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Measurement of Carbon Dioxide, Carbon Monoxide, and Oxides of Nitrogen in Diesel Exhaust

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1. Scope—The method presented applies to the analysis of the indicated constituents in diesel engine exhaust, or vehicles using diesel engines, when operating at steady-state conditions.

The measurements of carbon monoxide, carbon dioxide, and nitric oxide are based on continuous sampling and analysis by nondispersive infrared (NDIR) methods. Measurements of total oxides of nitrogen by chemiluminescence and NDIR methods is discussed.

1.1 Purpose—This SAE Recommended Practice provides for the measurement of carbon dioxide, carbon monoxide, and oxides of nitrogen in diesel exhaust.

2. References

2.1 Applicable Publications—The following publications form a part of this specification to the extent specified herein.

2.1.1 "Cooperative Evaluation of Techniques for Measuring NO and CO in Diesel Exhaust," CRC Report No. 443, March 1971 (SAE Paper 720104).

2.1.2 "Effect of Humidity of Air Intake on Nitric Oxide Formation in Diesel Exhaust," CRC Report No. 447.

2.1.3 "Cooperative Evaluation of Techniques for Measuring NO and CO in Diesel Exhaust—Phase IV," CRC Report No. 472, Aug. 1974 (SAE Paper 750204).

2.1.4 "Cooperative Study of Some Heavy Duty Diesel Emission Measurement Methods," CRC Report No. 487, July 1976.

2.1.5 "Effect of Intake-Air Humidity and Temperature on Diesel Emission with Correlation Studies," Ethyl Report ER442 (SAE Paper 730213).

2.1.6 NIST Standard Reference Materials, Office of SRM, B311 Chemistry, National Institute of Standards and Technology, Washington, DC 20234.

2.1.7 Federal Register, Vol. 42, No. 174, Thursday, Sept. 8, 1977, "EPA—Heavy Duty Engines for 1979 and Later Model Years—Certification and Test Procedures."

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2.1.8 Atkins Psychrometer #ZO2B-3, Atkins Technical Inc., P.O. Box 14405, Univ. of Florida.

2.1.9 EG&G Environmental Equipment Model 911 Humidity Analyzer, 151 Bear Hill Rd., Waltham, MA 02154.

2.1.10 K. M. Cole and J. A. Reger, “Humidity Calibration Techniques,” Instruments and Control Systems, Jan. 1970, p. 77.

2.1.11 A. Wexler and W. G. Brombacher, “Methods of Measuring Humidity and Testing Hygrometers,” NBS Circular 512, Washington, DC, 1951.

2.1.12 A. Wexler (Editor), “Humidity and Moisture: Measurement and Control in Science and Industry,” Reinhold Pub. Corp., NY, 1965, (Vol. 1–4), Vol. 1, R. E. Ruskin, "Principles and Methods in Measuring Humidity in Gases."

2.1.13 ASTM E 337-72, “Standard Method for Determining Relative Humidity by Wet and Dry-Bulb Psychrometer,” American Society for Testing Materials, 1916 Race St., Philadelphia, PA 19103-1187.

2.1.14 Keenan and Keyes, “Steam Tables.”

2.1.15 R. L. Beatty, L. B. Berger, and H. H. Schenk, “Determinations of the Oxides of Nitrogen by the Phenoldisulphonic Acid Method,” U.S. Bureau of Mines Report of Investigations, No. 3687, Feb. 1943.

2.1.16 “Research Technique for the Determination of Oxides of Nitrogen in Gaseous Combustion Products,” CRC Designation A-2-857.

2.1.17 B. E. Saltzman, *Anal. Chem.*, Vol. 26 (1954), p. 1949.

2.1.18 Ibid, Vol. 32 (1960), p. 135.

2.1.19 R. F. Davis and W. E. O'Neill, “Determination of Oxides of Nitrogen in Diesel Exhaust by a Modified Saltzman Technique,” U.S. Bureau of Mines Report of Investigations, No. 6790, 1966.

2.1.20 SAE Recommended Practice, “Measurement of Carbon Dioxide, Carbon Monoxide and Oxides of Nitrogen in Diesel Exhaust,” SAE J177a, SAE Handbook.

2.1.21 D. B. Kittelson, et al, SAE Paper 770720, “Sampling and Physical Characterization of Diesel Exhaust Aerosols,” and SAE Paper 780110, “Diesel Exhaust Aerosol Particle Size Distributions—Comparison of Theory and Experiments.”

2.1.22 W. H. Lipkea, J. H. Johnson, and C. T. Vuk, “The Physical and Chemical Character of Diesel Particulate Emissions,” SAE SP-430, Feb. 1978.

2.1.23 J. M. Perez, et al, “Cooperative Study of Heavy Duty Diesel Emission Measurement Methods,” SAE Paper 780112, Feb. 1978.

2.1.24 Balston Filter Assembly Type 33, with Filter Element Type D. H., Balston Filter Corp.

2.1.25 Lipson and Sheth, “Statistical Design and Analysis of Engineering Experiments,” McGraw-Hill, 1973, p. 80.

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3. Definitions of Terms and Abbreviations

3.1 Terms Used

3.1.1 EXHAUST EMISSION—Any substance (but normally limited to pollutants) emitted to the atmosphere from any opening downstream from the exhaust port of the combustion chamber of an engine.

3.1.2 DIESEL ENGINE—Any compression ignition internal combustion engine using the basic diesel cycle, that is, combustion results from the spraying of fuel into air heated by compression.

3.1.3 STEADY-STATE CONDITION—An engine operating condition at a constant speed and load and at stabilized temperatures and pressures.

3.1.4 KILOWATTS—Observed kilowatts unless otherwise indicated (brake power x 0.7457).

3.1.5 NIST—National Institute of Standards and Technology

3.1.6 RATED KW OUTPUT—The maximum brake power output of an engine in kilowatts (kW) as stated by the manufacturer.

3.1.7 RATED SPEED—The engine speed at which the rated kW is obtained.

3.1.8 TOTAL OXIDES OF NITROGEN—The sum total of the measured ppm of nitric oxide (NO) plus the measured ppm of nitrogen dioxide (NO_2) expressed as an equivalent mass of NO_2.

3.1.9 CALIBRATION GAS—A gas used to establish instrument response. Concentration known to ±2%, traceable to National Institute of Standards and Technology Standard Reference Materials (Reference 2.1.6).

3.1.10 SPAN GAS—A gas used routinely to check instrument response. Concentration traceable to calibration gas.

3.2 Abbreviations Used

C—Degrees Celsius
CHEMI—Chemiluminescence
cm—Centimeters
CO_2—Carbon dioxide
CO—Carbon monoxide
conc—Concentration
DI—Direct injection
dia—Diameter
DIR—Dispersive Infrared
DUV—Dispersive Ultraviolet
EXH—Exhaust
F/A—Fuel/Air ratio
g—Gram(s)
h—Hour
kg—Kilogram
kPa—Kilopascals
kW—Kilowatt
L—Liter(s)
m—Meter(s)
max—Maximum
min—Minimum, minute(s)
mL—Milliliter(s)

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NA—Naturally aspirated
NDIR—Nondispersive Infrared
NIST—National Institute of Standards and Technology
N_2—Nitrogen
No.—Number
NO—Nitric Oxide
NO_2—Nitrogen Dioxide
NO_x—Total oxides of nitrogen
O_3—Ozone
OD—Outside Diameter
PC—Prechamber
ppm—Parts per million by volume
s—Second(s)
SS—Stainless steel
TC—Turbocharged
wt—Weight
%—Percent

4. ***Sections—***This document contains the following sections:

3. Definition of Terms and Abbreviations
5. Equipment and Operating Procedures for Carbon Dioxide, Carbon Monoxide, and Nitric Oxide Analyses by NDIR Method
6. Engine Emissions Measurement Procedures
7. Information to be Recorded
8. Data Preparation and Report
9. Supplemental Discussion
10. Determination of Total Oxides of Nitrogen in Diesel Engine Exhaust
11. Equivalency

This procedure is based in part on technical information found in References 2.1.1 to 2.1.5 and experiences of the SAE J177 task group members of the SAE Diesel Emissions Subcommittee.

