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Quantitative Analysis of Nitric Oxide in Presence of Nitrogen Dioxide at Atmospheric Concentrations

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■ Chromium trioxide (CrO_3) was tested as a replacement for the potassium permanganate-sulfuric acid solutions designed to oxidize NO for conversion and detection as NO_2. The CrO_3 oxidizer was prepared by soaking firebrick in a 17% solution of pure CrO_3, draining, and drying at 105°C. The final loading was about 10% by weight. Since the optimal relative humidity (R.H.) working range of the CrO_3 oxidizer without sulfuric acid is higher (35-90% R.H.) than the material mixed with sulfuric acid, a humidifier with a shortened inlet tube was used so that the airstream was blown over water rather than bubbled through it. This gave a relative humidity of about 70–80%. Three to 5 grams of the hydrated oxidizer was placed in a midget impinger. An interesting and desirable feature of the CrO_3 oxidizer is its color change when hydrated (dull yellow) or dehydrated (dull pink) and when its oxidizing ability is spent (greenish brown). The midget impinger should be changed before more than half has depleted. At ambient levels of NO the oxidant should last at least 3 months. The oxidation efficiency is close to 100%.

The development of suitable analytical procedures for determining NO paralleled the historical sequence of improvements in NO_2 analysis. Chronologically, the need for trace analysis of NO started with the manufacture of city gas from coal. Methods for oxidizing NO with a mixture of $KMnO_4$ and H_2SO_4 were described by Guyer and Weber (1933), Hollings (1937), and Shindman and Yeaw (1942).

Other systems for oxidizing NO to NO_2 were described by Johnston (1954), Thomas et al. (1956), Remy (1956), and Ripley et al. (1964). Such systems used such compounds as ozone, heated I_2O_5, acidified MnO_2, periodate, persulfate, N_2O_5, ClO_2, and oxygen. Each method, however, has certain disadvantages for continuous sampling and analysis. An excess of ozone converts nitrogen oxides all the way to nitric acid in the presence of atmospheric moisture. Therefore, ozone must be precisely metered into the gas stream with no more than a 100% excess over the amount of NO. A disadvantage of the use of heated iodine pentoxide is the fact that many other reducing pollutants also liberate iodine from this reagent. Gaseous oxygen (O_2) oxidizes nitric oxide slowly and can be used only for concentrations above 100 ppm. Periodate, persulfate, and acidified permanganate are not quantitative oxidizers, and acidified manganese dioxide is not stable. Chlorine dioxide has been demonstrated to give good conversions. However, it is not readily available, and any large excess bleaches the azo dye reagent and must, therefore, be precisely metered into the air stream, similarly to ozone (Thomas et al. 1956).

Remy (1956) mentioned the use of CrO_3 as an oxidizing substance for NO. During development of an NO_2 galvanic monitor, Hersch (1963), used a heated column with CrO_3 + H_2SO_4 on Chromosorb to oxidize NO to NO_2. Glass fiber paper was then tried as suitable supporting material for the CrO_3 + H_2SO_4 mixture, or for CrO_3 alone, by Ripley et al. (1964). They also checked the usefulness of other oxidizing substances, a study which was followed recently by Hartkamp (1970). After 1964, it was found by Ripley et al. (1964) and by Saltzman and Wartburg (1965a) that these mixtures containing CrO_3 gave up to 30% more output for the same concentration of incoming NO than the liquid 2.5% $KMnO_4$ + 2.5% H_2SO_4 oxidizing system. Earlier observation of inconsistency in NO conversion by acidified CrO_3 mixtures was reported by Jones et al. (1965) to be caused by a relative humidity dependence.

During the development of a suitable scrubber for SO_2, chromic acid oxidizers oxidized SO_2 (Schulze, 1966) or SO_2 + NO (Saltzman and Wartburg, 1965a). The same authors found a suitable scrubber for the determination of ozone when drying a mixture at 120°C containing an excess of H_2SO_4 over CrO_3 on silica gel. This mixture oxidized all gases, including NO_2, but was very humidity sensitive. Wilson and Kopczynski (1968) verified a better response toward higher relative humidity by reducing the concentration of the sulfuric acid in the CrO_3 + H_2SO_4 mixture. Forwerg and Crecelius (1968), working with a commercial oxidizing mixture, regulated the relative humidity with a prewash of phosphoric acid.

