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(R) INSTRUMENTATION AND TECHNIQUES FOR EXHAUST GAS EMISSIONS MEASUREMENT

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***Foreword*—**This Document has also changed to comply with the new SAE Technical Standards Board format.

1. Scope

***Scope*—**This SAE Recommended Practice establishes uniform laboratory techniques for the continuous and bag-sample measurement of various constituents in the exhaust gas of the gasoline engines installed in passenger cars and light-duty trucks. The report concentrates on the measurement of the following components in exhaust gas: hydrocarbons (HC), carbon monoxide (CO), carbon dioxide (CO_2), oxygen (O_2), and nitrogen oxides (NO_x). NO_x is the sum of nitric oxide (NO) and nitrogen dioxide (NO_2). A complete procedure for testing vehicles may be found in SAE J1094.

This document includes the following sections:

1. Scope
2. References
3. Emissions Sampling Systems
4. Emissions Analyzers
5. Data Analysis
6. Associated Test Equipment
7. Test Procedures

1.1 Purpose—The purpose of this document is to describe means for the analysis of exhaust emissions. This procedure has been developed after thorough review and consideration of test techniques in use in laboratories of federal and state governments, and the automobile and petroleum industries.

2. References

2.1 Applicable Publications—The following publications form a part of this specification to the extent specified herein. The latest issue of SAE publications shall apply.

2.1.1 SAE PUBLICATIONS—Available from SAE, 400 Commonwealth Drive, Warrendale, PA 15096-0001.

SAE J1094—Constant Volume Sampler System for Exhaust Emissions Measurement
SAE J1263—Road Load Measurement and Dynamometer Simulation Using Coastdown Techniques

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3. Definitions

3.1 **Bag Sample—**Ambient air or vehicle exhaust collected during various segments of the driving test cycle for analysis.

3.2 **Calibrating Gas—**A precisely analyzed gas of known concentration, used to determine the response curve of an analytical instrument.

3.3 **Chemiluminescent Analyzer—**An analytical method for determining the NO_x concentration in exhaust gas.

3.4 **Chassis Dynamometer—**A laboratory-power absorption unit, capable of simulating the inertia and road-load power developed by a vehicle.

3.5 **Cooler—**A device capable of sufficient refrigeration to maintain condenser temperatures in the analytical train at 2 °C ± 1 °C (35 °F ± 2 °F).

3.6 **Curb Weight—**The weight of the vehicle in operational status, with all standard and commonly installed optional equipment, and the gas tank filled to nominal capacity.

3.7 **Detector—**That component in an analytical instrument which responds to a particular exhaust gas constituent.

3.8 **Driver's Aid—**An instrument intended to guide the vehicle driver in operating the vehicle in accordance with the specified acceleration, idle, deceleration, and cruise operating modes of a specific driving procedure.

3.9 **Exhaust Emissions—**Any substance (but normally limited to pollutants) emitted to the atmosphere from any opening downstream from the exhaust point of the combustion chamber of an engine.

3.10 **Flame Ionization Detection Analyzer (FID)—**An analytical instrument used for determining the carbon concentration of hydrocarbons in a gas sample.

3.11 **Hang-up—**The absorption-desorption of sample (mainly higher molecular weight hydrocarbons) from the surface of the sample system that can cause a delay in instrument response and lower concentration at the analyzer, followed by higher readings in subsequent tests.

3.12 **Inertia Masses—**A series of rotating masses on a chassis dynamometer, used to simulate the test mass of a vehicle.

3.13 **Loaded Vehicle Mass—**The manufacturer's estimated mass of a vehicle in operating condition. For the purpose of emission testing, it is the curb mass of a light-duty vehicle plus 136 kg (300 lb).

3.14 **Lox-Service Cleaning—**Process where sampling system plumbing is cleaned thoroughly prior to flowing liquid oxygen (LOX). Hydrocarbon contamination is removed by rinsing with a solvent that will not generate emission constituents.

3.15 **Mode—**A particular event (for example, acceleration, deceleration, cruise, or idle) of a test cycle.

3.16 **Nondispersive Infrared (NDIR) Analyzer—**An analytical instrument currently used to determine CO and CO_2 in exhaust gas.

3.17 **Probe—**A device inserted into some portion of an engine or vehicle system in order to obtain a representative gas or liquid sample.

3.18 **Reference Cell—**That portion of the NDIR instrument which contains the reference gas for comparison with the sample.

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3.19 Response Curve (Calibration Curve)—A line drawn through at least six points established by calibration gases, which determines the analytical instrument's sensitivity to unknown concentrations.

3.20 Sample Bag—A container made of nonabsorbent material, used to collect ambient and exhaust samples.

3.21 Sample Cell—That portion of the analytical instrument through which the sample gas being analyzed passes.

3.22 Sampling, Bag—A technique for collecting a sample of exhaust gas during a period of a test cycle and storing it for future analysis.

3.23 Sampling, Continuous—A technique in which a portion of the exhaust is continuously withdrawn for immediate analysis.

3.24 Span Gas—A single calibrating gas blend routinely used to adjust the calibration of an analyzer just prior to its use.

3.25 Test Cycle—A sequence of engine or vehicle operating modes, usually designed to simulate road usage of the vehicle.

3.26 Zero Gas (Zero Air)—A pure gas, such as nitrogen or air, used to determine the zero point of an analyzer's response curve.

4. Emissions Sampling Systems

4.1 Continuous (Undiluted Exhaust Gas)—Figure 1 shows a typical sampling system for the continuous measurement of exhaust-gas products emitted from the tailpipe of a vehicle. Such a system generally consists of sample probes, sample lines, coolers, particulate filters, positive displacement pumps, flow regulators and flow meters, and desiccators.

4.1.1 SAMPLE PROBE—The sample probe is the inlet to the sample system. It is recommended that this probe be constructed of stainless steel tubing, typically 6 mm (0.25 in) OD; it is usually part of a fixture which adapts to the end of the tailpipe of the vehicle. To minimize induction of ambient air, the end of the probe is extended into the tailpipe 30 to 45 cm (12 to 18 in) (if possible). The most desirable probe location is parallel to the exhaust flow, facing upstream. The sample probe fixture may slip over the outside of the tailpipe and be used with either a flexible adaptor (silicone rubber) or thermosetting-fiberglass-backed adhesive tape. This arrangement provides a seal which does not allow dilution of the exhaust gas with ambient air. Design of the probe fixture should also allow for unrestricted exit of the remaining exhaust gas (that which is not inducted into the probe) to either an exhausting system or another test apparatus such as a constant volume sampler (see SAE J1094). A valve should be located at or near the tailpipe fixture to allow purging of the sample probe and the rest of the analysis system with prepurified dry nitrogen gas or clean, dry air. The test probe for engine dynamometer testing should be located to approximate the sampling location in an actual exhaust system of the vehicle.