5. Equipment and Operating Procedures for Carbon Dioxide, Carbon Monoxide, and Nitric Oxide Analyses by NDIR Method

5.1 System—Figure 1 is a sketch of the sampling and analytical system that is recommended for the continuous analysis of CO_2, CO, and NO in diesel engine exhaust (see 8.1).

5.2 Component Description—The following components are prescribed for the sampling and analytical systems for the analysis of diesel exhaust gas for CO_2, CO, and NO.

5.2.1 Flowmeters, FL1 and FL2, to indicate the sample flow through the system.

5.2.2 NDIR with cell(s) of appropriate length for testing constituents. The accuracy of the instrument(s) should be ±1% full scale deflection or better. Typical ranges are shown in Table 1. The ranges can differ from those recommended if accuracy is maintained.

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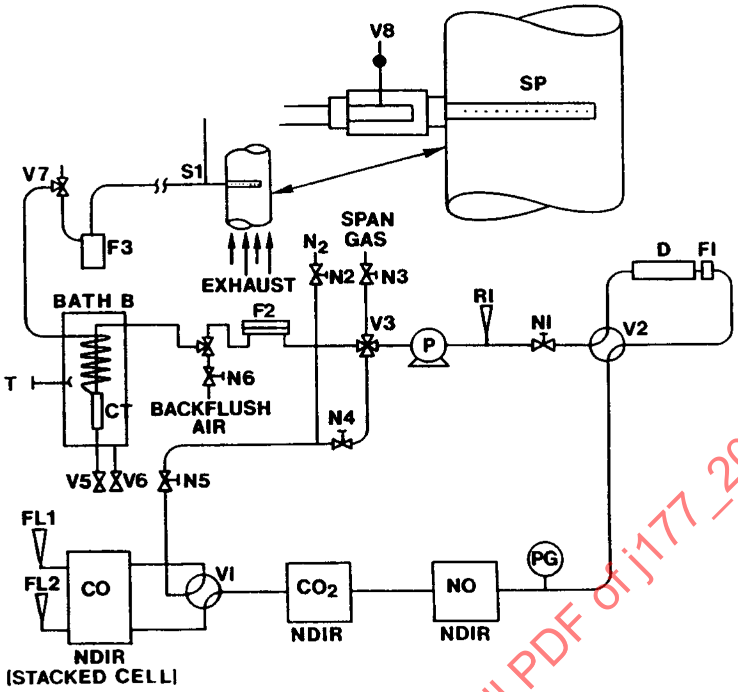

FIGURE 1—FLOW DIAGRAM OF EXHAUST GAS ANALYSIS SYSTEM FOR NITRIC OXIDE, CARBON DIOXIDE, AND CARBON MONOXIDE

TABLE 1—TYPICAL RANGES FOR ANALYSIS OF CO_2, CO, AND NO IN DIESEL EXHAUST

Component	Ranges[1]
CO_2	0–5% and 0–16%
CO	0–500 ppm
	0–1000 ppm
	0–2500 ppm
NO	0–500 ppm
	0–1000 ppm
	0–1500 ppm

1. Dual range cells or stacked cells may be used. Cell lengths as recommended by instrument manufacturer. Other ranges may be employed if the accuracy in determining the component concentration is equivalent to or better than the above (±1% full scale deflection).

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5.2.3 Selector valve, V1, to direct sample flow through high or low range CO analyzer and simultaneously purge the other analyzer.

5.2.4 Pressure gage or manometer, PG, to indicate the analyzer sample pressure (capable of detecting a 10 cm water pressure change).

5.2.5 Selector valve, V2, drier, and filter bypass.

5.2.6 Filter, F1, to prevent particles of drier from entering the analyzer.

5.2.7 Chemical drier, D, to remove moisture in sample stream. Approximately 2 cm in diameter, 15 to 20 cm length containing approximately 60 g of 6 to 8 mesh nonindicating Drierite™ and a band of indicating Drierite™ Figure 2. (Indicating Drierite™ can be mixed with nonindicating Drierite™, about 1 part to 10 parts.)

NOTE—Need not be used if a NDIR with water discriminating cells is used.

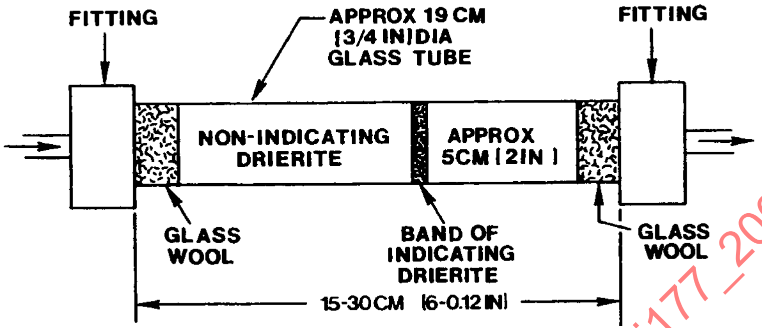

FIGURE 2—DRYING TUBE (EXAMPLE)

5.2.8 Needle valve, N1, to regulate the sample flow to the analyzer.

5.2.9 A pressure relief valve, R1, to vent excess flow and prevent pressure effects on the analyzer. (The relief pressure should be set for 15 kPa or higher if needed.)

5.2.10 Pump, P, to move sample through system.

5.2.11 Selector valve, V3, to direct sample, N_2, or calibrating gas streams to analyzer.

5.2.12 Needle valves, N2, N3, N4, and N5, as required by analyzer types to regulate N_2 or dry air and calibration gas flows. Valve N6 to regulate backflush air.

5.2.13 Filter, F2, for removing particulate contaminants from sample prior to analysis. A glass fiber type of at least 7cm diameter is suitable.

5.2.14 Selector valve, V4, to direct sample to analyzer or air back through the system to clear condensate from trap.

5.2.15 Toggle or solenoid valves, V5 and V6, to drain condensate traps and bath, respectively.

5.2.16 Bath or refrigerator, B, to cool and condense water from exhaust sample. Should be capable of maintaining a condenser gas exit temperature no greater than 7 °C.

5.2.17 Cooling coil and trap, CT, to condense and collect water vapor. A coiled 2.5 to 3 m, 0.63 cm dia SS line attached to a 2.54 cm dia, 15 cm length trap would be typical.

5.2.18 Temperature readout, T1 and T2, of bath and condenser exit gas temperature.

5.2.19 Selector valve, V7, to select room air to sample flow through the sampling and analytical system (optional).

5.2.20 Selector valve, V8, attached to stack probe to enable injection of span gas for response time check (optional).

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5.2.21 Prefilter, F3, to remove soot and some moisture from exhaust sample. Type of filter is optional but must not affect CO_2, CO, or NO concentration. An example is shown in Figure 3. Commercial elements, such as a high-efficiency, cylindrical, disposable filter element of resin-bonded borosilicate glass microfibers in an appropriate housing, are available (Reference 2.1.24).

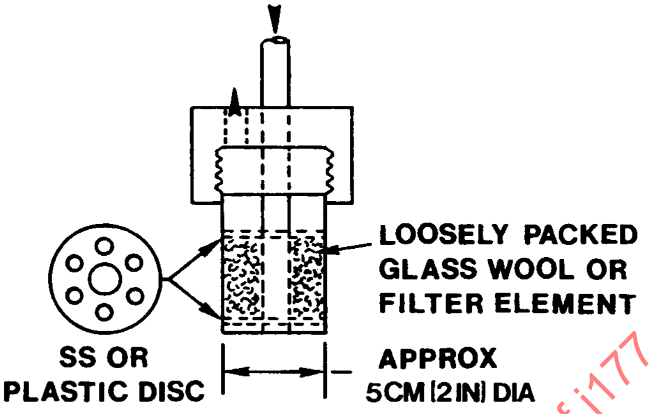

FIGURE 3—PREFILTER, F3, OR SOOT KNOCKOUT TRAP (EXAMPLE)

5.2.22 Sampling line, SL, from exhaust system to analysis system. Various materials can be used providing they can withstand the temperature and don't affect the sample integrity. SS, Teflon™, and polypropylene materials are currently used. The sample line size and length should be selected to meet the response time constraints specified in 4.3.1.

