapid formation of nitrous acid followed by diazotization and coupling long before the gas-phase oxidation of nitric oxide is allowed to proceed to completion.

In this investigation we used reaction kinetics to explain our quantitative yield (factor = 1.00) for the overall reaction employing

the modified Saltzman reaction. This method was chosen because we recognized that several competing reactions (discussed later) take place in the gas phase oxidation of nitric oxide. The routine analytical results which we obtain using the modified Saltzman procedure correspond closely with the quantitative results obtained by the well-known phenoldisulfonic acid nitration procedure,<sup>4</sup> which depends on conversion to nitric acid followed by ring nitration and spectrophotometric measurement.

### *Kinetics of the Gas Phase Oxidation*

The gas phase reaction  $2 \text{NO} + \text{O}_2 = 2 \text{NO}_2$  was shown by Bodenstein<sup>5</sup> to be third order and, for the most part, homogeneous. Hasche<sup>6</sup> and others investigated the effects of water vapor and of surface and found that these were measurable but of minor significance. Although there is some doubt as to the simple termolecular reaction path,<sup>7,8</sup> the overall kinetics are third order over a wide range of temperature and concentration. Treacy and Daniels<sup>9</sup> studied the reaction kinetics over the pressure range of 1 to 20 mm and the temperature range of 0 to 65° C. Their values for the rate constant.

$$K = \frac{d\text{NO}_2}{dt} \cdot \frac{1}{(\text{NO})^2(\text{O}_2)}$$

and those of the other investigators mentioned were from  $0.8$  to  $2.1 \times 10^{10}$  cc<sup>2</sup> mole<sup>2</sup>-sec. over the concentration ranges investigated.

In our experiments the oxygen concentration was in the ambient air range and therefore could be considered constant throughout the experiments. The classical third order equation  $dx/dt = Kc^2NO$ .  $CO_2$  can be expressed as equation 1

$$\frac{dx}{dt} = Kb(a-x)^2$$

where  $K$  = the rate constant in liters<sup>2</sup> per mole<sup>2</sup> — sec.

$b$  = the initial oxygen concentration in moles per liter.

$a$  = the initial NO concentration in moles per liter.

$x$  = the  $NO_2$  concentration at time,  $t$  (seconds) in moles per liter.

Integration of equation 1 and solving for  $x$  yields equation 2.

$$x = \frac{Ka^2bt}{1 + Kabt}$$

Then let  $F$  = the fraction of NO converted or

$$F = \frac{x}{a} = \frac{Kabt}{1 + Kabt}$$

At the ambient conditions of 25°C and 740 mm, under which we carried out our tests, the oxygen concentration in air is ( $3.98 \times 10^{-4} \times \% O_2$ ) moles per liter. Using this value of  $b$ , substituting  $3.98 \times 10^{-8} \times \text{ppm NO}$  for  $a$ , and selecting  $K$  as  $1.5 \times 10^4$  liters<sup>2</sup> per mole<sup>2</sup> — sec., then:

$$Kabt = 1.43 \times 10^{-5} (\text{ppm NO})(\%O_2)T$$

where  $T$  = time in minutes

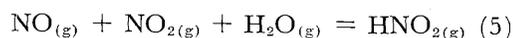
Equation 3 then becomes:

$$F = \frac{1.43 \times 10^{-5} (\text{ppm NO})(\%O_2)T}{1 + 1.43 \times 10^{-5} (\text{ppm NO})(\%O_2)T}$$

A half-life value can be obtained by placing  $F = 0.5$   $O_2 = 21\%$  and converting  $T$  to hours. Then  $T_{1/2} = 55.5$  hours/ppm NO.

Equation 4 will be employed for evaluation

of our experimental results. It should be recognized that the aqueous spectrophotometric results depends not only upon the above-described gas phase reaction but also entails several others such as the gas phase reaction:



described by Wayne and Yost.<sup>10</sup> This reaction is very rapid and should promote the heterogeneous dissolution in aqueous reagent. The experimental contribution to time,  $T$ , (equation 4) required for formation, solution and diazotization reaction of nitrous acid can only be very roughly guessed at. This, as well as the contribution to  $T$  resulting from the initial mixing of gases, will be discussed later. From the value of  $F$  (equation 4) the excess of nitrogen dioxide over the 1:1 ratio of NO to  $NO_2$  required for quantitative formation of nitrous acid by reaction 5 can be calculated and its effect upon the overall yield observed.