All these developments led us to consider further reduction of the H_2SO_4 concentration and the use of a Na acetate prefilter as a relative humidity buffer for manual sampling (Intersociety, 1972). Therefore, we tested an acid-free CrO_3 oxidizer which has high oxidative efficiency over a wide range of relative humidity. The work reported here was prompted by the favorable results obtained with that oxidizer (Levaggi et al. 1971).

Equipment

NO Oxidizer. An oxidizer less susceptible to humidity than acidified CrO_3 was prepared by soaking 14-16-mesh firebrick C-22 (Johns Manville) or molecular sieve 1/16-in. pellets (Linde) in a 17% CrO_3 solution (without sulfuric acid) for 10–30 min. After the material was drained and dried in an oven at 105°C for 30 min, the support contained about 10% CrO_3 by weight and had a dull pink color. The oxidizer changed to a rich yellow (the active form) upon 24-hr hydration by equilibration with ambient air at 40–70% relative humidity. It can also be conditioned by drawing ambient air at a flow rate of 0.5 l./min for 1 hr through the tube or impinger containing the material. A change in color to a greenish brown indicates the exhaustion of oxidizing ability and progresses with a sharp boundary. This color change provides an easy visual check of the activity of the oxidizer. For the evaluation study, about 3 grams of the material were placed in a midget impinger (of 30 ml total volume, 2.5 cm diameter) whose dip tube was within a few mm of the bottom of the outer tube. Alternatively a 5-mm tube was filled to an 80-mm height, and the support was held in place with a glass wool plug on each end.

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NO_2 Absorber. A 20% aqueous solution of triethanolamine (TEA = nitrilotriethanol) was used to soak 14–16-mesh firebrick C-22 (Johns Manville) or molecular sieve 1/16-in. pellets (Linde). After the material was drained and dried, the solid support was loaded into 2-cm diameter polyethylene tubes to a length of about 10 cm and held in place by two glass wool plugs, according to details given elsewhere (Levaggi et al. 1972).

Continuous Analyzer. For the continuous evaluation, a dual channel photometric analyzer was operated with modified Saltzman reagent and used in the simultaneous mode, so that NO and NO_2 could be analyzed separately (Figure 1).

Steel Tank. As a primary source of gas for the continuous analyzer, preferably a stainless or a conditioned steel tank containing about 12 ppm NO_2 + 3 ppm NO was used. When a diluter was used, a 0.5% NO_2 in air or a 0.5% NO in N_2 mixture was required.

Dilution Panel. Secondary dilution was done on a dilution panel which contained sufficient flowmeters and gas lines to dilute the pollutant gas to a level of 0–4 ppm NO_2 or 0–1 ppm NO with reliability and reproducibility (Kothny et al. 1972). The sample gases were single-component mixtures. A chromic oxide tube was used upstream to remove traces of nitric oxide by oxidation in nitrogen dioxide streams. A TEA tube was inserted upstream to remove nitrogen dioxide traces in nitric oxide streams.

Synthetic Air. This gas mixture was used as the diluting gas and as zeroing gas. Alternatively, compressed air which has been filtered through an oil separator, a molecular sieve, and an active charcoal filter in series can also be used.

Manual Sampler. A fritted bubbler containing 10 ml of modified Saltzman reagent was located at the output end of the dilution panel for manually measuring the concentration of the calibrating gases.

Diluter. The 0.5% NO in N_2 or NO_2 in air mixture was diluted through the asbestos-plug restricted orifice into a stream of purified or synthetic air, as described by Saltzman and Wartburg (1965b).

Humidifier or Dehumidifier. The humidifier which normally precedes the oxidizer was modified by shortening the inlet tube so that the airstream was blown over water rather than bubbled through it (as opposed to the acidified $KMnO_4$ bubbler). This gave a relative humidity of about 70–80% instead of nearly 100%. No dehumidifier was needed, since the optimal relative humidity working range of the CrO_3 oxidizer without sulfuric acid is higher (35–80%) than the material mixed with sulfuric acid (for the mixture containing two parts of CrO_3 to one part H_2SO_4, the optimal working range was 15–45% relative humidity) as found by Jones et al. (1965). Alternatively, humidity may be controlled by saturating incoming air by bubbling through 5% H_2SO_4. The oxidizer is placed in this case in a heated box. A 10–15°C temperature increase over ambient is enough to reduce the humidity to an adequate level. Heat for the box may be generated by a small 7½-W bulb. Orthophosphoric acid has also been proposed for regulation of the relative humidity (Forwerg and Crecelius, 1968).