5.2.23 Stainless steel probe, SP, to extract a representative sample from the engine exhaust system (see 8.2). A multihole probe extending 75% of the way across the stack is suitable if the total area of the sampling holes does not exceed the cross-sectional area of the probe.

5.3 Operating Procedure—Follow the start-up or operating instructions of the instrument manufacturer. The following minimum requirements should be included.

5.3.1 SYSTEM RESPONSE TIME—An effect of sample residence time on NO measurements has been observed (Reference 2.1.4). The stabilized reading should give a deflection of at least 50% of full scale. (A valve can be attached to the stack probe or the sample introduced directly into the probe.) To test response, introduce the NO span gas at the sample gas flow rate at the sample probe. Measure the time elapsed before a deflection of 90% response of stabilized reading is observed on the readout meter or recorder. A response time to the NO analyzer of 20 s or less is desired.

5.3.2 CALIBRATION AND INSTRUMENT CHECKS

5.3.2.1 *Monthly*—The following should be conducted on initial startup of the system and monthly for all equipment in use. Instruments not in use for over 30 days should be calibrated before reuse.

Calibrate the instrument assembly and check calibration curves using calibration gases. Use the same gas flow rates as used for sampling engine exhaust. Flow has affected results obtained with some systems. A minimum flow rate of 4 L/min is recommended. The upper flow rate restriction is dependent on system design but should not exceed manufacturer's recommended flow.

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a. Allow 2 h minimum warmup of analyzers.
b. Tune analyzer.
c. Set zero and gain using purified dry air or nitrogen and the 100% range calibration gas.
d. Recheck zero and repeat step (c) if necessary.
e. Check possible interference of CO_2 on NO and CO analyzer. Inject 10% CO_2 in N_2 into the sample stream and observe response of CO and NO analyzers on the most sensitive or lowest range used. Observed changes should not exceed 2% of full scale response. If larger response does occur, consult instrument manufacturer's manual for correction of problem.
f. Calibrate each analyzer with a minimum of four calibrating gases that are approximately 25, 50, 75, and 100% response of each range (see 8.3) and establish a least squares curve. The calibration curve should fit the data points within ±1% full scale or ±2% of point, whichever is less. If the discrepancy is greater and cannot be resolved, check calibration gases or consult the instrument manufacturer. Depending on response characteristics of the instrument, a greater number of gases may be required to define the calibration curve.
g. Compare calibration response values with previous curves. Any significant change may indicate some problem in the system. Follow manufacturer's recommended procedures for locating and correcting any problems within the analyzers. Use best judgment for selecting a calibration curve for data reduction.

5.3.2.2 Pretest Check

a. Allow a minimum 2 h warmup if analyzers have been turned off; however, if the analyzers are being used on a daily basis, it is preferable that the analyzer power be left on continuously. The chopper motors may be turned off when the analyzers are not in use.
b. Zero on dry air or nitrogen and obtain a stable zero on the amplifier and/or recorder.
c. Introduce span gas and set gain to match the calibration curve. Use the same sample flow rate for calibration, span, and exhaust sampling. Use span gas having a concentration of the constituent that will give approximately 75 to 100% full-scale deflection. If amplifier gain shifts significantly, check for possible analyzer problems and correct. If necessary, check analyzer calibration with calibration gases.
d. Check zero and repeat steps (a) and (b) if required.
e. Check flow rates.
f. Check both refrigeration and condenser exit gas temperatures.
g. Check system for sample leaks by blocking off probe or probe end of sample line. If leaks exceed 1% of total flow, correct problem.
h. Check system response time, 4.3.1.

6. Engine Emissions Measurement Procedures

6.1 Engine Test Procedure—The following analysis procedure is recommended for emission measurements at steady-state operating conditions. The engine operating cycle is not dictated by this procedure, and the engine break-in, pretest conditioning, and measurement procedure may be modified depending on the purpose of the test, that is, emission certification test or routine laboratory development test. For emission certification see Federal Register (Reference 2.1.7).

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6.2 Emissions Measurement

a. Install sample probes and attach instrument package to prepare for data cycles.
b. Start the engine and warm it up under load until all temperatures and pressures have reached equilibrium.
c. If Drierite™ is used, during warmup, precondition Drierite™ by flowing exhaust gas through system for at least 5 min. If more than one Drierite™ tube is to be used during the test, they also must be preconditioned.
d. Measure CO_2, CO, and NO emissions as follows:

  1. Operate for at least 10 min in each mode, allowing at least 5 min for emission measurement.
  2. Check and reset zero and span after each mode or as needed to validate the data; if either changed more than 2% of full scale repeat the mode(s).
  3. Backflush condensate traps and prefilter after each mode or as needed.

6.3 Chart Reading

a. Locate the last minute of each test mode and average the chart reading for NO, CO, and CO_2 over this period. Correct chart reading for any obvious trace abnormalities.
b. Determine the concentration of NO, CO, and CO_2 in each mode from the chart reading [5.3(a)] and the calibration curve for the constituent (4.3.2.1).
c. Record chart reading from 5.3(a) and concentration from 5.3(b). Additional mass emission calculations may be required, depending on the purpose of the test.

7. Information to be Recorded—The following information should be included as part of the recorded data for each test performed:

7.1 Record Items

a. Test number.
b. Engine or vehicle tested:

  1. Identification number.
  2. Brief description including type (NA or TC, PC or DI) two- or four-stroke cycle, bore, and stroke.

c. Date of test.
d. Instrument operator and test engineer or vehicle operator.
e. Starting and finishing time.
f. Analyzer identifications.
g. Ambient temperature, start and finish.
h. Number of engine conditions tested.
i. Engine data at each test point (fuel rate, air flow, rpm, kW, temps, etc.).
j. Analysis results at each test point.
k. Atmospheric pressure, start and finish.
l. Fuel used, identification number and type (No. 1, No. 2 Diesel, etc.).
m. Sample flow rate, start and finish (should be checked at each test point).
n. Oil used, identification number and type.
o. Cooling bath exit gas temperature, start and finish (should be checked at each test point to be sure it is below 7 °C).

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7.2 Recorder Chart Notations

a. Items 6.1(a) to (h) inclusive.
b. Identify zero traces, calibration or span traces, steady-state test point identification, start and finish of each condition.
c. Instrument range used at each test point.
d. Humidity at each test point or at start and finish if no changes occurred.
e. Time of analysis, start and finish.
f. Calibration curve identification by number or date.
g. Remarks as required.

8. Data Preparation and Report

a. The data obtained in 5.3 should be checked for obvious errors.
b. The concentration of the constituents in the exhaust gas are measured on a dry basis in this procedure. To convert the measured values to concentrations present in the exhaust (wet basis), the following relationship can be employed:

$$\text{ppm (wet basis)} = \text{ppm (dry basis)}[1 - a(F/A)] \qquad \text{(Eq. 1)}$$

where:

A = Atomic hydrogen to carbon ratio = y/xin fuel with formula C_xH_y

c. More accurate calculations for this conversion are found in 8.4. The humidity of the inlet air also has an effect on the amount of NO chemically formed in combustion (Reference 2.1.5). The correction in Equation 2 should be applied to the NO value (wet basis) at each mode or test point. This conversion puts the values on a basis of 10.71 g of water per kilogram of dry air (75 grains per pound) and a temperature of 29.44 °C.

$$NO_{corr} = \frac{NO_{wet}}{K} \qquad \text{(Eq. 2)}$$

where:

$K = 1 + 7 \cdot A\,(H - 10.714) + 1.8 \cdot B\,(T - 29.444)$
$A = 0.044\,(F/A) - 0.0038$
$B = -0.116\,(F/A) + 0.0053$
T = Intake Air Temperature °C
F/A = Fuel-Air Ratio (Dry Basis)
H = Specific humidity, grams of water per kilogram of dry air (see 9.6)

where:

d. Mass calculations can be made using the ppm (wet basis and humidity corrected) and the measured exhaust flow. The exhaust flow can also be obtained from Equation 3.

$$\text{MASS EXHAUST (kg/min)} = \text{(MASS INLET AIR, kg/min)}\,(1+F/A) \qquad \text{(Eq. 3)}$$

The emissions on a mass basis are obtained as follows:

$$CO_2,\ g/kWh = 9.09(10^{-2})(\text{MASS EXH})(\text{ppm } CO_2)/kW \qquad \text{(Eq. 4)}$$

$$CO,\ g/kWh = 5.79(10^{-2})(\text{MASS EXH})(\text{ppm CO})/kW \qquad \text{(Eq. 5)}$$

$$NO,\ g/kWh = 6.20(10^{-2})(\text{MASS EXH})(\text{ppm NO})/kW \qquad \text{(Eq. 6)}$$

$$\text{NO as } NO_2\text{: } NO_2,\ g/kWh = 9.50(10^{-2})(\text{MASS EXH})(\text{ppm NO})/kW \qquad \text{(Eq. 7)}$$

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9. *Supplemental Discussion*

9.1 Analyzer Arrangement—The method as presented in the foregoing sections is considered to be a practical method of conducting continuous steady-state analyses for CO_2, CO, and NO. Adequate precision and accuracy for routine analyses are obtained using the procedures as defined.