In work with single-cylinder engines, or with the exhaust of a single cylinder of a multicylinder engine operating over a transient duty cycle, the proper probe location is difficult to define because of a varying degree of stratification of the concentrations of the various exhaust products which exist along the length of the exhaust pipe.

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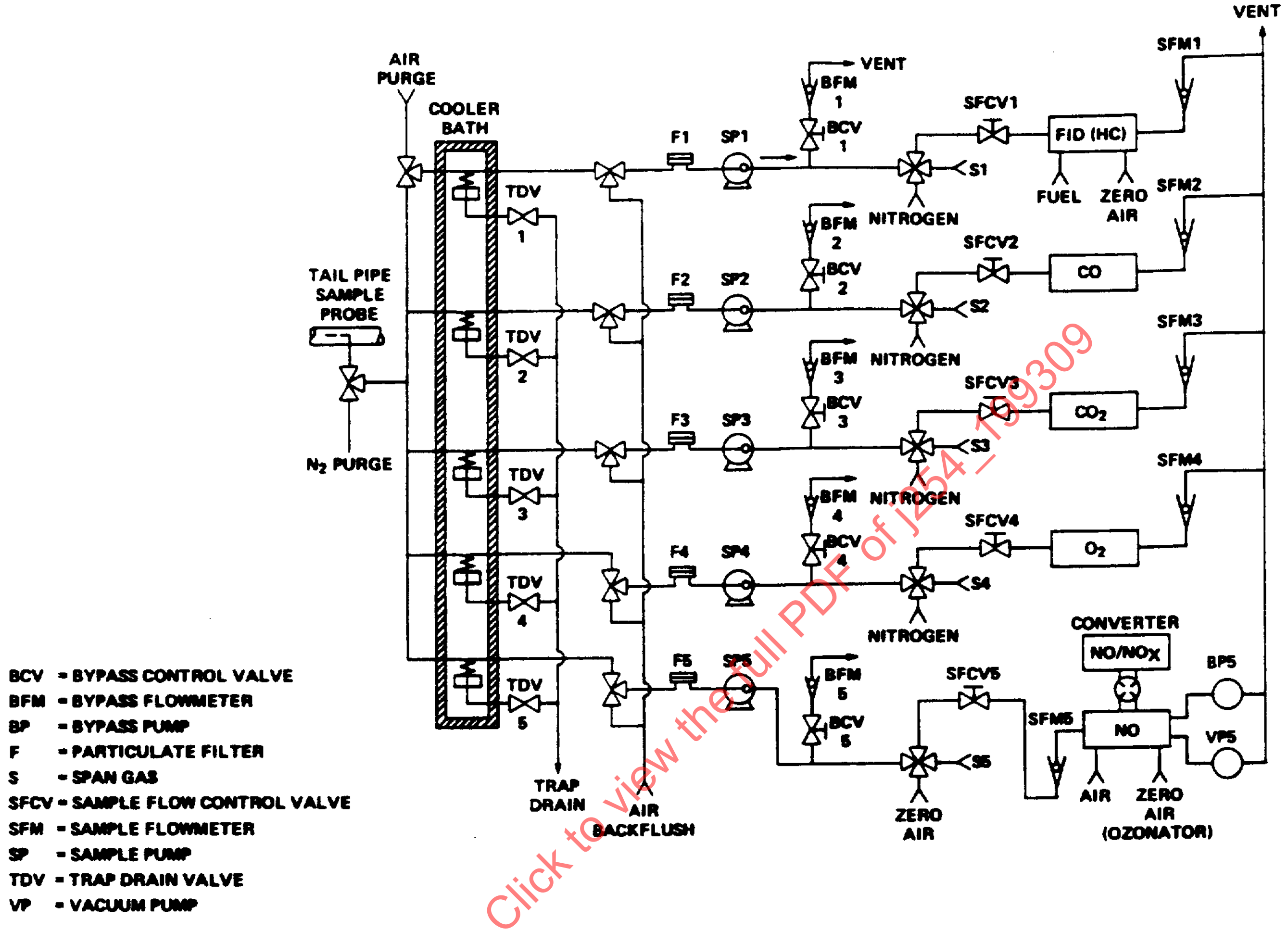

FIGURE 1—A CONTINUOUS UNDILUTED EXHAUST GAS ANALYSIS SYSTEM

4.1.2 SAMPLE LINE—The sample line carries the exhaust gas inducted into the sample probe to the condensers which are usually located close to the analysis system. This line is typically 6 mm (0.25 in) OD and should be made of stainless steel or Teflon (or equivalent). Teflon tubing with a flexible outside protective covering is recommended because it practically eliminates the hang-up from this part of the sampling system. If the ID is 6 mm (0.25 in), it can easily be joined to 6 mm (0.25 in) OD stainless steel tubing. The length of this sample line should be kept to a minimum, since its length is directly related to the delay time of the entire system; in many cases, it will be found to be responsible for the major portion of the delay time. Excessive delay times usually result when the line from the sample probe to the cooler is too long, or the sample flow rate is too low. Room restrictions may prohibit the use of short sample lines; therefore, other means, such as increasing the sample flow rate or simply determining the extent of the delay and accounting for it when processing the data, may have to be used. All tubes connecting the various components of the sampling system should be either stainless steel or Teflon, and should also be as short as possible.

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4.1.3 COOLER—The cooler condenses and removes the water contained in the exhaust gas sample. This is required because many analyzers have a strong response to water vapor, and also to prevent condensation of water in the analyzers.

There are a number of acceptable cooler configurations. Two types which have proved effective are the ice-bath cooler and the refrigerated-water bath. Both of these utilize a cooling coil of 6 mm (0.25 in) OD [uncoiled length is approximately 3 m (10 ft)] which empties into a trap with a volume not to exceed 60 to 80 cm^3 (4 to 5 in^3) for each leg of the analysis system. Figure 1. A drain and toggle valve are provided to remove the water collected in each trap. The cooling coils are usually clustered in a common, insulated chest which can be filled with ice and water, or a water glycol solution, which can be kept near 2 °C (36 °F) with an electrically-powered refrigeration system. Keeping the coolant slightly above 0 °C (32 °F) eliminates water freezing in the trap. A mixer in the coolant helps to maintain a constant temperature. (Corrections for water removed may be needed. See Section 6.)

4.1.4 SAMPLE FILTER—Borosilicate glass fiber filters of approximately 7 cm in diameter with an appropriate holding fixture of low internal volume should be used (one in each leg of the sample system, Figure 1), to remove any particulate matter which may be present. These filters also tend to stop water droplets which may have passed the cooler. Contaminated filters can result in excessive hangup and should be changed frequently (as often as each test, and if experience indicates the need, even during a test).

