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TENTATIVE METHOD FOR THE CALIBRATION OF NITRIC OXIDE, NITROGEN DIOXIDE, AND OZONE ANALYZERS BY GAS PHASE TITRATION

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ABSTRACT

A detailed procedural description of a technique developed and applied within the U. S. Environmental Protection Agency for the dynamic calibration of ambient air monitors for ozone, nitric oxide, and nitrogen dioxide is presented. A gas phase titration technique utilizing the rapid gas phase reaction between nitric oxide and ozone is used in such a manner that, with the concentration of one of the three gases known, the concentrations of the other two are determined. Initially a cylinder of nitric oxide in nitrogen is standardized by gas phase titration with ozone, in concentrations that have been determined iodometrically. Cylinder nitric oxide is then used as a secondary standard for routine calibrations. Ozone is added to excess nitric oxide in the dynamic calibration system, and a chemiluminescent nitric oxide monitor is used as an indicator of changes in concentration. The decrease observed on the spanned nitric oxide monitor upon addition of ozone is equivalent to the concentration of nitric oxide consumed, the concentration of ozone added and the nitrogen dioxide concentration produced. The advantages of the procedure are that a primary standard for only one of the gases is required and that rapid and routine calibrations of ozone, nitric oxide, and nitrogen dioxide monitors may be performed at a common manifold.

TENTATIVE METHOD FOR THE CALIBRATION OF NITRIC OXIDE, NITROGEN DIOXIDE, AND OZONE ANALYZERS BY GAS PHASE TITRATION

PRINCIPLE AND APPLICABILITY

Basic Principle

The following paragraphs describe, in general terms, a gas phase technique for the dynamic calibration of ambient air monitors for nitric oxide (NO), nitrogen dioxide (NO_2), total oxides of nitrogen (NO_x), and ozone (O_3). The technique basically utilizes the rapid gas phase reaction between NO and O_3 to produce a stoichiometric quantity of NO_2 in accordance with the following equation:[1,2]

$$NO + O_3 = NO_2 + O_2 \qquad k = 1.0 \times 10^7 \text{ liters moles}^{-1} \text{ sec}^{-1}$$

The quantitative nature of the reaction is used in such a manner that, with the concentration of one of the three basic components known, the concentrations of the other two are determined.

As illustrated in Figure 1, NO from a calibrated cylinder of NO in nitrogen (N_2) (50 to 100 parts per million) is diluted with a constant flow of clean air to provide NO concentrations at the exit manifold in the range from 0.05 to 1 ppm. Upstream of the point of NO addition, the clean air stream passes through an ozonizer,[3] which produces variable O_3 concentrations from 0 to 1 ppm at the sample manifold. Between the point where the ozonized air is mixed with NO (shown in Figure 1) and the sample manifold, a reaction chamber provides a residence time long enough for quantitative reaction to occur when O_3 concentrations up to 75 percent of the initial NO concentration are added.