Procedure

The diluted gas obtained by appropriate dilution was split. One stream was taken up by the automatic NO_x analyzer, another portion was connected with a manual sampler for checking the input concentration under standardized conditions, and the excess was vented.

The intake of the automatic analyzer was split into the simultaneous mode. The NO leg had in series the NO_2 absorber, the humidifier, the CrO_3 oxidizer, and finally a helical glass contact column wetted concurrently with the Saltzman reagent through which the gases were aspirated. The other leg was fed directly into another helical glass contact column, for NO_2 measurement. The NO_2 absorbers were used in two ways: on the output end of the dilution panel to generate a stream of pure NO, or in-line on the NO side of the automatic analyzer to selectively absorb NO_2 from the mixed stream of gases as explained before.

The manual procedure for NO_2 (Intersociety, 1972) was performed by assembling a gas line in series composed of a rotameter and a fritted bubbler with the azo dye reagent. The gas was drawn by a vacuum line controlled by a needle valve. In the mode for NO analysis, TEA absorber, humidity controller, and oxidizer were inserted between the rotameter and the fritted bubbler. It was more accurate to determine the concentration of NO by careful dilution of the pure gas with pressurized N_2 in the tank (deVera and Tokiwa, 1968), than with the method of multiplying the concentration with the corresponding asbestos-plug dilution factor. This latter factor was calculated from the asbestos-plug leakage rate and the dilution flow rate. When diluting NO_2, it was simpler to determine the outlet concentration with a standardized Intersociety Committee method (1972) (or Calif. Dept. Public Health, 1968; USDPH, 1965).

Results and Discussion

Absorption of NO_2 by NO_2 Filter. The absorption of NO_2 by the TEA absorber was quantitative. The TEA Absorber generated 2–4% NO from the dilute NO_2 gas stream (Table I), and did not absorb NO when this gas was mixed with incoming NO_2.

Absorption of NO_2 and Lag in Response by Oxidizer. In properly soaked and humidity-equilibrated fresh material, no initial lag in response occurred on the continuous analyzer.

Bleed-off of NO_2 from Oxidizer. There was no noticeable bleed-off of NO_2 when zero gas abruptly replaced a dilute (0.4–1.5 ppm) NO gas stream.