4.1.5 SAMPLE PUMPS—A pump that supplies a constant flow rate (typically 20 L/min with pump inlet and outlet at atmospheric pressure) can be used in each leg of the analysis system to pull the sample from the probe and then push the sample through the analyzer. Arrangements with a single-sample pump are also possible. To minimize hangup, pumps with stainless steel metal bellows or Teflon coated diaphragms should be used. Carbon vane or piston pumps which may introduce a hydrocarbon lubricant into the sample gas are to be avoided. The pump and motor should be mounted to eliminate the transmission of mechanical vibrations to the connecting sample lines and analyzers. An effective means of accomplishing this is to use short, flexible Teflon tubing (stainless steel braided for safety), to carry the sample gas to and from the pump, and to isolate the pump and motor with shock mounts. Small mechanical vibration of the analyzers may affect their output.

4.1.6 FLOW CONTROL AND MEASUREMENT—The pump for each analyzer should be allowed to pull as much sample as it can through the sample system to reduce the lag time required to move the sample from the tailpipe to the analyzer. An optional means of increasing the sample flow rate is to use a sample flow bypass. Immediately following each pump, a bypass line allows sample gas to be dumped to a waste system with the remaining 5 L/min proceeding through the analyzer. The bypass flow is regulated by an adjustable needle valve (stainless steel), and monitored with a rotameter-type flowmeter with at least 10 L/min capacity using a stainless steel or inert material float. [High sample rates for raw (undiluted) exhaust analysis should not be used simultaneously with dilute CVS-type analysis, as the raw sample flow will cause an error in the mass emissions obtained from the CVS calculations.]

4.1.7 Extreme care must be taken to assure that all sample system connections are leak free.

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4.2 Emissions Sampling Systems--Bag Analysis—These tests yield average emission values for various periods of a complete test by a single measurement of each bag sample. The analysis can determine whether a vehicle will pass surveillance or compliance tests. SAE J1094 describes this technique. Figures 2 and 3 show a six-bag sample gathering system and an analytical system, respectively.

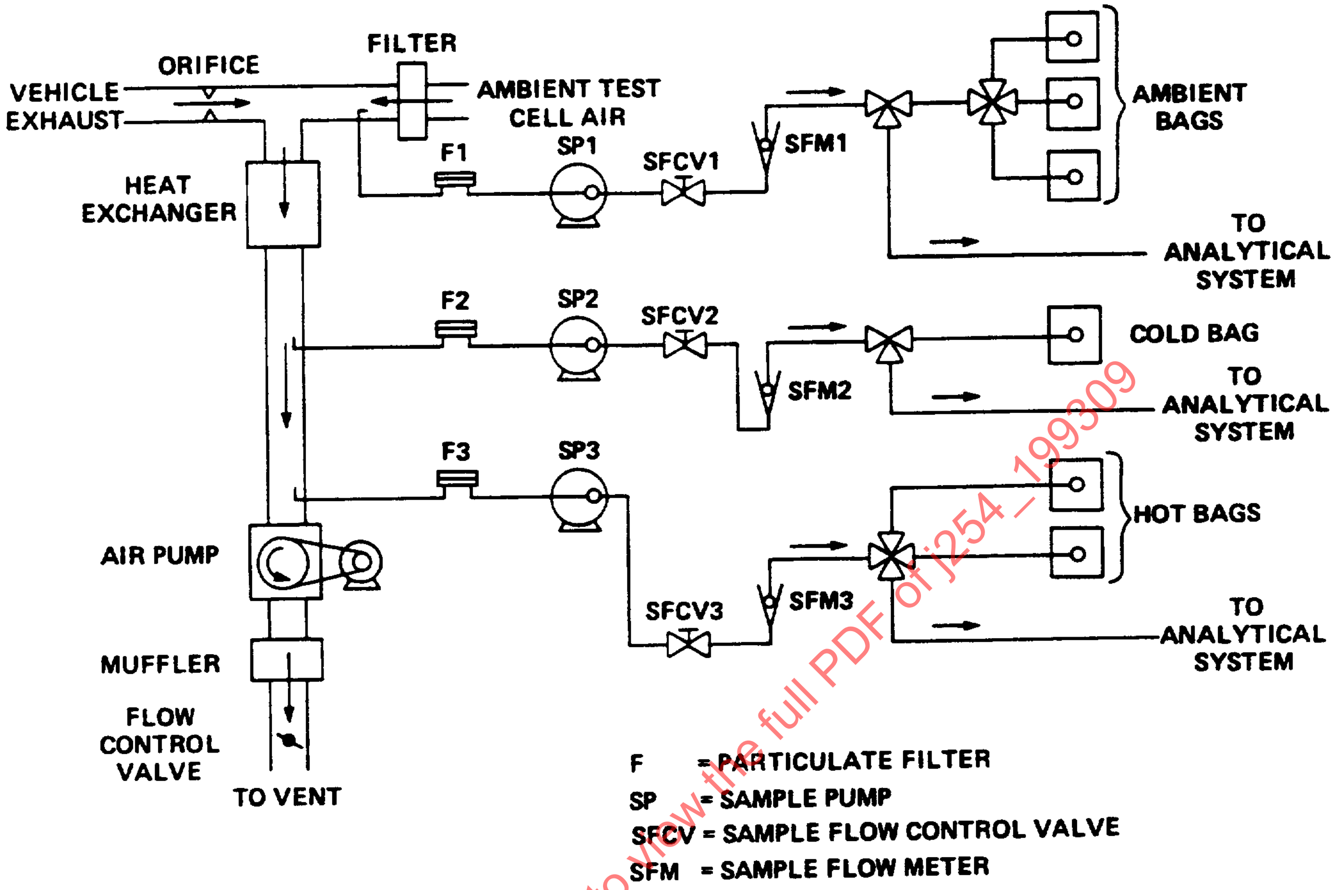

FIGURE 2—A REPRESENTATIVE SIX-BAG EMISSIONS SAMPLE GATHERING SYSTEM (CONSTANT VOLUME SAMPLER)