It should be pointed out that the reactions described are not the only reactions which occur. J. K. Rieke<sup>11</sup> postulated that the solution of nitric oxide and nitrogen dioxide in water can involve eleven separate reactions. For this reason we have included an experimental study of the reaction of low concentrations of nitrogen dioxide as well as nitric oxide with aqueous reagent. It was reasoned that if a given initial concentration of nitric oxide in air was allowed to stand for a sufficiently long time, such as two hours, it would behave similarly to the same initial concentration of nitrogen dioxide when allowed to react with Saltzman reagent.

### Materials

The volume of a 12-gallon borosilicate bottle is measured accurately by water displacement. It is fitted with a rubber stopper carrying two glass stopcocks. A mercury manometer, motor-driven air compressor, two-stage vacuum pump, Hamilton gas syringes (50, 100 and 1000 ml) and 250-ml vacuum bottles are provided. The latter contain Griess-Isoyay reaction mixture and are evacuated prior to sampling as described by Davis and O'Neill.<sup>3</sup> A UV-visual double-beam spectrophotometer is employed for mea-

TABLE I  
Results of Oxidation of Nitric Oxide  
Using Modified Saltzman Procedure<sup>a</sup>

Reaction Time, <i>T</i> (min)	Conversion Fraction NO to NO <sub>2</sub> , <i>F</i> , and Spectrophotometric Yield, <i>Y</i> (%), at Indicated Concentration (ppm)					
	567 <sup>b</sup>		1277 <sup>b</sup>		2137 <sup>b</sup>	
	<i>F</i>	<i>Y</i>	<i>F</i>	<i>Y</i>	<i>F</i>	<i>Y</i>
2.5	0.30	100			0.62	95
3.0	0.38	100			0.66	91
4.0	0.40	100	0.60	93	0.72	89
7.0	0.54	96	0.73	86	0.82	82
17	0.74	90	0.87	80	0.92	75
32	0.84	88	0.92	76	0.95	72
62	0.91	84	0.96	73		
122	0.95	80			0.99	72

<sup>a</sup> Values tabulated represent average of three runs each.

<sup>b</sup> These concentrations are the averages of the constant total oxide concentrations obtained using phenoldisulfonic acid as a reference method. About 50 ml of pure NO is required to give 1000 ppm of mixture.

surement of absorbance: Pure nitric oxide and nitrogen dioxide, contained in lecture bottles, are used for making up mixtures.

### Procedure

The large reaction bottle is taped to minimize implosion hazard. The manometer is connected to one stopcock and the vacuum pump to the other. The bottle is evacuated to about 50 mm Hg. The manometer stopcock is closed, and the calculated amount of nitric oxide or nitrogen dioxide is injected through the second stopcock by means of syringes. Nominal initial concentrations of from 400 to 2100 ppm for NO and 400 to 2800 ppm for NO<sub>2</sub> are injected. In calculating the volume of oxide to add, nitric oxide does not deviate very far from perfect gas behavior. Nitrogen dioxide, however, is largely associated to tetroxide in the pure state,<sup>7</sup> so that about half the ideal gas volume should be injected into the bottle.

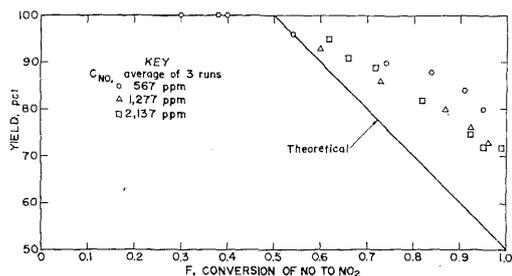


FIGURE 1. Spectrophotometric yield of nitrous acid as a function of estimated fractional conversion of NO to NO<sub>2</sub>.