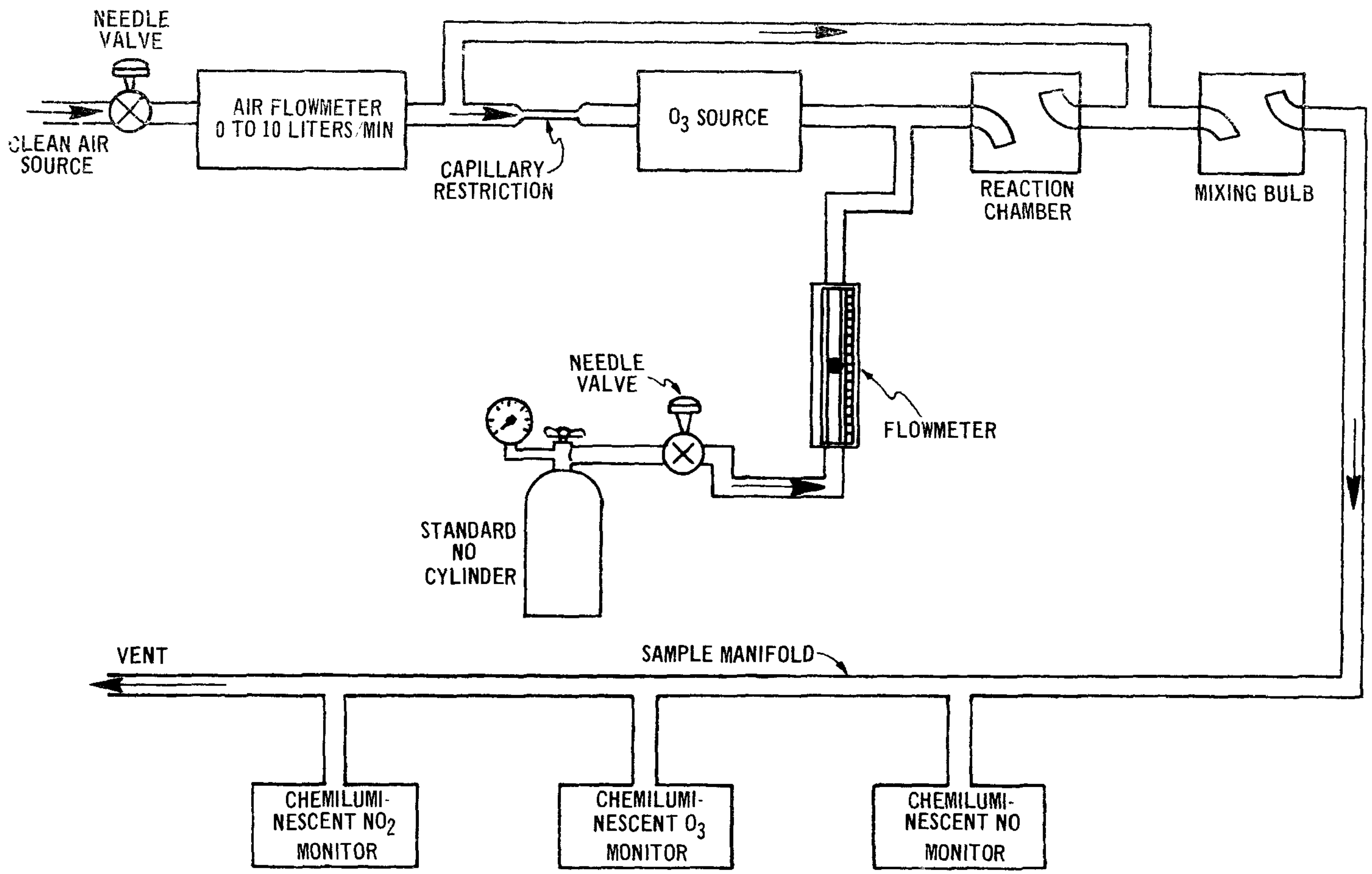

Figure 1. Flow scheme for calibration of NO, NO_2, NO_x, and O_3 monitors by gas phase titration.

Upstream of the ozonizer, the air stream is split so that 10 percent of the flow passes through the O_3 source and 90 percent through a bypass line. The ozonized 10 percent flow mixes directly with the NO stream and recombines with the 90 percent bypass flow downstream of the reaction vessel. The stream is split in order to produce locally high concentrations of O_3 and NO in the reaction chamber ($[O_3]$, reaction chamber = 10 X $[O_3]$, sample manifold), which in turn provides a quantitative reaction within a small volume. The concentrations produced at the manifold are independent of the ratio of bypass flow to source flow and depend only on total flow rate.

When excess NO is present, the amount of O_3 added is equivalent to (1) the amount of NO consumed and (2) the concentration of NO_2 formed. This interrelation is fundamental among concentrations of the three gases.