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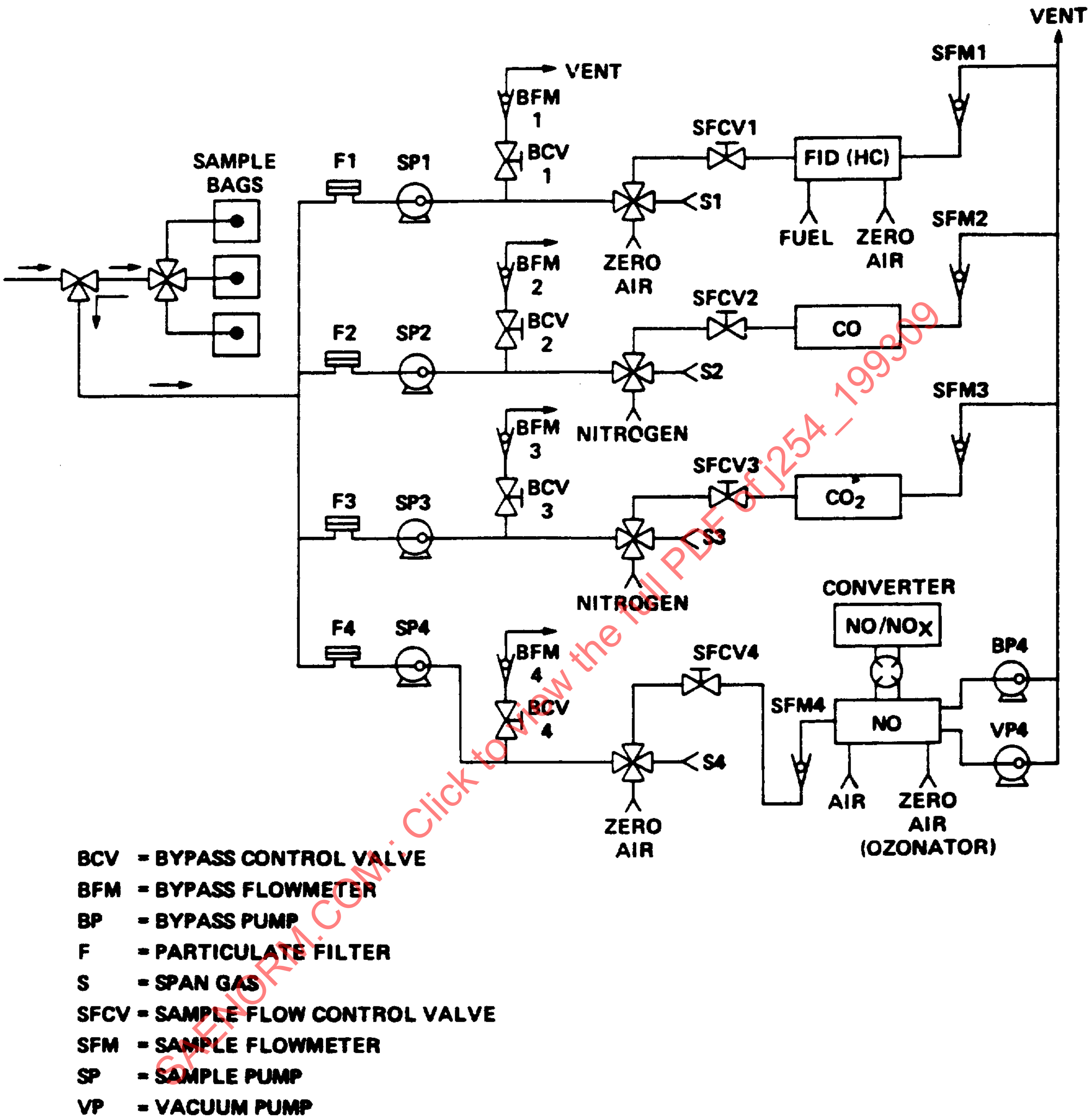

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FIGURE 3—A REPRESENTATIVE ANALYTICAL SYSTEM FOR SAMPLE BAG MEASUREMENT

In this constant volume (variable dilution) proportional sampling technique, a sampling pump draws a constant volume flow rate, for example, 8.5 m^3/min (300 scfm). This flow consists of the total exhaust of a vehicle with the remainder made up of dilution air. The technique allows for monitoring of continuous emissions on a mass basis and also, with the addition of a second pump, provides an aggregate total mass sample from a vehicle operated through an entire test cycle.

5. *Emissions Analyzers*

5.1 Nondispersive Infrared Analyzer—NDIR analyzers shown in Figure 4 are primarily used to determine concentrations of CO and CO_2 in exhaust gas. Although not recommended, NDIR analyzers can also be used to measure NO and HC.

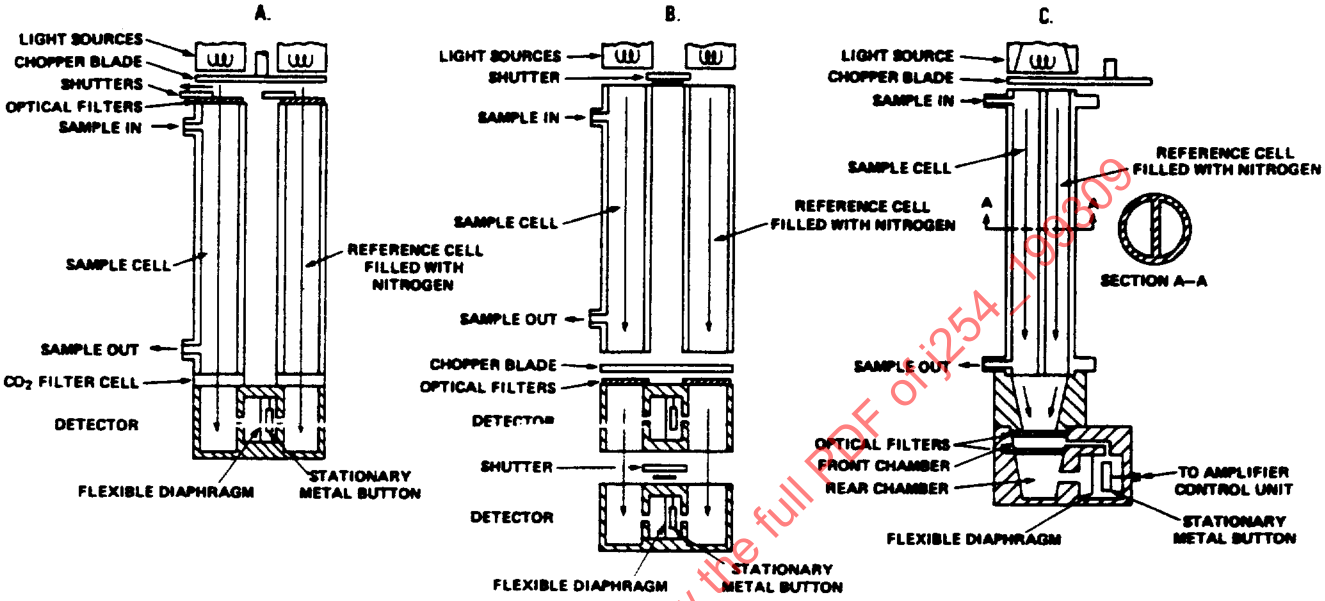

FIGURE 4—THREE NONDISPERSIVE INFRARED ANALYZERS SHOWING DIFFERENT DESIGNS USED TO MINIMIZE THE EFFECTS OF INTERFERING GASES

5.1.1 Theory—The NDIR analyzer detects the infrared energy absorption differential between two gas-filled columns. The gas whose concentration is to be determined is flowed through the sample column. The reference column is filled with a nonabsorbing gas such as dry air. In a nondispersive instrument, no attempt is made to separate the infrared energy into discrete wavelengths, but rather to make use of the principle that gas molecules absorb discrete bands of infrared energy.