The arrangement of analyzers as shown in Figure 1 allows the use of a single cart system with a minimum of hardware and span gases for the analysis of CO_2, CO, and NO. Use of individual analyzer systems or of analyzer systems connected in parallel may be desired by some users. A typical parallel system is shown in Figure 4. In some research activities and in abatement or control analyses only individual analyzers or two instruments in series or parallel may be desired. These modifications can be used if proper attention is paid to flow rates and system temperatures. Any modifications should be in basic agreement with Section 5.

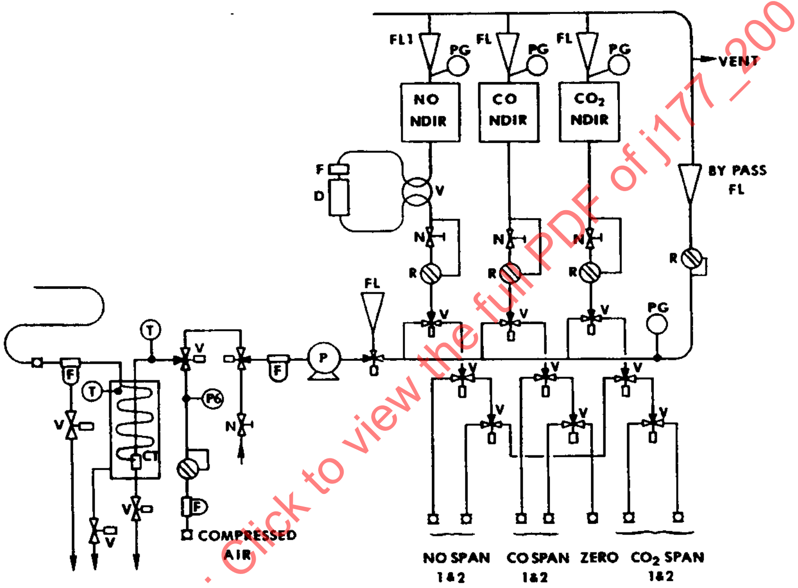

FIGURE 4—FLOW DIAGRAM OF A TYPICAL PARALLEL FLOW SYSTEM

9.2 Probe Location—The probe location should be governed by the purpose of the test. For routine emissions measurements, the probe should be located in the exhaust line at a distance of 1 to 3 m from the exhaust manifold outlet flange or the outlet of the turbocharger. Longer lengths can be used if results can be shown to be equivalent to those at 1 to 3 m.

9.3 Calibration and Span Gases—There are several suppliers of gases in the ranges used in this procedure. These can be obtained with concentration analysis accuracy of ±2% or better. However, it is recommended that internal cross checks be performed on all incoming gas standards. NIST Standard Reference Materials (Reference 2.1.6) should be used when available to verify calibration gases. Span gases can be checked with calibration gases traceable to NIST gases.

The CO and CO_2 gases can be purchased mixed. NO gases should not be obtained mixed with either CO or CO_2. All gases should be obtained in zero-grade N_2.

For NO_x analyzers discussed in Section 9, the NO should not contain over 5% NO_2 and the concentration will be named as total NO_x.

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9.4 **Dry-Wet Basis Calculations—**Diesel emissions as exhausted are wet and mass calculations based on the exhaust should employ concentration data that is on a wet basis. The conversion of emission data from a dry to wet basis is approximated by Equation 1, Section 8. A more accurate conversion can be obtained if desired. The calculations are described in the following paragraph.

The combustion of diesel fuel can be defined by the general equation:

$$CHy + nO_2 + n(3.76N_2) + mH_2O \rightarrow CO_2 + \left(\frac{y}{2} + m\right)H_2O + xO_2 + n(3.76N_2) \qquad \text{(Eq. 8)}$$

where:

y = Atomic H/C ratio in the fuel
n = Moles of oxygen in air to engine = (1 + y/4 + x)
m = Moles of water in 4.76 n moles of air
x = Moles of excess oxygen
Mass of fuel per unit time, F = 12.01 + 1.008y
Mass of air per unit time, A = 105.28n + 32.00n + 18.016m

$$F/A = \frac{12.01 + 1.008y}{137.28n + 18.016m} \qquad \text{(Eq. 9)}$$

F and A can be measured and y determined. Then, if the humidity, h, is determined in grams of water per kilogram of dry air (0.1429 x grains of water per pound of dry air), n can be determined:

$$n = \left(\frac{A}{F}\right)\left(\frac{12.01 + 1.008y}{137.28 + 0.1375h}\right) \qquad \text{(Eq. 10)}$$

The fractional volume of water in the exhaust, W, is:

$$W = \frac{0.5y + (7.63 \times 10^{-3})}{(4.76 + 7.63 \times 10h)n + 0.25y} \qquad \text{(Eq. 11)}$$

The conversion factor, CF, to be applied to the dry values is then

$$CF = 1 - w \qquad \text{(Eq. 12)}$$

Table 2 can be used to interpolate the conversion factor over the normal diesel F/A operating range.

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TABLE 2—CONVERSION FACTOR, CF

y	h	Fuel/Air Ratio 0.00(1) Conversion Factor	Fuel/Air Ratio 0.01 Conversion Factor	Fuel/Air Ratio 0.02 Conversion Factor	Fuel/Air Ratio 0.03 Conversion Factor	Fuel/Air Ratio 0.04 Conversion Factor	Fuel/Air Ratio 0.05 Conversion Factor
2.0	0 (0)(2)	1.000	0.980	0.960	0.940	0.920	0.900
2.0	14.2 (100)	0.978	0.958	0.938	0.919	0.901	0.882
2.0	28.5 (200)	0.957	0.939	0.918	0.898	0.880	0.860
1.9	0 (0)	1.000	0.981	0.961	0.943	0.925	0.906
1.9	14.2 (100)	0.978	0.958	0.940	0.921	0.904	0.886
1.9	28.5 (200)	0.957	0.938	0.919	0.901	0.883	0.886
1.8	0 (0)	1.000	0.982	0.963	0.945	0.928	0.911
1.8	14.2 (100)	0.978	0.959	0.942	0.925	0.907	0.890
1.8	28.5 (200)	0.957	0.939	0.920	0.904	0.889	0.870

1. Correction for humidity in inlet air.
2. Numbers in parentheses are grains water per pound dry air.

9.5 Humidity Measurement—The measurement of the inlet air water content is required in Section 8(c). It is recommended that the wet and dry bulb temperatures of the inlet air be measured in accordance with ASTM E 337-62 at a point that is representative of the air entering the engine. Wet and dry bulb thermometers or equivalent should be used. There are available wet and dry bulb thermistor type psychrometers that are portable and can be adapted for stack sampling. Two such instruments can be found in References 2.1.8 and 2.1.9. The device used should be capable of measuring wet bulb/dry bulb temperatures to within ±0.6 °C or dew point to within ±1.2 °C.

