Rapid Determination of Nitrogen Oxides with Use of Phenoldisulfonic Acid

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■ A rapid, quantitative batch procedure for analysis of atmospheric nitrogen oxide samples ($NO + NO_2$, commonly referred to as NO_x) from mines, tunnels, and raw or dilute diesel exhaust is described. This modification of the phenoldisulfonic acid nitration procedure eliminates the time-consuming evaporation step and two transfer steps of the original procedure. Samples are collected in evacuated bottles containing an absorbent solution and hydrogen peroxide to completely oxidize the gas-phase NO_x to nitric acid. After destruction of excess oxidant, an aliquot of the absorbed sample is added to the phenoldisulfonic acid reagent in a 25-ml. volumetric flask which is used as the reaction vessel for subsequent nitration and neutralization. This modified method can double or triple the number of analyses per day by the original method.

The phenoldisulfonic acid nitration procedure (Beatty *et al.*, 1949) has long been considered a reliable method for determining NO and NO_2, commonly referred to as NO_x. The NO_x gas-phase mixture is oxidized completely to nitric acid by hydrogen peroxide, followed by ring nitration of 1-phenol-2,4-disulfonic acid and visible spectrophotometric determination of the trialkali salt formed on neutralization.

The phenoldisulfonic acid (PDSA) method is not as sensitive as the Saltzman (1954) procedure and other modifications of the Griess-Ilsovay reaction. The latter methods use diazotization and coupling to form azo dyes and are particularly useful for the low levels of nitrogen oxides encountered in air pollution work. The PDSA method, however, can be readily used for the NO_x levels found in raw diesel engine exhaust (50 to 2000 p.p.m.) or atmospheres resulting from the use of explosives (10 to 200 p.p.m.).

Chlorides and organics are major interferences in the determination of nitrates by the PDSA method (Boltz, 1958; Scott, 1930). Both materials are likely to be present in auto exhaust. However, in the Bureau of Mines schedule testing program we found that the level of total organic compounds or chlorides is very low (in the part per million range) in the exhaust of a properly adjusted diesel engine. Removal of both chlorides and organics from samples prior to analysis is detailed by Boltz (1958). Dimitriades (1968) reported that tetraethyl lead (TEL) in amounts equivalent to 2 ml. per gallon produces auto exhaust containing 25 p.p.m. (Cl + Br). Assuming an NO_x content of 1500 p.p.m., the halide interference is equivalent to a -1.7% error in the nitrate determined. Organic matter interferes mainly through the off-colors imparted to the original sample solution. Additional decomposition of organic substances may be caused by charring the residue during evaporation or by the strongly acidic PDSA reagent.

The PDSA procedure requires lengthy absorption and evaporation steps and careful attention to avoid spattering losses. For this reason, it is often supplanted by modifications of the Saltzman procedure even for the higher ranges of NO_x concentration. In most cases, a factor must be used since side reactions are known to occur (Koshlov and Ulitin, 1966; Murphy, 1967; Shaw, 1967).

However, a modification of the Saltzman procedure, developed by Davis and O'Neill (1966), provided quantitative results only under the very specialized conditions such as those in the testing of diesel engines for suitability for safe underground operation. Here, the gas issues from the exhaust with the oxides almost entirely in the form of nitric oxide. Samples are taken almost immediately under conditions where nitrous acid forms exclusively due to the very high ratio of nitric oxide to nitrogen dioxide, thus promoting the overall reaction $NO + NO_2 + H_2O \rightarrow 2HNO_2$. The available diazotization-coupling reagent acts very rapidly to consume the nitrous acid nearly as fast as it is formed.

A relatively rapid, quantitative batch procedure was sought for the analysis of nitrogen oxide samples obtained from mines, tunnels, and raw or dilute diesel engine exhaust. Modification of the PDSA method by eliminating the evaporation step was thought to be the best approach.

Experimental

Reagents. A solution for absorption of gas samples is prepared containing 1.5 ml. of 30% hydrogen peroxide per liter of $0.1N$ sulfuric acid, which is stable for at least 12 months (Beatty *et al.*, 1949). A standard $0.0025M$ potassium nitrate is prepared by using the absorbent solution for dilution. The standard is equivalent to that obtained by absorption of 224 ml. of 1000^{V}_{V} p.p.m. NO_x (10 μmoles) in 4.00 ml. absorbent solution at STP. The PDSA reagent is available (Hartman-Leddon Co., Philadelphia, Pa.) as phenoldisulfonic acid, APHA, Item 1913. Water used for dilution should be distilled and passed through a double ion-exchange bed to eliminate nitrates and other ions.

Equipment. An electrically operated rotator is used which is capable of holding several 250-ml. Bureau of Mines air sample bottles (Beatty *et al.*, 1949). These are round-bottomed tubes, approximately 150-mm. long and 55 mm. in diameter, which are evacuated and sealed after the addition of 4 ml. of absorbent solution. An ultraviolet-visible range spectrophotometer is used with matched quartz 1-cm. cells for measurement of absorbance.

Summary of Preliminary Experiments. Time studies were made to determine the effect of agitation upon the gas sample absorption and oxidation. In the nitration of phenoldisulfonic acid reagent, the maximum amount of aqueous dilution that could be tolerated was measured to determine whether the neutralization and evaporation steps could be eliminated. Conditions under which the reaction mixture could be heated to provide for rapid color formation without charring were studied.