The infrared radiation is passed through the sample and reference columns into a detector that has two cells which are physically separated by a flexible, metal diaphragm. These two detector cells contain the same gas that is to be analyzed. When the gas in the detector receives infrared energy, the pressure increases in that cell because the absorbed energy heats the gas. With no infrared absorbing gas in the sample column, both cells of the detector receive the same amount of energy and the pressure in the two cells is identical. However, if a gas sample is flowing in the sample column, some of the infrared energy will be absorbed by the gas. This means less energy will arrive at the sample cell side of the detector and the pressure in that cell will be less. This will cause the flexible metal diaphragm to move. The metal diaphragm is used as one plate of a variable plate capacitor in a tuned electric circuit.

To make the diaphragm oscillate, thus creating a detector output signal, a chopper blade driven by a synchronous motor periodically interrupts the sample and reference energy beams in the range of 5 to 10 Hz. In some cases, the 5 to 10 Hz signal can modulate a carrier frequency of 10 MHz or so, which is demodulated to obtain a DC signal that is more practical. The amplitude of the diaphragm oscillation, which is a measure of the concentration of the gas, is converted from a variable capacitance into an AC signal, amplified, and synchronously rectified to give a DC output signal.

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5.1.2 INTERFERENCES—Since exhaust gas is a multicomponent gas mixture, several gases in it may have absorption bands that overlap the absorption bands for CO and CO_2. To make an NDIR analyzer insensitive to interfering gases, an optical filter, or a cell charged with the interfering gas, may be used to filter out unwanted portions of the infrared absorbing spectrum.

Various sample detection system configurations have been used to alleviate undesirable interference signals occurring in the low CO concentration ranges. Individual design variations are described in 5.1.3.

5.1.3 ANALYZER DESIGN VARIATIONS—The analyzer shown in Figure 4A produces infrared radiation from two separate energy sources. This radiation is beamed separately through a chopper. The beams pass through a combination filter cell and optical filter assembly that reduces the interference effects of water vapor and other interfering gases.

The analyzer shown in Figure 4B has dual collimated infrared radiation sources. The response of the detector to other infrared absorbing components in the sample stream is minimized by the stacked nature of its construction. The detector has two sets of chambers. The infrared beams enter the first set of chambers, pass through them by means of a transparent bottom into the second set of chambers. The signal detected in the first chamber consists of a large part of the IR absorption signal of the components of interest in the sample stream and a small part of the IR absorption signal of the other components. The second chamber signal provides a much lower-level absorption signal of the component of interest, but approximately the same signal from the interfering components. The interfering gas signal from the lower chamber is electronically subtracted from the upper chamber signal of interest. To further minimize interference, optical filters are placed in front of the detector to cut out those IR beams in the radiation sources which are not necessary for detecting the IR absorption of the component of interest.

Infrared source imbalance is eliminated through use of a single radiation unit in the CO analyzer shown in Figure 4C. The two measurement chambers of the detector are in series in the combined ray path and are connected via channels to the detector diaphragm. The absorption spectrum of the gases is a band composed of a number of absorption lines. In the shorter, front-measuring chamber of the detector, absorption of the radiation takes place primarily in the center of the absorption band as it does when CO is present in the sample cell. Radiation in the outer edges of the band is absorbed in the longer rear measuring chamber. Since absorption by interfering species falls in both the center and edges of the various CO bands, it can be nearly eliminated by subtraction of signals from the front and rear chambers.

In any of the previous configurations, the oscillating-diaphragm detector could be replaced by a microflow gas sensor.

5.1.4 CALIBRATION—The instrument is calibrated by passing several gases of known concentrations through the analyzer to establish a response curve as shown in Figure 5. Gases with nominal concentrations of 15, 30, 45, 60, 75, and 90% of the maximum level on a given analyzer range should be used. These gases should have values traceable to National Institute of Standards and Technology (NIST) reference gases. In addition, the response curve must be smoothed to the calibration data points by using a suitable curve fitting technique. If any point does not fall on a smooth curve, it must be considered suspect; that calibration standard gas should not be used until its concentration can be verified. Cylinder contamination, mislabeling, or some other reason may have resulted in an error.

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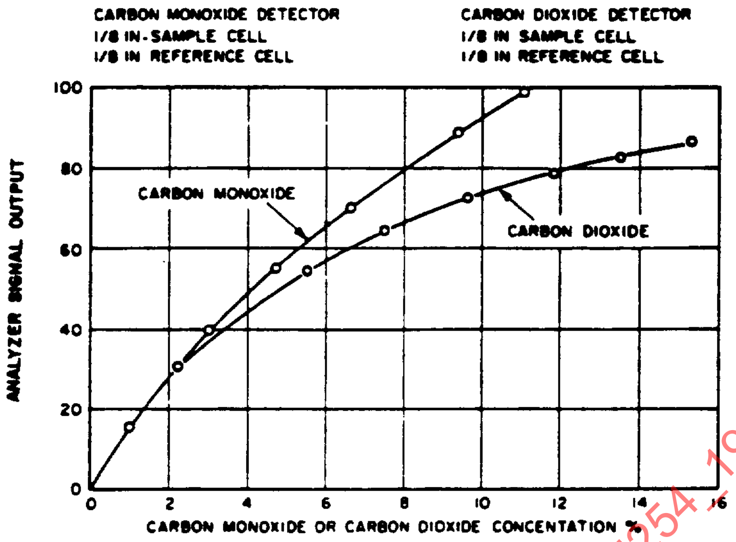

FIGURE 5—TYPICAL NDIR ANALYZER RESPONSE CURVES TO CARBON MONOXIDE AND CARBON DIOXIDE

5.1.5 CELL PRESSURE—An NDIR analyzer output depends upon the cell pressure. Since the cell is generally at atmospheric pressure, changes in atmospheric pressure between the main calibration and the sample readings are corrected with a span gas prior to the reading. Maintaining constant flow rates of the sample gases throughout the sample system will generally insure that the span and sample readings are made at the same pressure.

The exhaust of the emission analyzer should be plumbed to the laboratory exhaust system and then vented freely into the exhaust system. This plumbing must not put any significant back pressure on the analyzer cell. Care must be taken to avoid conditions at the analyzer sample gas outlet that could create variations in the back pressure to the sample cell. Pressure variation in the sample cell causes a sample-gas density variation which directly affects the analyzer output. If outlet pressure variations exceed 5 mm H_2O, a back pressure regulator may be required.

5.1.6 SPEED OF RESPONSE—The speed of response of NDIR instruments is usually limited by flow rate, the sample-cell volume, and the time constant of the electronics. The electronic amplification supplied in modern instruments is generally adequate. However, the speed of response is related to the instrument sensitivity. In order to be able to detect low concentrations, path length, and therefore, cell volume is increased to permit more of the energy to be absorbed in the sample. This means that as the cell volume is increased, the flow must be increased to maintain the same speed of response.