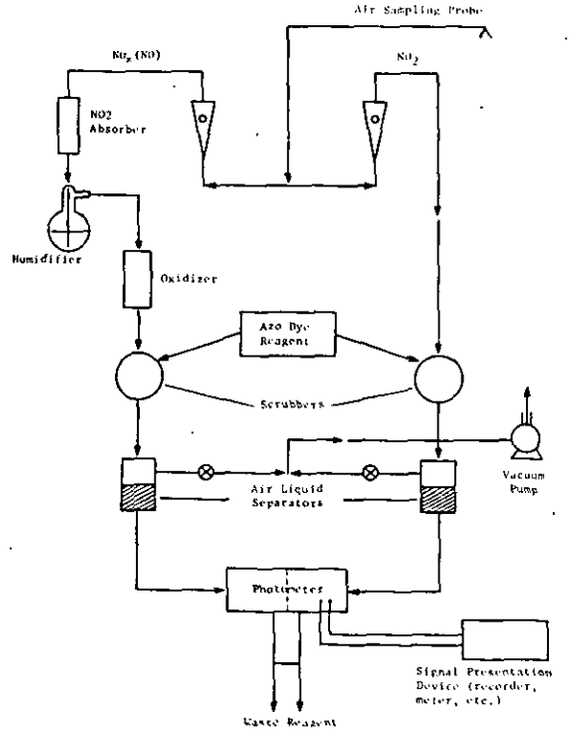

Figure 1. Flow diagram of the continuous air analyzer in the simultaneous mode

Table I

Sample gas	Components on NO side: NO_2 absorber	Components on NO side: NO oxidizer	Analyzer output: NO side, ppm	Analyzer output: NO_2 side, ppm	Parameter tested
A. Continuous Analyzer in Simultaneous Mode					
1a. 0.90 ppm NO_2	...	...	0.90	0.90	Absorption efficiency of TEA for NO_2
1b. 0.90 ppm NO_2	TEA	...	0.00	0.90	
2a. 0.42 ppm NO	...	CrO_3	0.42	0.00	Absorption of NO by TEA
2b. 0.42 ppm NO	TEA	CrO_3	0.42	0.00	
3a. 0.86 ppm NO_2	...	...	0.86	0.86	Reduction of NO_2 to NO by TEA
3b. 0.86 ppm NO_2	TEA	CrO_3	0.03	0.86	
4a. 0.46 ppm NO	TEA	CrO_3[a]	0.10	0.00	Oxidation efficiency (t = 0 hr)
4b. 0.46 ppm NO	TEA	CrO_3	0.46	0.00	Oxidation efficiency (t > 2 hr)
5a. 0.61 ppm NO	TEA	CrO_3	0.61	0.00	Efficiency at 80% R.H.
5b. 0.61 ppm NO	TEA	CrO_3	0.60	0.00	Efficiency at 35% R.H.
B. Manual Method in NO Mode					
1. 0.99 ppm NO_2	TEA	...	0.036	0.99	Reduction of NO_2 to NO by TEA
2a. 1.21 ppm NO	...	CrO_3	1.21	0.00	Efficiency of NO oxidizer
2b. 1.21 ppm NO	...	CrO_3-H_2SO_4	1.15	0.00	Efficiency of NO oxidizer
3a. 1.53 ppm NO	...	CrO_3	1.53	0.00	Efficiency of NO oxidizer
3b. 1.53 ppm NO	...	$KMnO_4$-H_2SO_4	1.07	0.00	Efficiency of NO oxidizer
C. Analyzer Operation with Gas Mixtures					
1a. 1.53 ppm NO_2 + 0.80 ppm NO	...	CrO_3	1.40	0.69	Lag time after 15 min
1b. 1.53 ppm NO_2 + 0.80 ppm NO	...	CrO_3	1.51	0.78	Lag time after 30 min
1c. 1.53 ppm NO_2 + 0.80 ppm NO	...	CrO_3	1.53	0.80	Steady output (t > 1 hr)

[a] Unequilibrated oxidizer, CrO_3 = NO oxidizer (this paper), TEA = NO_2 absorber (this paper), CrO_3-H_2SO_4 = chromic acid–sulfuric acid glass fiber paper, $KMnO_4$-H_2SO_4 = permanganate liquid bubbler.

Oxidation of NO to NO_2. For properly equilibrated material (70–80% relative humidity, at 0.5 l./min for 1 hr) incoming concentrations of NO below 1 ppm were quantitatively oxidized to NO_2 even when the incoming relative humidity fluctuated between 35 and 90%. The use of a humidifier to regulate the relative humidity from 70–80% is beneficial and could be done by blowing the air stream over an aqueous surface. The oxidation efficiency of the oxidizer dropped at sustained relative humidity values over 80%.

Durability. The amount used, 3 grams, should be useful for at least three months at ambient NO and hydrocarbon levels. The color change to greenish brown indicates exhaustion, and the tube should be changed before more than half is depleted.

Oxidation to Higher Oxides. It has been mentioned by Saltzman and Wartburg (1965a) that some CrO_3 oxidizers high in sulfuric acid oxidize NO_2 to N_2O_5 at very low relative humidities. With less sulfuric acid, Jones et al. (1965) reported that the oxidizers worked by quantitatively oxidizing NO to NO_2 at a relative humidity as low as 16%. When CrO_3 on firebrick is used at ambient concentrations of NO in a humidified stream of air, there is no noticeable loss (< 1%) of NO to higher nonvolatile oxides. A chemiluminescent NO_x analyzer gave the same NO and NO_x readings when CrO_3 was placed in the NO gas stream. Oxidation of NO to NO_3^-, for example, would have been indicated by a decrease in the NO_x trace; there was none. However, if CrO_3 is used unhumidified at high NO concentrations (10–50 mg/m³; 8–40 ppm) to convert the NO to NO_2, then losses on the order of 50% can occur.

Performance. The oxidative capacity of the material stays at a constant level and quantitatively converts NO to NO_2 throughout its lifetime after proper conditioning.

Summary and Conclusions

It has been demonstrated that chromic oxide on an inert support can be used to quantitatively oxidize NO to NO_2 when the relative humidity of the incoming gas mixture is regulated between 35 and 80%, for manual analysis as well as for continuous recording instruments.

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