An outline of the general calibration scheme follows. The standard cylinder of NO in N_2 is initially recalibrated by the use of gas phase titration (GPT) with O_3 concentrations that have been analyzed by iodometry (this procedure is discussed in more detail later). An acceptable alternative method, not described, for cylinder calibration would be by comparison of NO_2 concentrations produced by GPT with the output of a gravimetrically calibrated permeation tube. Once the NO concentration in the cylinder has been confirmed, this cylinder may be used over its lifetime to provide a working standard for routine calibrations.

In routine calibrations, NO analyzers are calibrated by dynamic flow dilution of the cylinder gas. To calibrate NO_2 and O_3 analyzers, a constant concentration of NO at approximately 1 ppm is produced in the flow system. Ozone is added in increments from the variable O_3 source. The incremental decreases of NO, observed on the spanned NO detector,* are then equivalent to the concentrations produced by the O_3 source and serve to calibrate the source. Since NO_2 produced is equivalent to O_3 consumed, the calibrated O_3 source also serves as a calibrated NO_2 source when NO is present in excess.

Application of Technique

This technique has been designed primarily for the calibration of chemiluminescent analyzers for NO, NO_2, NO_x and O_3. Any detector that has a rapid and linear response to NO could be used as the indicator in the GPT step. With minor modifications in the flow scheme shown in Figure 1, any O_3 analyzer could be used as the concentration indicator. Since GPT is used to provide a working calibration of the O_3 source, any type of O_3 or oxidant analyzer may be calibrated. Only those types of NO_2 analyzers that do not respond to NO may be calibrated, since the NO_2 calibration samples will contain a small excess of NO.

RANGES

The procedures described in this document apply to the generation of calibration samples for NO in the range from 0.05 to 1 ppm, for O_3 in the range from 0 to 0.5 ppm, and for NO_2 in the range of 0 to 0.5 ppm.

INTERFERENCES

No other interfering gases are present in calibration samples produced for O_3 and NO. Nitrogen dioxide analyzers that suffer interference

*A "spanned NO detector" is an instrument that has been calibrated with a known concentration of NO; the output reads directly in concentration units.

from NO cannot be calibrated by this method, since some NO is present in the NO_2 calibration sample produced.

PRECISION, ACCURACY, AND STABILITY

Precision

The definition of the term precision as applied to the generation of calibration gases is generally uncertain at present. A given concentration of any of the three gases (NO, NO_2, O_3) can, however, be generated from day-to-day with an estimated reproducibility of ± 2 percent.

Accuracy

The accuracy in the concentrations of the calibration gases produced (NO, NO_2, or O_3) is estimated to be ± 3 percent. This value is determined by the accuracy of the primary calibration scheme used, in this case iodometric O_3 analysis.

Stability

The concentrations of calibration gases produced by GPT are stable to within ± 1 percent over a 1-hour period.

APPARATUS

Figure 1, a schematic of the GPT apparatus, shows the placement of most of the components listed below:

1. Air Flow Controller. A device capable of maintaining constant air flow; e.g., a differential pressure regulator.
2. Air Flowmeter. A flowmeter capable of monitoring air flows between 0 and 10 liters per minute; also a wet test meter or volumetric soap bubble meter for calibration and absolute flow measurements in this range.
3. Pressure Regulator for Standard NO Cylinder. All regulators

used should have stainless steel internal parts with teflon or Kel-F seats.

4. Nitric Oxide Flowmeter. A flowmeter capable of monitoring NO flows between 0 and 100 cubic centimeters per minute (cm^3/min) and a 25-cm^3 soap-bubble meter for absolute flow measurements in this range. The NO flow must be measured and controlled within an accuracy of ± 2 percent.

5. Capillary Restriction. Glass or stainless steel capillary of sufficient length and internal diameter to allow approximately 1.0 liter/min of air to flow through the O_3 generator at a total air flow of 10 liters/min.

6. Ozone Generator. The O_3 source consists of a quartz tube into which O_3-free air is introduced and then irradiated with a stable low-pressure mercury lamp. The level of irradiation is controlled by an adjustable aluminum sleeve that fits around the lamp. Ozone concentrations are varied by adjustment of this sleeve. At a fixed level of irradiation, O_3 is produced at a constant rate. This generator is described completely in Reference 3.