5.1.7 RESPONSE—The response of NDIR CO and CO_2 instruments is nonlinear due to energy absorption characteristics as approximately described by Beer's law Figure 5. The output of the instrument can be made linear using appropriate linearizing circuits. Beer's law states that the exponential output signal, E, is related to the sample gas concentration, c, by the expression;

$$E = A(1 - e^{-kcx}) \qquad \text{(Eq. 1)}$$

where A is the amplification factor, k is the gas absorption factor for a particular gas, and x is the length of the sample cell. This expression is useful in qualifying an instrument, but because of detector characteristics and characteristics of the signal conditioning by the electronics, it should not be used in place of a multipoint calibration. Even with linear instruments, at least 6 calibration gases spread evenly over each range of the instrument must be used to verify the linearity of the instrument.

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5.1.8 Signal Noise—Noise is the unwanted part of the signal that degrades instrument accuracy. Noise can be caused by many things, but the most common are:

a. Cell misalignment
b. Low detector signal output
c. Dirty cells
d. Poor electrical connections
e. Improper chopper blade alignment and synchronization
f. Pressure fluctuations from changes in flow rate

Connecting an active filter between the first stage of signal amplification and the phase inverting network of the analyzer signal conditioner reduces the noise level considerably, with little effect on response time. Care should be taken when making this type of modification.

5.2 Flame Ionization Detector—Hydrocarbons—The flame ionization detector (FID) is used to measure the total hydrocarbon content of complex-hydrocarbon mixtures on a carbon-mass basis. This measurement can be converted to a hydrocarbon-mass basis by assumption of a specific carbon to hydrogen ratio.

5.2.1 Description—The burner of a typical FID is similar to that shown in Figure 6. A small stream of fuel, hydrogen diluted with an inert gas, is premixed with the sample gas and burned at the outlet of the jet in a diffusion flame with air.

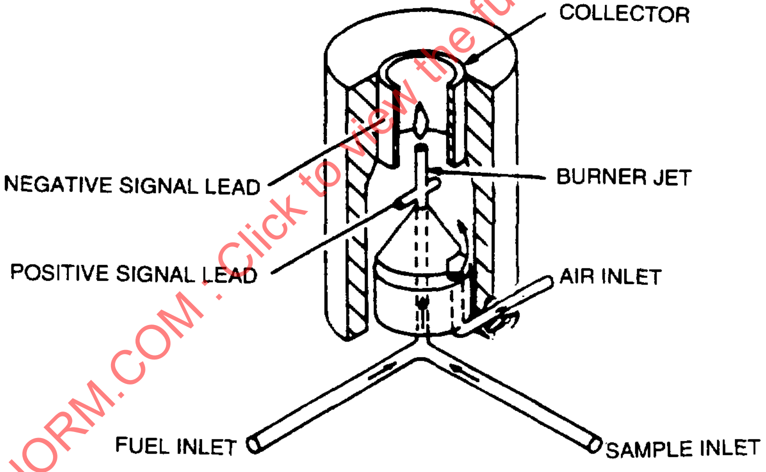

FIGURE 6—TYPICAL BURNER OF FLAME IONIZATION DETECTOR

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The FID operates on the principle that the introduction of a gas sample containing hydrocarbon into a hydrogen diffusion flame will increase the concentration of ions within the flame. This increase in ionization is almost directly proportional to the mass flow rate of carbon atoms into the flame. A DC voltage between the burner tip and a collector electrode, which surrounds the flame, collects the ions within the flame, causing current to flow through the associated electronic measuring circuits.

5.2.2 Interferences—Under normal operating conditions, a FID has no significant response to any non-organic carbon constituent found in exhaust gas. The presence of O_2 in the sample, though, can interfere with the accuracy of the hydrocarbon measurement.

5.2.3 RELATIVE RESPONSE—To obtain accurate analysis of complex hydrocarbon mixtures, it is necessary that the FID response to each carbon atom in the sample be the same as the single hydrocarbon calibration gas, i.e., uniform relative response. The presence of O_2 in the sample can cause the relative responses of the various sample gas hydrocarbon constituents to differ substantially from that of the calibration gas. It has been suggested that this is due to preflame oxidation of the hydrocarbons at the core of the flame which prevents later ionization. Since the ease of oxidation of a hydrocarbon is different for each species, preferential oxidation takes place, which results in differing sensitivities for each hydrocarbon, i.e., nonuniform relative response. Several investigators have shown that more uniform relative response can be obtained by the following steps.

a. Maintain sample flow rate to the FID burner at a minimum to reduce the O_2 concentration within the core of the flame available for preflame oxidation.
b. Use high fuel flow rate to the FID burner to dilute any O_2 entering with the sample, again reducing the O_2 concentration.
c. Use H_2-He mixed fuel instead of H_2-N_2 fuel. Since the fuel type changes the response to various hydrocarbons, it is important to use the specified fuel in complying with governmental standards.
d. Select a calibration and zero gas with an oxygen content approximating that of the sample to be analyzed, as this will tend to normalize the relative response between sample and span gas.

Because sample, fuel, and air flow rates affect the uniformity of relative response of a FID to the various exhaust hydrocarbons, good correlation between FID's of the same model will occur only when their flow rates are the same. To establish correlation between dissimilar FID's, it may be necessary to actually determine their relative response to several major hydrocarbon species and normalize them by adjustment of sample, fuel, and air flow rates for equal relative response. As an initial guide in setting flow rates, the following is recommended:

a. Sample Flow — 3 to 5 cm^3/min
b. Fuel Flow — Adjusted for maximum response
c. Air Flow — 3-1/2 to 4 times the fuel flow rate

The response of the FID to the carbon in oxygen-containing organic compounds (such as alcohols, ethers, and aldehydes) will usually be less than to the carbon in hydrocarbons.

5.2.4 VISCOSITY—The response of an FID is directly proportional to the volumetric sample flow to the FID burner. Therefore, a stringent control of sample flow rate is mandatory. Because most FID's use a pressure-regulated capillary flow control system, the sample flow to the burner is dependent on both sample pressure and viscosity. Any change in sample viscosity will, therefore, result in an inversely proportional change in apparent reading, though pressure has remained constant. It is, therefore, necessary to use a calibration gas whose viscosity approximates that of the sample being measured. In actual practice, this is usually neglected because the error is small.

5.2.5 OPERATION—The typical FID, with proper use, is capable of accurate measurement of hydrocarbon concentrations over a very wide dynamic range—commonly several orders of magnitude. To best optimize the accuracy of measurements, especially when using FID ranges of 300 ppmC (C = carbon atoms) or less, the following guidelines are recommended.

5.2.5.1 *Fuel and Air*—Many problems are caused by impurities in the gases and/or lack of cleanliness of regulator and external connecting tubing. The utmost care should be exercised to insure that tubing, fittings, and regulators are not only clean upon installation, but that they remain clean during use. Contaminated burner air is a common cause of high background noise level. Consequently, the use of pure air of less than 3 ppm hydrocarbon impurity is recommended for low level hydrocarbon measurements. An elastomer diaphragm regulator may be used for the burner air, but should be LOX-service cleaned. The hydrogen fuel gas must be essentially hydrocarbon-free, i.e., less than 1 ppmC. A metal diaphragm LOX-service cleaned fuel regulator is required. It is also important that supply gases and lines be maintained at a

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relatively constant temperature as temperature fluctuation will result in absorption-desorption of hydrocarbons which will appear as analyzer drift.

