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Determination of Sulfur Compounds in Automotive Exhaust

Foreword—Automotive engines, depending upon the amount of sulfur in the fuel burned, emit varying quantities of sulfur compounds in the exhaust. Catalytic converters, which oxidize carbon monoxide and hydrocarbons also may alter the proportion of the various forms of sulfur emitted. This SAE Information Report describes equipment, procedures, and the measurement of normal sulfur compounds in automotive exhausts, and presents analytical methods related to this activity along with some comments on their suitability. The information contained in this document does not represent current testing techniques and equipment. It is being retained because of its historical value.

1. Scope

Scope—This SAE Information Report deals exclusively with the determination of sulfur compounds in automotive exhaust. Engine operating cycles and interpretation of results are not covered. Methods described in detail are those that have been or are being used by various laboratories. None are specifically recommended as superior to others. Since intensive measurement of automotive sulfur compounds is a relatively new activity, methods and practices have changed rapidly. Some methods are more experimental than others and are so noted in the test.

1.1 Environmental Protection Agency Action

Environmental Protection Agency Action—EPA has issued a detailed recommended practice on the determination of sulfates in automotive exhaust. Copies can be obtained by writing the Director, Emissions Control Tech., Environmental Protection Agency, 2565 Plymouth Rd., Ann Arbor, MI 48105.

2. References

2.1 Applicable Publications

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

SAE Paper 770166 “Automotive Sulfate Emissions—A Baseline Study,” Somers, Garbe, Lawrence, and Baines.

2.1.2 FEDERAL AND MILITARY STANDARDS—Available from U. S. Government, DOD SSP, Subscription Service Division, Building 4D, 700 Robbins Avenue, Philadelphia, PA 19111-5094

Federal Test Procedure—Federal Register 40 CFR 86

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2.2 Related Publications—The following publications are provided for information purposes only and are not a required part of this document.

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

G. J. Barnes and J. C. Summers, "Hydrogen Sulfide Formation Over Automotive Oxidation Catalysts." SAE Paper 750093. February 1975.
C. R. Begeman, et al., "Sulfate Emissions from Catalyst-Equipped Automobiles." SAE Paper 741060. October 1974.
M. Beltzer, et al., "Measurements of Automotive Exhaust Particulate Emissions." SAE Paper 740286. February 1974.
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D. A. Trayser, et al., "Sulfuric Acid and Nitrate Emissions from Oxidation Catalysts," SAE 750091, February 1975.
D. A. Trayser, et al., "Effect of Catalyst Operating History on Sulfate Emissions." SAE Paper 760036, February 1976.

2.2.2 CRC PUBLICATIONS—Available from the Coordinating Research Council, 219 Perimeter Center Parkway, Atlanta, GA 30346.

J. F. Foster, et al., "Fifth Annual Summary Report on Chemical and Physical Characterization of Automotive Exhaust Particulate Matter in the Atmosphere." CRC Project CAPE-19-70. March 1976.
D. A. Trayser, et al., "Sixth and Final Annual Summary Report on Chemical and Physical Characterization of Automotive Exhaust Particulate Matter in the Atmosphere," CRC Project CAPE-19-70, September 1976.

2.2.3 MISCELLANEOUS PUBLICATIONS

M. Beltzer, “Particulate Emissions from Prototype Catalyst Cars.” EPA-650/2-75-054. May 1975.

J. B. Burkart, et al., “Catalytic Converter Exhaust Emissions.” Paper No. 74-129, APCA 67th Annual Meeting, Denver, CO. June 1974.

J. W. Butler and D. N. Locke, “Photometric End-Point Detection of the Ba-Thorin Titration of Sulfates.” J. Environmental Science Health—Environmental Science Eng., A11(2), 79–92 (1976).

J. S. Fritz and S. S. Yamamura, “Rapid Microtitration of Sulfate.” Anal. Chem., 27 (1955), p. 1461.

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E. S. Lisle and J. D. Sensenbaugh, “The Determination of Sulfur Trioxide and Acid Dew Point in Flue Gases.” Combustion 36, 12 (1965).

M. Mikkor, et al., “Effect of Hydrocarbons, Carbon Monoxide and Oxygen on Sulfuric Acid Emissions from an Automotive Catalyst.” Paper No. 43, Symposium on Auto Emission Catalysts, Div. of Colloid and Surface Chemistry, ACS 170th National Meeting, August 1975.

H. N. S. Schafer, “An Improved Spectrophotometric Method for the Determination of Sulfate with Barium Chloranilate as Applied to Coal Ash and Related Materials.” Anal. Chem. 39, 1719 (1967).

M. J. Van Der Zijden, et al., “SO_2 and SO_3 in Exhaust Gases of Internal-Combustion Engines,” J. Inst. Pet., 36, 561 (1950).

P. W. West and G. C. Gaeke, “Analytical Chemistry,” Vol. 28, P. 1816 (1956).

“Method 8—Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources.” Federal Register, Vol. 36. No. 247, December 23, 1971, pp. 24893–24895.

3. Definitions

3.1 **Aerosol—**A finely divided, noncondensable liquid and/or solid dispersed in a gas.

3.2 **Dilution Tube (Or Tunnel)—**One of several types of ducts used to dynamically mix engine exhaust with dilution air in a stationary test set-up. Conditioned air, supplied by a blower, is mixed with engine exhaust at a mixing orifice in the upstream end of the tube while sampling takes place at a downstream location.

3.3 **Goksoyr-Ross—**A controlled condensation coil named for its co-inventors. Fluid with condensable material is passed through a coil surrounded by a flowing, controlled-temperature liquid. Condensate trapped within the coil is recovered for analysis.