Procedure. Prepare a calibration curve by using 4.00 ml. of standard nitrate solution. Destroy excess peroxide present in the standard by adding 3 to 4 drops of $0.6N$ potassium permanganate. Remove excess oxidant and manganese dioxide which is present as a brown precipitate (MnO_2 results from reduction of $KMnO_4$ by H_2O_2) by adding 1 to 2 drops of $0.6N$ oxalic acid. This operation results in a colorless solution. If only 3 drops of permanganate or only 1 drop of oxalic acid is required, add one drop of water in either case to provide a total volume close to 4.30 ml. The volume of the drop may vary, depending on the type of dropper used; therefore each dropper should be calibrated. The use of drops in place of accurately measured volumes does not contribute significantly to error. This method of addition is preferable to making up to a definite volume since it avoids an unnecessary transfer step and is sufficiently accurate. Add small aliquots of the resulting solution up to a maximum of 2.00 ml. (4.66 μmoles) to 2 ml. of PDSA contained in 25-ml. volumetric flasks which are cooled under cold running water and shaken to prevent local overheating. Heat each flask for 10 min. on a steam bath, then cool. Make flasks up to volume by slowly adding 1:1 NH_4OH. Flasks should be shaken and cooled during neutralization. Measure the absorbance against a reagent blank at 410 nm. Draw a calibration curve of absorbance *vs.* μmoles NO_x. This curve is linear up to at least 2 μmoles and has a slope of approximately 0.00240.

Collect gas samples in evacuated air sample bottles containing 4.00 ml. of absorbent. If immediate analysis is required, rotate bottles for 1 hr. After destruction of excess peroxide in the bottles, add 0.50- to 2.00-ml. aliquots of absorbed sample to the PDSA reagent, according to the expected concentration range. Perform nitration, neutralization, and absorbance measurements as with the standard. Determine NO_x levels from the calibration curve after making suitable pressure, volume, and temperature corrections. Use the accurately known volumes of the individual gas bottles (measured by water displacement) in the calculations.

Comparison with PDSA Method. The modified PDSA method was compared directly with the currently used PDSA method. Three nitric oxide standards, nominally 600, 1100, and 1600 p.p.m., were used. In addition, exhaust gas samples taken from a one-cylinder CFR engine were compared directly by both methods to check accuracy.

Results and Discussion

Absorption and oxidation of 600 to 1600 p.p.m. of nitric oxide in a gas sample was found to be complete after the sample bottles were rotated for 1 hr. Total absorption was also obtained when sample bottles were allowed to stand for 24 hr. In contrast, only 90% of the maximum absorption was obtained after 3 hr. of standing.

The reaction also could be safely carried out by heating on a steam bath. When a hot plate was used, charring occasionally resulted.

In the dilution studies varying amounts of standard nitrate solution were added to 2 ml. of PDSA reagent. It was determined that a maximum of 2-ml. aqueous standard nitrate could be used to ensure completion of the reaction at 100° C. Thus, a maximum aliquot of 2 ml. of the 4.3 ml. of an absorbed gas sample can be taken, since the reaction will not go to completion with an acid concentration of less than 50%.

The modified method eliminates the time-consuming evaporation step of the original procedure. Two transfer steps, with attendant rinsing, are avoided by adding a sample aliquot directly to a volumetric flask which is used as the reaction vessel. The 10 to 12 samples normally handled per day with the original method can be increased two to three times by this modified procedure. Since none of the basic chemical reactions of the original method have been changed by the suggested modifications, the rapid method is suitable for any type of samples which would normally be analyzed by the PDSA method. The sensitivity is comparable to the original method.

No interference studies were made since it had been our experience that neither chlorides nor charable organics, two major interferences in the PDSA method, are found in the exhaust from properly adjusted diesel engines. To apply this method to auto exhaust samples, however, studies of such interferences would be required.

Table I. Precision of Modified PDSA Method

Mean concn, p.p.m.	Standard deviation	Coefficient of variation, %
557	24	4.3
1117	50	4.5
1630	65	4.0

Table II. Comparison of PDSA Methods to Determine Accuracy

Test no.	NO$_x$, p.p.m. PDSA	Modified PDSA
1	896	925
2	1071	1063
3	948	902
4	520	474
5	839	792
6	594	512
7	938	974
8	470	490

The precision of the modified PDSA method was estimated by using 20 replicate samples of each of three nitric oxide standards. Sampling was carried out on two days, and the results obtained by two chemists using both 1-hr. rotation and 24-hr. standing absorption. A 0.50-ml. aliquot of the treated solution was taken in each experiment. Results are given in Table I.

Previously determined precision of the conventional PDSA method was of the same order.

Eight pairs of samples were taken under varying conditions over a period of several days directly from the exhaust of a CFR engine. Results are given in Table II. Each sample pair was taken simultaneously.

Based upon the data in Table II, a regression line (Crow *et al.*, 1960) was obtained with a slope of 1.0506 and an intercept of −57.6957. A standard deviation of $Sy/x = 45.35$ and a correlation coefficient of 0.98 indicate that the methods can be readily interchanged without significant loss of precision or accuracy.

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