CAUTION—When sampling from a restricted engine intake system, the minimum velocity as stated in Reference 2.1.12 must be maintained.

Wet and dry bulb measurements should be taken at least immediately prior to and after each set of measurements. There are a number of references on humidity measurements (References 2.1.10 to 2.1.13) that can be consulted for additional guidance. Psychrometric tables for use in determining humidity values can be obtained from the U.S. Weather Bureau, Washington, DC.

Rather than use the psychrometric tables, the specific humidity can be calculated as shown in 9.6.

9.6 Humidity Calculation—Wet and dry bulb temperatures can be used to calculate the specific humidity as follows:

Given:

Wet bulb temperature, T_w, °C
Dry bulb temperature, T_a, °C
Barometric Pressure Observed, P_b, kPa

Procedure:

Find the saturation pressure of water vapor, P_w, at the wet bulb temperature, T_w.

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$$P_w\text{, kPa} = 0.6109579 + (4.440515 * 10^{-2} * T_w) + (1.425658 * 10^{-3} * T_w^{4}) + (2.629981 * 10^{-5} * T_w^{3}) + (3.115099 * 10^{-7} * T_w^{4}) + (2.201172 * 10^{-9} * T_w^{5}) \quad \text{(Eq. 13)}$$

Equation 13 is applicable over the temperature range of –30 to +40 °C. Below 0 °C, the equation follows the temperature-water vapor pressure relationship for super-cooled liquid water. (Source: Psychrometric Tables and Charts, by Zimmerman and Lavine.)

Next calculate the experimentally derived constant A for use in Ferrel's equation as recommended by NIST (Reference 2.1.13).

$$A = 3.67 \cdot 10^{-4}(1 + 0.001152 \cdot T_w) \quad \text{(Eq. 14)}$$

where:

T_w is in °C

Next find the partial pressure of water vapor, P_v, from Ferrel's equation:

$$P_v\text{, kPa} = P_w - 1.8 \cdot A\ P_b(T_d - T_w)\text{kPa} \quad \text{(Eq. 15)}$$

Then find the specific humidity, H:

$$H = \frac{621.98\,P_v}{P_b - P_v}\text{g}H_2O\text{ per kg of dry air} \quad \text{(Eq. 16)}$$

Dew point temperature can be used to calculate the specific humidity as follows:

Given:

Dew point temperature T_{dp}, °C
Barometric pressure observed, kPa

Procedure:

Find the partial pressure of water vapor, P_v, kPa.

$$P_v\text{, kPa} = 0.6109579 + (4.440515 * 10^{-2} * T_{dp}) + (1.425658 * 10^{-3} * T_{dp}^{2}) + (2.629981 * 10^{-5} * T_{dp}^{3}) + (3.115099 * 10^{-7} * T_{dp}^{4}) + (2.201172 * 10^{-9} * T_{dp}^{5}) \quad \text{(Eq. 17)}$$

Equation 17 is applicable over the temperature range of –30 to +40 °C. Below 0 °C, the equation follows the temperature-water vapor pressure relationship for super-cooled liquid water. (Source: Psychrometric Tables and Charts, by Zimmerman and Lavine.)

Substitute the result into Equation 16 to find the specific humidity.

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9.7 Determination of Oxides of Nitrogen in Engine Exhaust—Supplementary Analysis Methods

9.7.1 INTRODUCTION—The chemical kinetics of combustion reactions highly favor the formation of NO over NO_2. The NO formed does convert to NO_2 in the presence of oxygen with the degree of conversion being time related. In diesel exhaust, the conversion of NO to NO_2 under conditions of sampling in Section 5 is generally less than 5%. The procedure in the preceding sections is adequate for most analyses where conversion of NO to NO_2 is minimized.

9.7.2 TOTAL OXIDES OF NITROGEN—The method and procedures described in Sections 10 and 11 are recommended if NO_2 and NO_x measurements are required.

9.7.3 WET CHEMICAL BATCH METHODS—The methods presented in this section are useful in obtaining noncontinuous or batch type sampling procedures and in checking gases. The methods measure total oxides of nitrogen within the range of 100 to 3000 ppm. By varying the sample to reagent ratio, higher or lower concentrations can be measured. The methods utilize conventional laboratory glassware but do take more time to accumulate data than instrumental methods.

9.7.3.1 *Phenoldisulphonic Acid (PDS) Method*—This method is one of the older established wet methods and an accurate method for analysis of NO_x. This method is described in References 2.1.15 and 2.1.16.

The major drawback of the PDS method is that it is a very time-consuming method.

9.7.3.2 *Saltzman Methods*—Various modifications of the Saltzman method have been used (References 2.1.17, 2.1.18, and 2.1.19). It is felt that the procedure described in 9.7.3.3 is one of the better and a tested Saltzman modification.

9.7.3.3 *Greiss-Saltzman (Broering) Modification*—This method is rapid, accurate, and less tedious than most Saltzman modifications and the PDS method.

The method (Figure 5) uses a 30 mL syringe partially filled with Greiss reagent to a volume of 20 mL. The sample (10 mL) is drawn into the syringe so that it is placed in contact with the reagent which turns red when it reacts with the nitrogen dioxide. The nitrogen dioxide is the product of the nitric oxide-oxygen reaction which takes place while the sample is stored in the syringe plus any nitrogen dioxide in the gas sample. The intensity (absorbance) of the color is measured with a colorimeter or spectrophotometer and converted to ppm NO_x from calibration curves. The method is discussed in detail in Reference 2.1.20.

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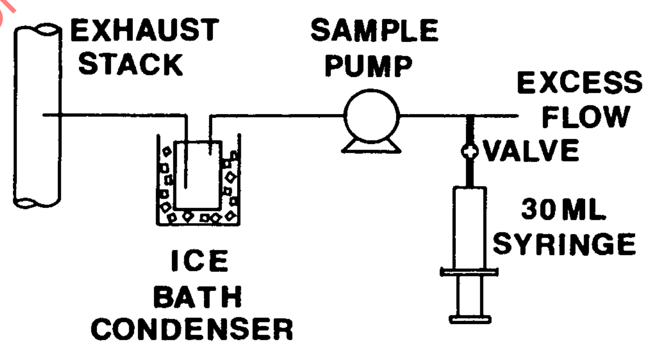

FIGURE 5—WET-CHEMISTRY NO_x SAMPLING SETUP

10. Determination of Total Oxides of Nitrogen in Diesel Engine Exhaust—There are several species of oxides of nitrogen but, with the exception of NO and NO_2, their presence in diesel exhaust is essentially nil. The measurement of total NO_x as described in this section pertains to the measurement of the total NO and NO_2.

The oxidation of nitric oxide to nitrogen dioxide is a reversible reaction:

$$NO + 1/2\ O_2 \Leftrightarrow NO_2 \qquad \text{(Eq. 18)}$$

The reverse reaction is favored by heat and the reduction rate can be accelerated by specific catalysts. One principle of measuring total NO_x utilizes the use of converters through which the sample is passed. NO_2 is converted to NO and the total ppm NO is measured by various detectors. The two most widely used are the NDIR and the CHEMI analyzers, with the CHEMI analyzer being the dominant analyzer in recent history. The use of CHEMI analyzers is mandated by many environmental regulatory agencies.

The NDIR detectors employ a dual beam infrared cell in which the energy absorbed by the sample as it flows through the sample side of the cell is compared to the energy absorbed by a standard gas mixture, Figure 6. The instrumentation is designed to minimize interferences from other molecules (e.g., CO, CO_2, and H_2O).