5.2.5.2 *Calibration Gases*—As with the fuel and air, care should be exercised to insure that all lines, fittings, and regulators used with the calibration gases are contamination-free. LOX-service cleaned, metal diaphragm regulators are especially recommended for low concentration (less than 300 ppmC) calibration gases and the zero gas.

As discussed previously, it is important that the calibration and zero gases have approximately the same oxygen content and viscosity as the sample gas.

5.2.5.3 *Sample Lines*—The sampling system should be kept short with minimum volume to minimize sample transit time. Sample line, fittings, filters, and pumps should be constructed of stainless steel or Teflon. Sample system cleanliness is extremely important. Contamination, such as scale, grease, or fingerprints, will not only contribute to high sample backgrounds, but absorption of sample hydrocarbons by the contamination will retard the sample and increase response time. A particulate filter should be used to prevent blockage of the fine capillary used to control sample flow. Samples with a dew point above room temperature, such as tailpipe exhaust, must be dried to prevent condensation of water within the system. The use of a heated FID, which allows heating of both internal and external sample lines, eliminates the necessity for water removal.

5.2.5.4 *Response Curve*—Typically, an FID requires calibration with a zero gas and with only one other, one-component, calibration gas at full scale, since response is generally linear with carbon content of the sample. However, this should be verified for each FID because some instruments at certain conditions are nonlinear and require a response curve.

5.3 Chemiluminescent NO_x Analyzer—The chemiluminescent (CL) analyzer (Figure 7) can be used for the direct measurement of oxides of nitrogen (NO_x) concentrations in continuous or bag samples. The CL analyzer measures only the concentrations of nitric oxide (NO) in a gaseous sample. By the use of a high-efficiency converter that changes any nitrogen dioxide (NO_2) present into NO, the total concentration of NO_x ($NO + NO_2$) present can also be determined.

5.3.1 THEORY—The analyzer measures the light from the chemiluminescent reaction of NO and O_3. When a gaseous sample to be measured is blended with dilute O_3 in a reaction chamber, some of the NO_2 produced exists in an excited state (NO_2^*). The excited NO_2^* can return to its ground energy state by emitting a photon according to the following equations:

$$NO + O_3 \rightarrow NO_2^* + O_2 \qquad \text{(Eq. 2)}$$

$$NO_2^* \rightarrow NO_2 + hV \qquad \text{(Eq. 3)}$$

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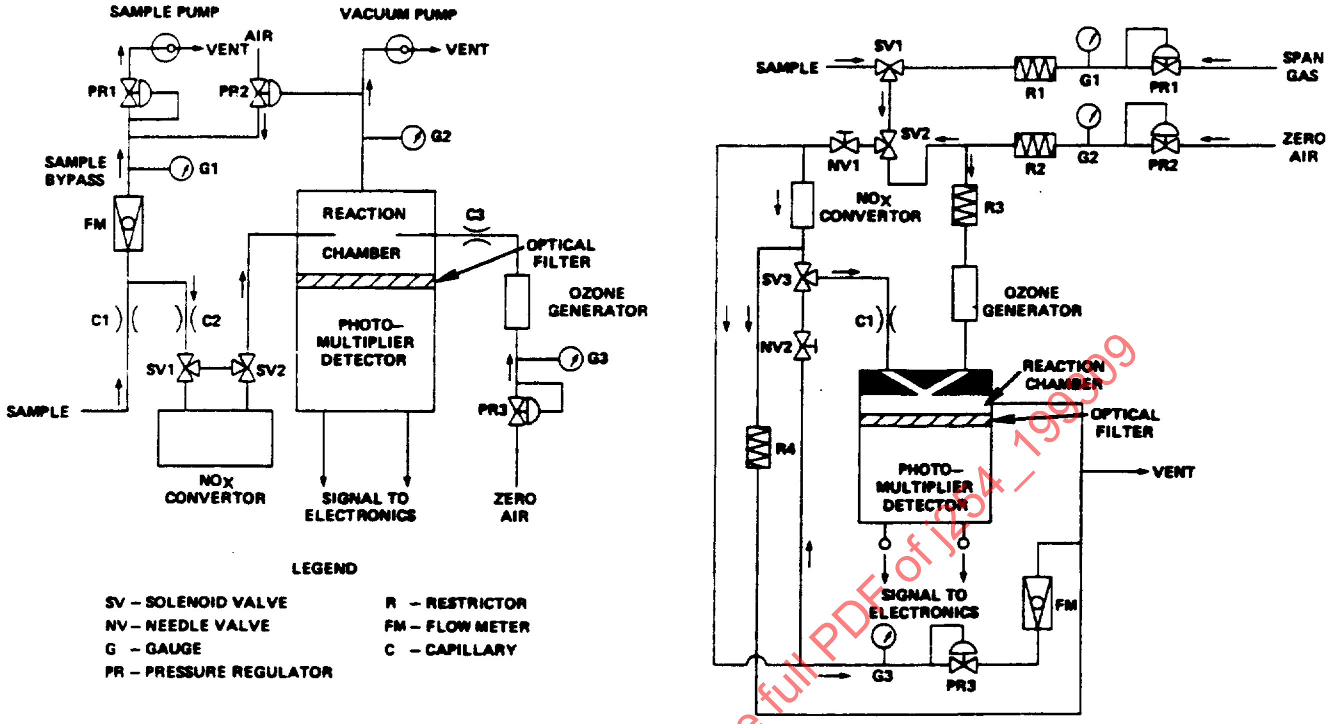

FIGURE 7—SCHEMATICS OF TWO CHEMILUMINESCENT ANALYZERS SHOWING A LOW PRESSURE TYPE(LEFT) AND AN ATMOSPHERIC PRESSURE TYPE (RIGHT)

In the presence of an excess of O_3, the light emitted by this specific reaction is proportional to the concentration of NO. This light can be detected by an optical filter-photomultiplier combination to produce an output which is essentially linear with respect to the NO concentration of the sample. To measure the concentration of NO_x in a sample, a converter which converts NO_2 into NO at high efficiency is inserted into the input sample flow stream.

5.3.2 CALIBRATION—Since the CL analyzer produces an essentially linear response with respect to NO concentration of the sample, a two-point calibration (at zero and full scale) is required. However, linearity should be verified periodically. Some CL instruments may be nonlinear, and may require a response curve with known gases having nominal concentrations equal to 15, 30, 45, 60, 75, and 90% of full-scale concentration. Calibration gases should consist of a known mixture of NO with nitrogen as the balance gas. The actual concentration should be known to within ± 1% of the true values. Zero-grade nitrogen or zero-grade air shall be used to obtain zero response of the CL analyzer.