Immediately following the oxide injection, the partially evacuated bottle is pressurized with compressed air to about 150 mm of mercury above atmospheric as measured by opening the manometer stopcock. About 1 minute is required to fill the bottle. The extreme turbulence of inrushing air ensures complete mixing within that time. Samples are taken directly into vacuum bottles containing Griess-Ilsovoy reaction mixture at intervals. For nitric oxide these intervals range from 15 seconds to 24 hours. For nitrogen dioxide, duplicate samples are taken in about 2 hours. Over this period, a few samples are taken for analysis by the phenoldisulfonic acid method<sup>†</sup> in order to establish the reference concentration of total oxides of nitrogen. (In the phenoldisulfonic acid procedure the bottles containing acidified hydrogen peroxide<sup>4</sup> should be sealed with rubber tubing and screw clamps rather than by the usual glass seal employed for field testing.)

The absorbance of the reaction mixtures is measured and nitrogen oxide concentrations are calculated by the methods given in the literature references.<sup>3,4</sup>

### Results and Discussion

In Table I, values are given for the calculated fraction, *F*, of nitric oxide converted to nitrogen dioxide, and the measured spectrophotometric yield, *Y*, for azo dye formation in the Saltzman procedure, as the function of reaction time, *T*. The yields, *Y*, represent the percentages of the quantitative phenoldisulfonic acid nitrogen oxide values obtained by the use of the modified Saltzman procedure. The values of *F* are based on the assumption that the gas-phase reactions approximate pseudo-third-order kinetics according to equation 4. The values for time, *T*, are only approximately based on the time taken to fill the 46.2-liter bottle, the elapsed time in this bottle, the time required to transfer samples to the vacuum bottles, and the time required for depletion of the gas phase within the vacuum bottles. The last quantity is unknown but believed to be rapid. As an approximation the residence time (after pressuring with air) within the large bottle plus 2 minutes was taken as time, *T*.

A plot of  $Y$  versus  $F$  (Figure 1) shows a very rough compliance with the expected reaction path using the Table I values. The theoretical reaction path is shown based only on the nitric oxide oxidation,  $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ , and on the subsequent stoichiometric reactions  $\text{NO} + \text{NO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{HNO}_2$  and excess  $\text{NO}_2$  dissolving in water to give 50% nitric and 50% nitrous acid. As previously mentioned, the actual reactions are more complicated than those represented by the idealized path. The results of the three average concentrations of nitrogen oxides indicate that, up to about a 1:1 ratio of  $\text{NO}:\text{NO}_2$  ( $F = 0.5$ ), nitrous acid forms quantitatively and is converted to the azo dye in quantitative yield. Above  $F = 0.5$ , the excess nitrogen dioxide gives a higher yield of diazotate than expected. Some concentration dependence can be observed in the final yields obtained, showing that the lowest concentration gave the highest yield.

To investigate the effect of concentration on final yield (2-hour equilibration), the results of individual nitric oxide and nitrogen dioxide runs have been tabulated in Table II in order of increasing initial concentration. The yield was plotted against concentration in parts per million in Figure 2, using the data points from Table II. A regression line having a slope of  $-0.0067$  and an intercept of  $82.78$  was drawn through the points. Although a correlation coefficient<sup>12</sup> of  $0.89$  was obtained showing moderate linearity, a curved dotted line drawn through the points appeared to produce a better fit. An additional plot (Figure 3) of yield versus log concentration, in parts per million, had a calculated slope of  $-19.07$  and an intercept of  $131.98$  with a correlation coefficient of  $0.933$ . The standard deviation,  $S_y/s_x$ , equals  $2.63$ . Although there still is deviation from linearity, some improvement in fit is evident. This linearity can be claimed only over the concentration range tested. This range covers that to be expected in diesel engine exhaust.