7. Reaction Chamber and Mixing Bulb. The reaction chamber and mixing bulb are Kjeldahl mixing bulbs with volumes of 150 cm^3.

8. Sample Manifold. A multiport all-glass manifold is recommended. All connections in the calibration system should be glass or teflon.

9. Nitric Oxide Detector. An NO monitor is used as an indicator in the calibration procedure. The detector should be of the chemiluminescent type that is based on the light-producing

reaction between NO and O_3 at reduced[4,5] or atmospheric[6] pressure. Detectors of this type are available commercially from several companies.

10. Iodometric Calibration Apparatus. The iodometric apparatus required for the primary calibration of the NO cylinder is described in the Federal Register.[7]

REAGENTS

1. Nitric Oxide Standard Cylinder. Cylinder containing 100 ppm NO in N_2 with less than 1 ppm NO_2.
2. Clean Air Supply. Cylinder air or purified air containing no more than 0.002 ppm of NO, NO_2 and O_3.
3. Reagents for Potassium Iodide (KI) Procedure. (See Reference 7 for a list of these reagents.)

PROCEDURE

Primary Calibration of the NO Cylinder

Ozone Generator Calibration -- A multipoint calibration of the O_3 generator is obtained by the use of the neutral-buffered KI procedure as described in the Federal Register.[7]

Gas Phase Titration -- The NO concentration in the cylinder is determined as follows:

1. With the NO flow off, set the clean air flow at a value of approximately 5 liters/min; measure and record the absolute air flow, F_O.
2. Generate approximately 1.0 ppm NO by dilution and span the instrument on a range of 0 to 1 ppm. (If a 100 ppm range is available, the NO monitor may be spanned directly with cylinder gas.)

3. Measure and record the NO cylinder flow rate, F_{NO}, with soap-bubble meter in-line as described in the section below entitled Calibration of NO Monitors (0 to 1.0 ppm Range).

4. Record the initial detector reading and then add approximately 0.1 ppm O_3 by opening the sleeve on the O_3 generator.

5. Allow the NO response to stabilize and record the resultant detector readings.

6. Adjust sleeve to obtain 0.2 ppm O_3 and allow NO response to stabilize.

7. Continue this procedure until up to 0.8 ppm O_3 has been added in a stepwise fashion.

8. Remeasure the NO flow rate.

Calculation -- The calculation method is as follows:

1. As illustrated in the example given in Figure 2, plot the NO detector readings in ppm (y axis) versus O_3 concentration added (x axis).

2. Draw a straight line from the y axis through the linear portion of the titration curve and extrapolate to the x axis. (The concentration at the x axis intercept, C_0', is the O_3 concentration equivalent to the initial diluted NO concentration.)

3. Calculate the cylinder NO concentration by the following equation:

$$C_{NO} = \frac{F_0 \times C_0'}{F_{NO}}$$

where C_{NO} = cylinder NO concentration, ppm

F_{NO} = measured NO flow, cm^3/min

C_0' = equivalence point O_3 concentration, ppm

F_0 = total clean air flow, cm^3/min.