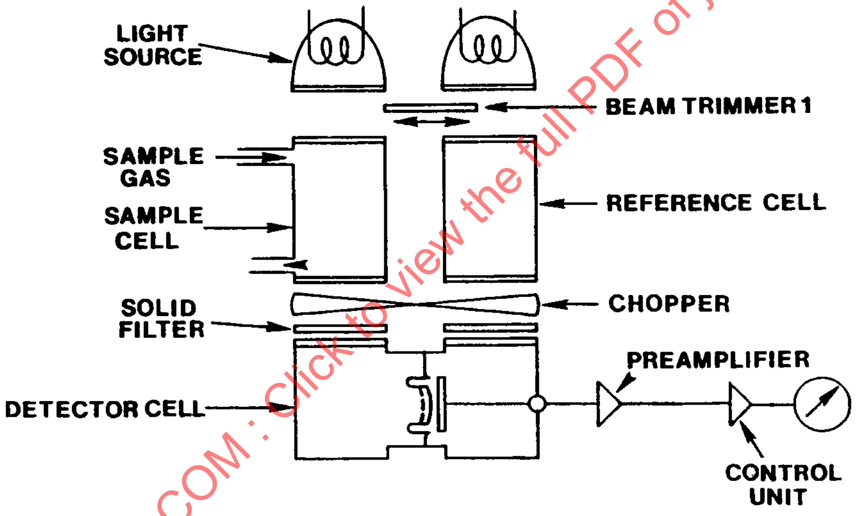

FIGURE 6—A DUAL BEAM NDIR DETECTOR

The operating principle of the CHEMI is based on the bimolecular gas phase reaction between nitric oxide and ozone:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad \text{(Eq. 19)}$$

About 10% of the NO_2 molecules produced in reaction (Equation 19) are in excited state, NO_2^*. The orbital electrons of the excited molecules subsequently return to their ground energy state by two competing reactions:

$$NO_2^* \rightarrow NO_2 + h\upsilon \qquad \text{(Eq. 20)}$$

$$NO_2^* + M \rightarrow NO_2 + M \qquad \text{(Eq. 21)}$$

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Reaction (Equation 20) results in the emission of light energy, $h\upsilon$, which is proportional to the concentration of NO in the sample. This energy is quantified by use of a photomultiplier tube and associated electronic instrumentation, Figure 7. Reaction (Equation 21) results in a quenching effect or a reduction of the amount of energy given off by the NO_2^* molecules as a result of inelastic collisions with other molecules designated by M in the reaction. The instruments are designed to minimize this quenching effect and improve analyzer sensitivity.

In summary, the current state-of-the-art utilizes instruments that measure NO and to determine NO_x requires a NO_2 to NO converter upstream of the instrument. The types of converters and instruments commonly used are discussed in the following sections:

10.1 Converters
10.2 NDIR System
10.3 CHEMI System
10.4 Other Systems

The information is based primarily on the technical literature and limited experience with these units in measuring diesel emissions by the SAE J177 task group.

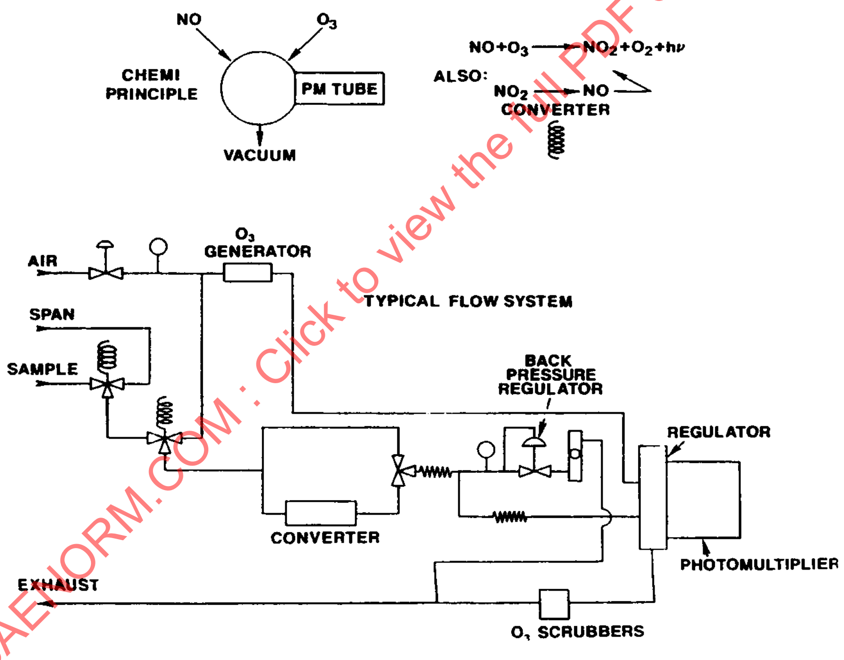

FIGURE 7—CHEMI PRINCIPLE AND TYPICAL SYSTEM

10.1 Converters—Two types of converters currently in use are the catalytic type and the stainless steel thermal type converters. There are several commercial variations of these converters. In general, the catalytic converters operate at temperatures below 400 °C while the thermal converters operate above 630 °C.

10.1.1 START-UP AND OPERATION—Follow manufacturer's instructions. Optimize the analyzer performance as directed by the manufacturer.

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10.1.2 CONVERTER EFFICIENCY CHECK—To insure the effectiveness of the converter, the efficiency should be checked at least every week and preferably before each use. For most cases, the use of zero-grade air will generally be adequate to generate a sufficient amount of NO_2 for converter efficiency checks. If higher concentrations of NO_2 are required, O_2 can be used instead. However, care should be taken to insure there are no leaks in the ozonator, due to the inherent danger of using O_2 in the proximity of electrical contacts.

To determine the efficiency, use the procedure described in 9.1.2.1.

10.1.2.1 Converter Efficiency Check Procedure

a. Start up instrument and optimize performance.
b. Zero and check the calibration of the NO analyzer and then attach the NO_x generator Figure 8.
c. Select an appropriate NO analyzer operating range and introduce NO span gas into the NO_x generator-analyzer system. The NO concentration should be selected to give about 80% deflection on one of the more common operating ranges. Record value.
d. With the oxides of nitrogen analyzer in the NO mode, record the concentration of NO indicated by the analyzer.
e. Turn on the NO_x generator O_2 (or air) supply and adjust the O_2 (or air) flow rate so that the NO indicated by the analyzer is about 10% less than indicated in step (d). Record the concentration of NO in this NO + O2 mixture.

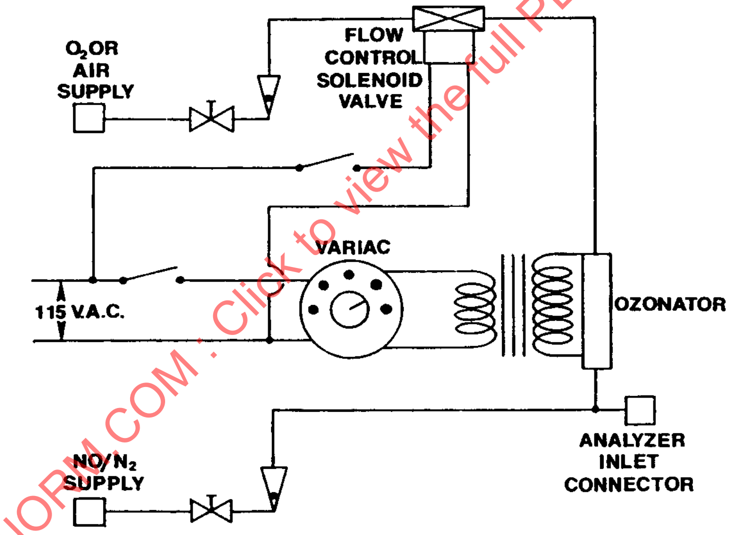

FIGURE 8—SCHEMATIC OF NO_x GENERATOR

f. Switch the NO_x generator to the generation mode and adjust the generation rate so that the NO measured on the analyzer is 10 to 20% of that measured in step (d). There must be at least 10% unreacted NO at this point. Record the concentration of residual NO.
g. Switch the oxides of nitrogen analyzer to the NO_x mode and measure total NO_x. Record this value.
h. Switch off the NO_x generator, but maintain gas flow through the system. The oxides of nitrogen analyzer will indicate the total NO_x in the NO + O_2 mixture. Record this value.
i. Turn off the NO_x generator O_2 (or air) supply. The analyzer will now indicate the total NO_x in the original NO in N_2 mixture. This value should be no more than 5% above the value indicated in step (c).

NOTE—If the No_x generator uses an electrical discharge to produce ozone, it will also produce NO_x from air flowing through it. (This effect will not occur if pure oxygen is used.) Therefore, an additional step is required to determine how much NO_x is produced by the electrical discharge and this amount is subtracted from the amount in step (g).