### Conclusions

1. The overall reaction consisting of the gas-phase oxidation of nitric oxide in a large excess of oxygen followed by solution in and

TABLE II  
Modified Saltzman Yields Obtained with Nitric Oxide and Nitrogen Dioxide after Equilibration for Two Hours

Gas	Concentration added		Yield (%)
	ppm	log <sub>10</sub> , ppm	
NO	420	2.624	80
NO <sub>2</sub>	490	2.690	80
NO	495	2.695	82
NO <sub>2</sub>	510	2.708	84
NO <sub>2</sub>	570	2.755	79
NO	635	2.803	78
NO <sub>2</sub>	790	2.898	78
NO <sub>2</sub>	840	2.925	76
NO	1200	3.080	72
NO	1200	3.080	71
NO	1300	3.115	71
NO <sub>2</sub>	1745	3.293	68
NO <sub>2</sub>	1845	3.267	68
NO	2040	3.310	73
NO	2127	3.329	69
NO	2241	3.351	71
NO <sub>2</sub>	2780	3.444	65

reaction with Saltzman's reagent is roughly pseudo-third order.

2. The complexity of the reactions involved precludes a clearcut description of the reaction paths. Several reactions appear to be occurring simultaneously and sequentially.

3. The overall reaction is quantitative using our engine sampling techniques as shown by comparison with the phenoldisulfonic acid method. Oxides of nitrogen exist almost exclusively as nitric oxide at engine temperatures, and very rapid sampling directly into Saltzman reagent provides insufficient time for the nitrogen dioxide to total nitrogen oxides ratio,  $F$ , to exceed  $0.5$ .

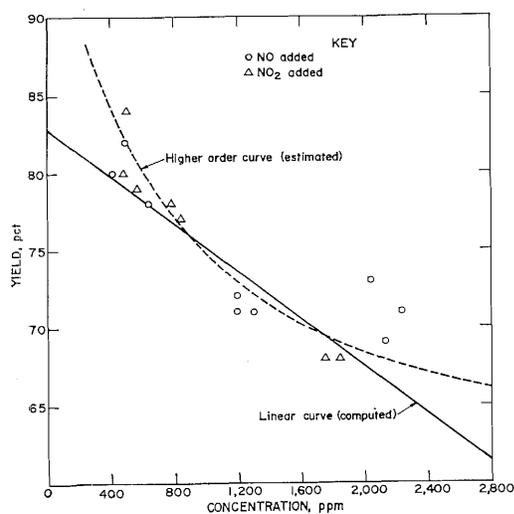


FIGURE 2. Yield versus initial concentration (ppm).

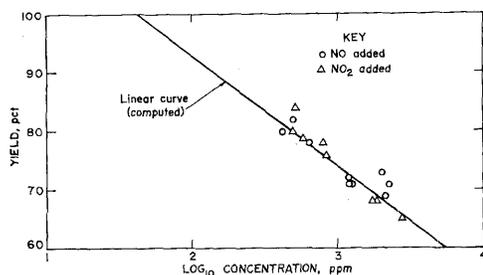


FIGURE 3. Yield versus  $\log_{10}$  initial concentration (ppm).

4. The Saltzman "factor" decreases roughly linearly with the log of initial concentration. This is true over the concentration range measured (400 to 2800 ppm) starting with either nitric oxide or nitrogen dioxide.

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#### Errata

In the article "The Adsorption of Aliphatic Acetate Vapors onto Activated Carbon" by E. R. Hermann and C. L. Fraust appearing in *American Industrial Hygiene Association Journal* 30: 494-499 (Sept.-Oct. 1969) two figures were reversed in their positioning although the correct caption appears with each figure. Figure 2 on page 496 should have been Figure 7 on page 497, and vice versa.

#### Bureau of Mines Report

On page 290 of the May-June 1969 issue of this Journal, there is a brief note concerning Bureau of Mines Report of Investigation 7077. Inadvertently this same note was carried on page 325 in the same issue. The work reported would merit this double exposure, however the brief note may have given some readers the impression that the low temperature problems reported in the information circular still apply to Bureau of Mines approved equipment. This is not the case. Schedule 13E, under which breathing apparatus is currently tested, requires satisfactory performance at -25°F. The malfunctions reported in the circular pertain only to apparatus approved prior to Schedule 13E.