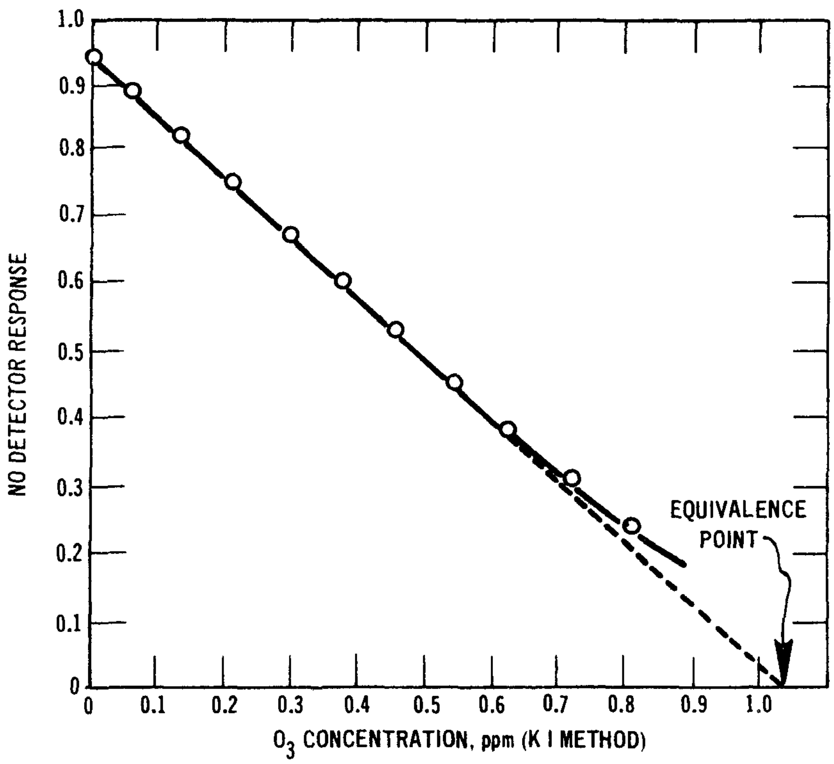

Figure 2. Gas phase titration of NO with O_3.

Procedure for Routine Calibration of NO, NO_2, NO_x, and O_3 Monitors

The following procedure is recommended for routine calibration:

Zero Adjustment --

1. Allow all instruments to sample clean air until a stable response is obtained. (Clean air supply should contain no more than 0.002 ppm of NO, NO_2, and O_3.)
2. After the response has stabilized, make proper zero adjustments.

Calibration of NO Monitors (0 to 1.0 ppm Range) --

1. Span the chemiluminescent NO detector on a range of 0 to 1.0 ppm generating an NO concentration in the range of 0.9 to 1.0 ppm by flow dilution. (The flow rate of NO added must be measured accurately, preferably with a soap-bubble meter in-line; i.e., meter the NO flow into the bubble meter and from the bubble meter into the system.)
2. After accurately measuring the NO flow, remove the bubble meter, and meter the NO flow directly into the system.
3. Calculate the exact NO concentration added by:

$$[NO] = \frac{F_{NO} \times C_{NO}}{F_T}$$

where [NO] = diluted NO concentration, ppm

C_{NO} = cylinder NO concentration, ppm

F_{NO} = NO flow rate, cm^3/min

F_T = total flow at manifold, cm^3/min

$= F_{NO} + F_0$

F_0 = total clean air flow, cm^3/min.

4. After the NO instrument response has stabilized, adjust the instrument span control until the instrument output reads directly the concentration calculated above.
5. Decrease the NO flow rate to yield a decreased NO concentration.
6. Calculate the concentration added and record the NO instrument response.
7. Repeat at several concentration values in the range of 0 to 1.0 ppm.
8. Plot instrument response versus calculated NO concentrations and draw the NO calibration curve. (If the initial instrument span is accomplished accurately, direct readout of concentration should be possible without reference to the calibration curve.)

Calibration of NO_2 Monitors (0 to 0.5 ppm Range) --

1. Adjust the NO flow rate to establish 1.00 ppm NO as measured on the NO monitor.
2. Open the sleeve on the O_3 generator to add enough O_3 to decrease the NO response to 0.5 ppm. (Note and record the sleeve setting on the O_3 generator. This action results in the generation of 0.5 ppm NO_2, which is used to span the NO_2 instruments.)
3. Allow the response of each NO_2 instrument to stabilize and adjust the span controls to give a direct readout of 0.5 ppm.
4. Decrease the added O_3 concentration by adjustment of the sleeve on the O_3 generator, again noting and recording the sleeve setting on the O_3 generator. (Allow the instrument responses to stabilize before measuring.) The decrease in response on the NO monitor yields the concentration of NO_2 generated and

the O_3 source concentration.