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j. Calculate the efficiency of the NO_x converter by substituting the concentrations obtained into the following equation:

$$\text{Percent efficient} = \left[1 + \frac{g - h}{c - d}\right] \times 100 \qquad \text{(Eq. 22)}$$

where:

g = Concentration obtained in step (g)
h = Concentration obtained in step (h)
c = Concentration obtained in step (e)
d = Concentration obtained in step (f)

The efficiency of the converter shall be greater than 90%. Adjustment of the converter temperature may be necessary to maximize the efficiency. If the converter does not meet the conversion efficiency specifications, repair or replace the unit prior to testing.

k. Repeat the efficiency check with the new or repaired unit.

10.1.2.2 *Regeneration of Converter*—If the converter is a catalytic type and does not meet the efficiency limitations, the converter may be rejuvenated by flowing air or oxygen through the converter overnight. This depletion of catalyst effectiveness occurs due to operation of the converter for extended periods in an oxygen deficient environment. In analyzing diesel exhaust this is not normally encountered unless prolonged use of span gases with a nitrogen diluent occurs. To minimize this effect, periodically flow air zero gas through the converter. Consult the manufacturer's literature for recommendations regarding converter regeneration requirements and procedures.

This procedure is not as effective for thermal converters but may also be tried.

10.1.3 FLOW CONSIDERATIONS—The commercially available converters are not designed to handle the total exhaust flows of current emission measurement systems. The flow requirements of the NO_x analyzer must be considered in the selection of the converter. The flow limitations can be established by use of the converter efficiency check, 10.1.2.1. (Excessive flow rates result in lower efficiencies and may affect the life of the converter.) The manufacturer's recommendations should be considered in selecting operating flows and pressures.

10.1.4 PROBLEM AREAS—As indicated earlier the information on use of converters in diesel emission systems is limited. Reference 2.1.4 was one of the first efforts to compare systems using these devices. The following paragraphs are some areas noted to which some attention should be paid if a NO_x converter system is used to measure diesel emissions.

10.1.4.1 It is not always evident when a converter loses efficiency during testing. Frequent efficiency checks, 10.1.2, are useful but do not guarantee reliability of the unit. A recommended check just prior to and after testing is to use a stabilized span gas of about 50 ppm NO_2 in nitrogen or any known source of NO_2 and run it through the converter. If the conversion to NO drops below 90%, run the efficiency check in 10.1.2.

The concentration of NO_2 in the bottle used previously should be checked at least monthly immediately after checking the converter efficiency as an internal cross-check on the stability of the NO_2 span bottle. This value should be recorded.

10.1.4.2 Test data in Reference 2.1.4 indicated NO_x readings can be obtained that are lower in value than NO values. The data were obtained at steady-state operating conditions and occurred more frequently at higher load engine operating conditions and with stainless steel converters. However, the crossover did occur with both stainless steel and catalytic types of converters. Some improvement was reported by adjusting the converter operating temperature when measuring diesel exhaust NO_x.

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NOTE—If adjustments are made on the converter, the efficiency has to be rechecked.

When this occurs, the system flow in the NO and NO_x modes should be checked for equal mass flow and the converter checked for leaks.

Three theories which appear to be relevant are:

a. At temperatures below 500 °C (catalytic converters), the reaction in Equation 23 becomes important. The CO value increases with F/A ratio or load in diesels. Directionally, this is what was observed.

$$2NO + CO \rightarrow CO_2 + N_2 \quad \text{(Eq. 23)}$$

b. In the reactors operating above 600 °C (thermal type), reaction (Equation 24) may be an important contributor to the problem. The carbon may be due to very fine organic-particulate matter (References 2.1.21 and 2.1.22) which again is concentration dependent and related to engine operating conditions.

$$C + 2NO \rightarrow CO_2 + N_2 \quad \text{(Eq. 24)}$$

c. A third possibility is that some species such as ammonia is present and is converted to NO at the high converter temperatures.

This phenomenon has to be resolved before truly accurate NO_x data can be obtained.

10.2 Measurement of Total Oxides of Nitrogen With a NDIR System—The use of a NDIR to measure NO_x requires that the NO_2 be converted to NO and interferences from gases such as CO_2 and H_2O be compensated for by the instrument. At least one commercial instrument is available that can be used for NO_x analysis. Instruments for this use should have a minimum water rejection ratio of 10 000:1 and a minimum CO_2 rejection ratio of 30 000:1.

10.2.1 CONVERTER—The converter used is similar to those discussed in 10.1 but they must have sufficient capacity to handle the required flow for the NDIR. One approach is to use a coiled 2 m stainless steel tube of about 0.635 cm OD heated to 630 °C. In building a converter, the contact time, conversion efficiency, and coil temperature profile is important and should be explored. An example of such an investigation is shown in Figure 9. The efficiency checks described in 10.1 are also apropriate here.

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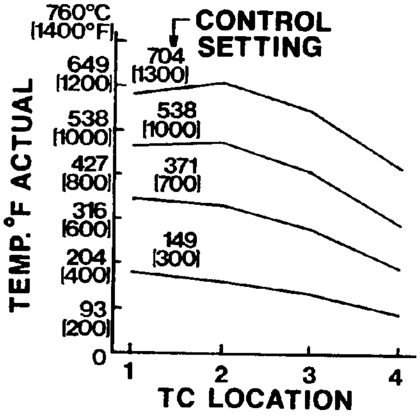
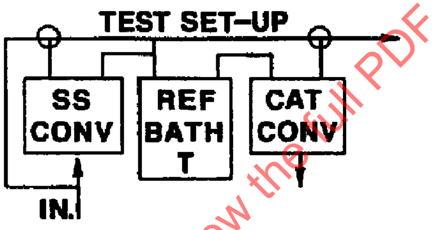
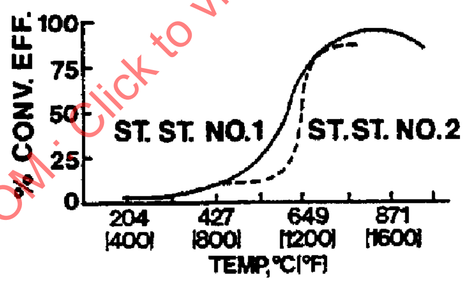


A. TEMPERATURE PROFILE
ST ST CONVERTER
ROOM AIR AT 4500CC/MIN.





B. EFFECT OF TEMP. ON EFFICIENCY

FIGURE 9A—TYPICAL RESULTS ST ST CONVERTER

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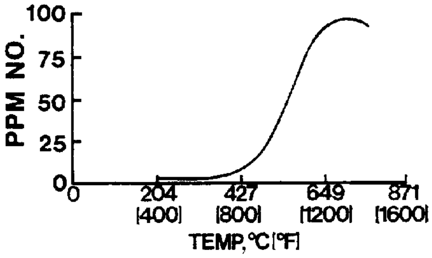

C. NO_2 CONVERSION
100 PPM NO_2
2000CC/MIN

FIGURE 9B—typical results st st converter (continued)

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10.2.2 DETECTOR—Detectors in most current instruments use single detectors as shown in Figure 6. The interferences are minimized satisfactorily by design of the cell and filters for CO and CO_2 analyzers but for NO analyzers, water interference remains a problem. In the system shown in Figure 1, water is removed by the use of a drier. Another method is to use an analyzer with a dual detector and an associated summing amplifier circuit to nullify response to interferences, Figure 10.