5.3.3 NO_x CONVERTER EFFICIENCY DETERMINATION—Periodically, the efficiency of the NO_x converter should be measured using the apparatus illustrated in Figure 8 to determine the NO_2 to NO conversion efficiency. Efficiency checks should be made using an NO span gas concentration appropriate to the instrument range to be used. Appropriate adjustments to the converter temperature should be made to obtain converter efficiency between 97 and 100%. The following procedure is to be used for determining the values for Equation 4.

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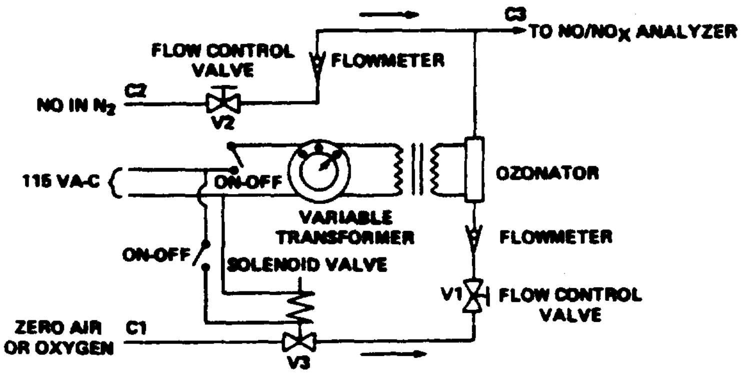

FIGURE 8—NO_X GENERATOR FOR CONVERTER EFFICIENCY DETERMINATION

a. Attach the NO/N_2 supply at C2, the O_2 supply at C1 and the analyzer inlet connection to the efficiency detector at C3 as shown in Figure 8. At low concentrations of NO, air may be used in place of O_2 to facilitate control of the NO_2 generated during Step d and to minimize the fire hazard.
b. With the variable transformer off, place the NO_2 converter in the bypass mode and close valve V3. Open valve V2 until sufficient flow and stable readings are obtained at the analyzer. Zero and span the analyzer output to indicate the value of the NO concentration being used. Record this concentration.
c. Open valve V3 (on/off flow control solenoid valve for O_2) and adjust valve V1 (O_2 supply metering valve) to blend enough O_2 to lower the NO concentration (b) about 10%. Record this concentration.
d. Turn on the ozonator and increase its supply voltage until the NO concentration of (c) is reduced to about 20% of (b). NO_2 is now being formed from the NO + O_2 reaction. There must always be at least 10% unreacted NO at this point. Record this concentration.
e. When a stable reading has been obtained from (d), place the NO_X converter in the converter mode. The analyzer now indicates the total NO_X concentration. Record this concentration.
f. Turn off the ozonator and allow the analyzer reading to stabilize. The mixture NO + O_2 is still passing through the converter. This reading is the total NO_X concentration of the dilute NO span gas used at step (c). Record this concentration.
g. Close valve V3. The NO concentration should be equal to or greater than the reading of (b). Calculate the efficiency of the NO_X converter by substituting the concentrations obtained during the test into the equation:

$$\%\ \text{Efficiency} = \frac{[(3)-(4)]-[(6)-(5)]}{[(3)-(4)]} \times 100\% \qquad \text{(Eq. 4)}$$

5.3.4 VISCOSITY—The response of a CL analyzer is directly proportional to the volumetric sample flow to the CL analyzer reaction chamber, making stringent control of sample flow rate mandatory. Because most CL analyzers use a pressure-regulated capillary flow control system, the sample flow to the reaction chamber is dependent on both sample pressure and viscosity. Any change in sample viscosity will result in an inversely proportional change in apparent reading, though pressure has remained constant. It is necessary to use a calibration gas whose viscosity approximates that of the sample being measured.

5.3.5 OPERATION—Prior to use, the CL analyzer should be calibrated with gases of known concentration. Pass zero gas through the analyzer and adjust the dark current suppression or amplifier zero control for zero instrument response. A known concentration of NO span gas is then applied and the photomultiplier high voltage supply or the amplifier gain is adjusted for the proper corresponding instrument response.

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5.3.6 ANALYZER PERFORMANCE IMPROVEMENT—Output signal drift is often encountered in analyzers using photomultiplier tubes (PMT). This drift is a characteristic of the PMT referred to as fatigue. Fatigue can be reduced in certain analyzers by providing illumination to the PMT during prolonged periods when there is no chemiluminescent reaction. A light emitting diode may be inserted into the reaction chamber to illuminate the PMT while the analyzer isn't being used for testing. Use of light during analyzer idle periods has been shown to reduce warmup drift and increase analyzer-to-analyzer correlation in certain instances.

Interference from H_2O and CO_2 quenching in atmospheric pressure CL analyzers can be reduced by moving the sample capillary further upstream from the reaction chamber, reducing sample flow rate, and increasing the ozone flow rate.

5.4 Oxygen Analyzers

5.4.1 POLAROGRAPHIC ANALYZERS

5.4.1.1 *Theory*—Polarographic oxygen analyzers operate on the principle that different gases are chemically reduced at different applied voltage potentials. Of the gases normally found in exhaust gas, oxygen is reduced at the lowest potential and can, therefore, be readily measured. The instrument actually measures the partial pressure of oxygen in the sample, but for fixed operating conditions, it can be calibrated in other units such as percent oxygen by volume.

The analyzer consists of two basic units, a sensor and an amplifier. The sensor, which detects oxygen content, normally consists of a gold cathode insulated from a silver anode between which a potential of approximately 0.8 V is applied. The anode is electrically connected to the cathode by a potassium chloride gel. The entire anode-cathode assembly is separated from the sample by a Teflon gas-permeable membrane.

5.4.1.2 *Interferences*—There are other gases, such as SO_2, Cl_2, Br_2, I_2, and NO_2 which will reduce at 0.8 V. These gases are not usually found in exhaust gas in sufficient concentrations relative to O_2 to give a significant interference.

5.4.1.3 *Continuous Operation*—In operation, the sensor is placed in the sample stream and oxygen diffuses through the Teflon membrane and is reduced, by the 0.8 V potential, at the cathode. This reduction causes a current flow which is proportional to the partial pressure of oxygen in the sample. The housing for the sensor should have a low dead volume to reduce the response time.

Since the partial pressure of oxygen changes with the total pressure, the system pressure must be closely controlled. For example, if the total pressure of the sample is doubled, the partial pressure of the oxygen will double, and, as a result, the output of the sensor will double while the actual percent oxygen in the sample will remain the same. Because of this characteristic, direct readings in percent oxygen are valid only if the gas mixture is analyzed under the same total pressure as when calibrated.

5.4.1.4 *Calibration Considerations*—Since sensor response is linear with oxygen partial pressure in the sample, a simple two-point calibration, at zero and full scale, is required. Span settings can normally be made using room air. However, if the room air is not relatively clean, blends of oxygen in N_2 should be used. The instrument is zeroed using nitrogen.

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