$$[NO_2]_i = [O_3]_i = [NO]_o - [NO]_i$$

where $[NO]_o$ = initial NO concentration measured on NO monitor, ppm

$[NO]_i$ = NO concentration after O_3 addition, ppm

$[NO_2]_i$ = resultant NO_2 concentration, ppm

$[O_3]_i$ = added O_3 concentration, ppm

5. Repeat at several added O_3 concentrations to obtain a multipoint calibration in the range of 0 to 0.5 ppm.
6. Plot the NO_2 instrument response versus the NO_2 concentration as determined above and draw the NO_2 calibration curve.

<u>Calibration of O_3 Monitors (0 to 0.5 ppm Range)</u> -- The calibration of the O_3 source, as described earlier, was determined by observation of the decreases on the NO monitor as a function of sleeve setting. The following steps are recommended for calibration of O_3 monitors:

1. In order to obtain $[O_3]_i'$, the output of the source, corrected for dilution of O_3 by the NO flow rate, multiply each of the differential readings obtained above by the ratio F_T/F_O. (The ratio F_T/F_O normally represents a small correction factor; e.g., $F_T/F_O = 1.02$ for $C_{NO} = 50$ ppm and $F_O = 5$ liters/min.)

$$[O_3]_i' = F_T/F_O \times [O_3]_i = F_T/F_O\ [NO_2]_i$$

2. Plot these corrected O_3 concentrations versus sleeve setting to yield a calibration curve for the O_3 source.
3. With the NO flow off, open the sleeve to the setting required to give 0.5 ppm as determined by the calibration curve above.

4. Adjust the instrument span control to give a full-scale readout of 0.5 ppm.

5. Reduce the sleeve setting in increments to give a series of O_3 concentrations in the range of 0 to 0.5 ppm.

6. Plot instrument response versus O_3 concentration determined from the O_3 source calibration curve.

7. Draw the calibration curve for the O_3 monitor.

GLOSSARY

cm^3/min	Cubic centimeters per minute
C_{NO}	Cylinder NO concentration, ppm
F_{NO}	NO flow rate, cm^3/min
F_0	Total clean air flow, cm^3/min
F_T	Total flow at manifold, cm^3/min
GPT	Gas phase titration
NO	Nitric oxide
NO_2	Nitrogen dioxide
NO_x	Total oxides of nitrogen
[NO]	Diluted NO concentration, ppm
$[NO]_i$	NO concentration after O_3 addition, ppm
$[NO_2]_i$	Resultant NO_2 concentration, ppm
$[NO]_o$	Initial NO concentration measured on NO monitor, ppm
O_3	Ozone
$[O_3]_i$	Added O_3 concentration, ppm
$[O_3]_i'$	O_3 output corrected for flow dilution, ppm

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16. ABSTRACT

A detailed procedural description of a technique developed and applied within the U. S. Environmental Protection Agency for the dynamic calibration of ambient air monitors for ozone, nitric oxide, and nitrogen dioxide is presented. A gas phase titration technique utilizing the rapid gas phase reaction between nitric oxide and ozone is used in such a manner that, with the concentration of one of the three gases known, the concentrations of the other two are determined. Initially a cylinder of nitric oxide in nitrogen is standardized by gas phase titration with ozone, in concentrations that have been determined iodometrically. Cylinder nitric oxide is then used as a secondary standard for routine calibrations. Ozone is added to excess nitric oxide in the dynamic calibration system, and a chemiluminescent nitric oxide monitor is used as an indicator of changes in concentration. The decrease observed on the spanned nitric oxide monitor upon addition of ozone is equivalent to the concentration of nitric oxide consumed, the concentration of ozone added and the nitrogen dioxide concentration produced. The advantages of the procedure are that a primary standard for only one of the gases is required and that rapid and routine calibrations of ozone, nitric oxide, and nitrogen dioxide monitors may be performed at a common manifold.

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