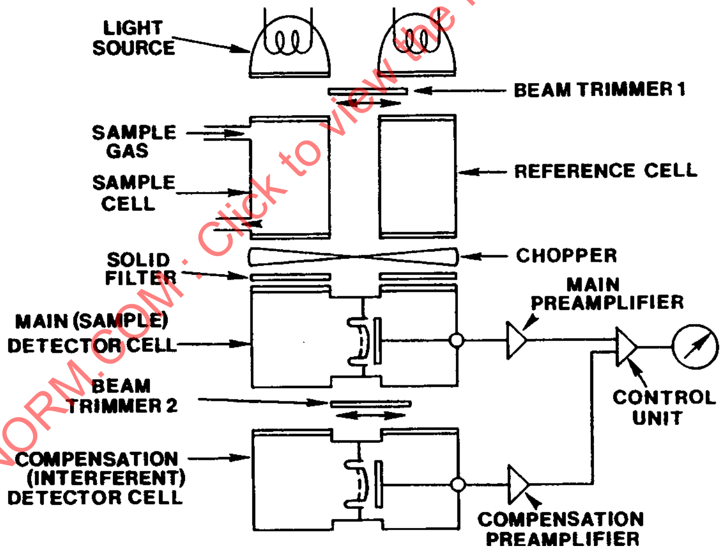

FIGURE 10—NDIR DUAL DETECTOR WITH WATER COMPENSATOR

10.2.3 ANALYTICAL SYSTEM—The system is essentially the same as Figure 4 except the drier tube and bypass valve are eliminated and the converter is placed ahead of the cold bath. It can also be arranged as shown in Figure 11 with the NDIR in place of the CHEMI.

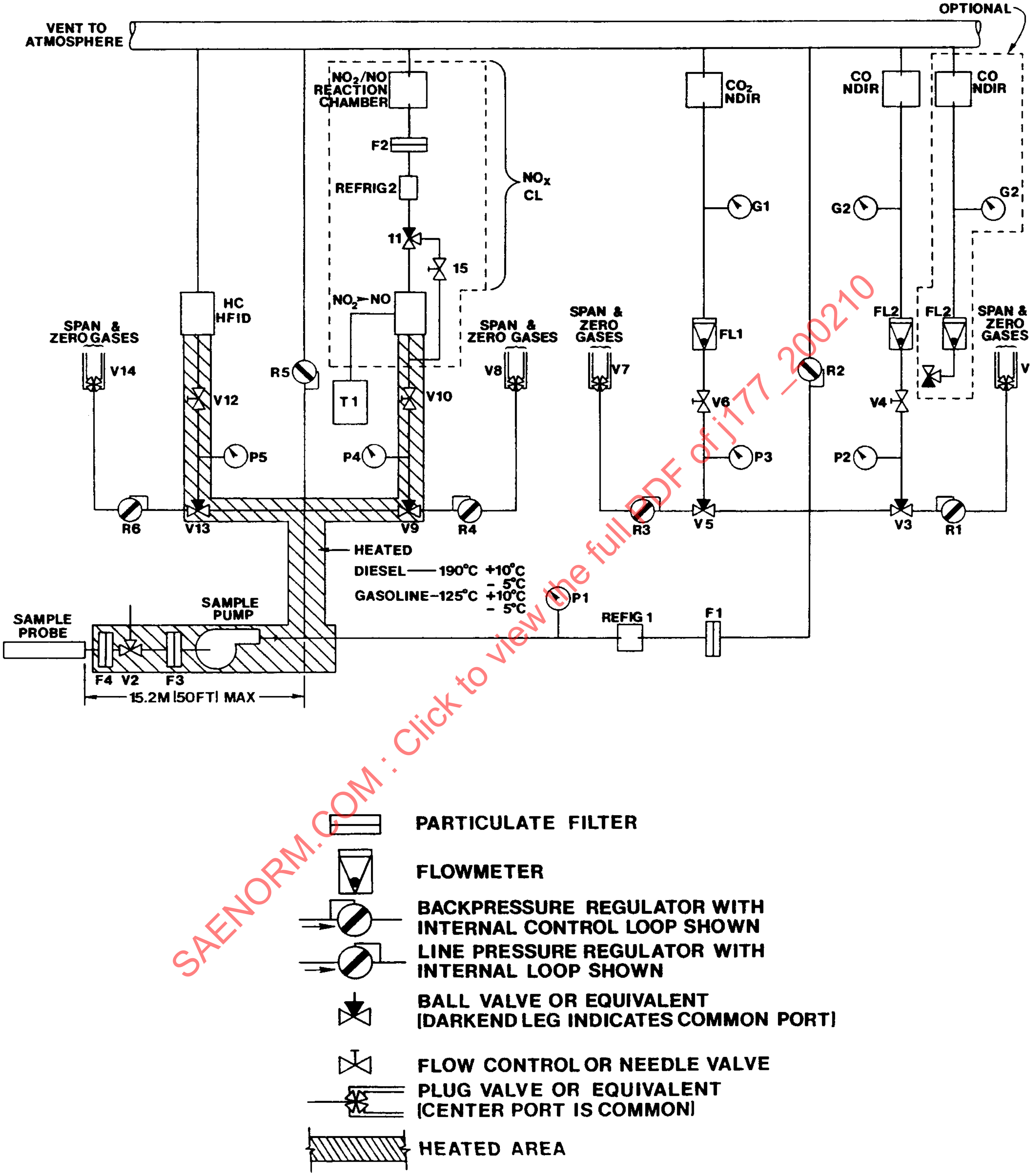

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FIGURE 11—FEDERAL REGISTER SYSTEM (REFERENCE 2.1.7)

10.2.4 DUAL DETECTOR INTERFERENCE ADJUSTMENT—The interference levels of the dual detector's NDIR analyzer should be adjusted prior to calibrating the instrument. Zero and span the analyzer in the most sensitive range. Offset the zero to 5 or 10% so that negative responses can be observed. Introduce zero air saturated with water at room temperature at a point that is downstream of the condenser. Following the manufacturer's instructions, adjust the summing amplifier so that the difference in response (after an adjustment) between dry zero gas and wet air is less than 5 ppm.

Next introduce about 15% CO_2 at a point downstream of the condenser. The difference in response between dry zero and the dry CO_2 should be less than 5 ppm. If additional adjustment of the summing amplifier is necessary, alternately check water interference and CO_2 interference until a satisfactory compromise is obtained. Computation of the water rejection ratio and the CO_2 rejection ratio is described in Reference 2.1.7. Recheck and adjust the zero and span settings if necessary.

10.2.5 OPERATING PROCEDURE—Follow procedures in 5.3 as appropriate.

10.2.6 ENGINE EMISSIONS MEASUREMENT PROCEDURES—Follow Section 6 with the exception of the following changes:

a. 6.2(c)—Not applicable.
b. 6.2(d)—Change to measure CO_2, CO, NO, and NO_x as follows:
    1. For CO, CO_2, and NO_x, operate for at least 10 min in each mode, allowing at least 5 min for emission measurement.
    2. For NO measurement, add an additional minute after NO_x measurement. For this minute, switch to the NO mode bypassing the converter.
    3. See 6.2(d)(2).
    4. See 6.2(d)(3).

10.2.7 CHART READING—See 5.3.

10.2.8 RECORDED INFORMATION AND CALCULATIONS—(See section 7) and (See section 8). Add the following to 7(d):

$$NO_x, g/kWh = 9.50(10^{-2})(\text{Mass Exhaust})(\text{ppm } NO_x)/kW \qquad \text{(Eq. 25)}$$

10.3 Measurement of Total Oxides of Nitrogen With a Chemiluminescence System—The use of the CHEMI for NO_x measurements requires the use of a converter to reduce the NO_x in the gas stream to NO. Interferences due to CO_2 and water have to be minimized. Several types of commercial instruments are available utilizing vacuum and nonvacuum systems (Reference 2.1.4).

10.3.1 CONVERTER—Several types of converters are commercially available. Usually the manufacturers of the CHEMI includes the converter as part of the instrument package or makes recommendations as to the best match-up. Both catalytic and thermal units are used. See 10.1 for additional information on converters.

10.3.2 DETECTORS—The principle of the detectors was discussed in Section 10. A typical unit is shown in Figure 8.

10.3.3 ANALYTICAL SYSTEM—A typical system would be similar to that in Figure 11 (Reference 2.1.7). Changes to Figures 1 and 4 would include:

a. The drier and drier-bypass would not be required.
b. The NO_2 converter would be located ahead of the refrigerator bath.
c. The refrigerated bath would not be required if the sample was heated up through the converter to the CHEMI. Some typical CHEMI arrangements (Reference 2.1.4) are shown in Figure 12.

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