3.4 **Impinger (Bubbler)—**A type of trap in which the sample stream impinges against a cool wall and then must flow through a liquid which retains the species of interest.

3.5 **Isokinetic Sampling—**Withdrawing a sample stream at the same velocity as the parent stream. This method is used to obtain a representative sample when particulate matter is of interest.

3.6 **Mass Median Equivalent Diameter—**The calculated diameter of a sphere of unit density which represents the midpoint particle obtained when the total particulate mass is divided into two equal parts.

3.7 **Mixing Orifice—**An orifice, usually sharp-edge, located near the upstream end of a dilution tube. Engine exhaust discharges near the center while dilution air flows through the remaining area. Turbulence downstream from the orifice merges the two into well-mixed, air-diluted, exhaust gas stream.

3.8 Particulate Matter—Any dispersed solid or liquid in which the individual aggregates are larger than 0.001 µm in diameter, excluding uncombined water.

3.9 Probe—The section of a sample line which is farthest upstream and thus is the first to encounter the material to be sampled. Typically, it is the part of the sample line physically located within the stream being examined.

3.10 Sulfates—Sulfuric acid or one of its salts.

4. Brief Introduction to Sampling Systems in Use

4.1 Undiluted Exhaust System—This technique involves extracting a small portion of the raw (undiluted) exhaust stream and passing it through collection equipment where sulfur-related components are trapped and held for analysis.

4.1.1 CONTROLLED-CONDENSATION COLLECTION (GOKSOYR-ROSS)—The probe and sample line are maintained above 200 °C followed by the G-R condensation coil maintained at about 60 °C. Sulfuric acid is condensed and held in the coil whereas sulfur dioxide passes through. After collection, the sulfuric acid is washed from the coil and analyzed by one of several methods. Sulfur dioxide is also commonly determined simultaneously by connecting the exit of the G-R coil to a bubbler containing 3% H_2O_2. SO_2 is oxidized in the bubbler to H_2SO_4, which is subsequently analyzed by the same method. Sample volume is measured by a gas meter.

4.1.2 BUBBLER/IMPINGER COLLECTION (MODIFIED METHOD 8)—The method was developed to determine H_2SO_4 in stationary stack gas (Method 8). One type is made up of a probe and heated sample line followed by two bubblers in an ice bath. The first bubbler contains an isopropyl alcohol (IPA)/water solution to trap H_2SO_4 but not SO_2, whereas the second bubbler contains a hydrogen peroxide/water solution to trap SO_2 by oxidation to H_2SO_4. Following the bubblers is a dry ice trap, sample pump, and gas meter. At the end of the sampling period, the material from each bubbler is analyzed for sulfate.

A second type consists of a probe followed by a series of several midget impingers, in an ice bath, each containing a solution of isopropyl alcohol (IPA) and water. Sample gas is pulled through the train by a pump with the flow rate measured by a suitable flow meter. Sulfur compounds trapped in the impingers are assumed to be sulfur trioxide or sulfate. Analysis of the impinger solution is by any method specific for sulfate.

4.2 Dynamic Dilution System (Dilution Tube)—In this technique the total exhaust gas stream is constantly emptied into a duct that also has a continuous supply of fresh, treated air. Flow is maintained by a constant-volume blower at one end of the duct. Exhaust and fresh air are mixed near the upstream end of the duct and the mixture sampled downstream. The purpose of air dilution is to cool the exhaust to condense sulfuric acid to form an aerosol but to prevent condensation of water. In cyclic operation, the dilution tube provides a mixture which when sampled at a uniform rate will yield a sample proportional to tailpipe output.

4.2.1 FILTER COLLECTION—Used for sample collection from diluted exhaust streams. The system employs a probe followed by one or more disc-type filters. Flow is maintained by a sample pump. Sulfur compounds deposited on the filter element are analyzed by one of several methods.

4.2.2 CONTROLLED CONDENSATION COLLECTION (GOKSOYR-ROSS)—Equipment and techniques are generally similar to those used for collection of undiluted exhaust samples (4.1.1). The probe is inserted at a downstream location in the duct. The entire sample probe and line to the inlet of the G-R coil must be maintained above 200 °C.

4.3 Static Dilution System (Dilution Chamber)—Partially diluted engine exhaust is directed into a large plastic chamber. Air in the chamber serves to dilute the exhaust further, cool it, and prevent condensation of sulfur-related compounds. Samples are withdrawn through special ports in the chamber wall.

4.3.1 Filter Collection—Filter collection systems used with static dilution chambers are similar to those employed with dynamic dilution. A measured volume of diluted sample is drawn through a disc-type filter element where the sulfate is trapped. Material held on the filter element is extracted and usually analyzed for sulfate by a barium iodate, spectrophotometric method. Other methods of analysis could be used.

4.3.2 Bubbler/Impinger Collection (Modified Method 8)—This system is essentially the same as that described in 4.1.1 for undiluted exhaust sampling.

5. Detailed Description of Systems in Use

5.1 Exhaust Handling Methods—There are three general methods of handling vehicle exhaust gas and preparing it for sample collection. Each is described in detail in the following paragraphs.

5.1.1 Undiluted Exhaust—The simplest method that has been used. A probe leading to the collection system is inserted into the vehicle exhaust pipe where it picks up a sample of raw undiluted gas. Quartz and stainless steel have been used as probe materials. A typical stainless steel design uses 6.35 mm OD tubing closed at one end with several 3.2 mm holes drilled around the circumference (Figure 1). Probes are inserted into the exhaust pipe at a location where the gas temperature is high enough to preclude condensation. Sample lines leading from the probe usually are heated to about 200 °C to prevent condensation ahead of the collection apparatus.

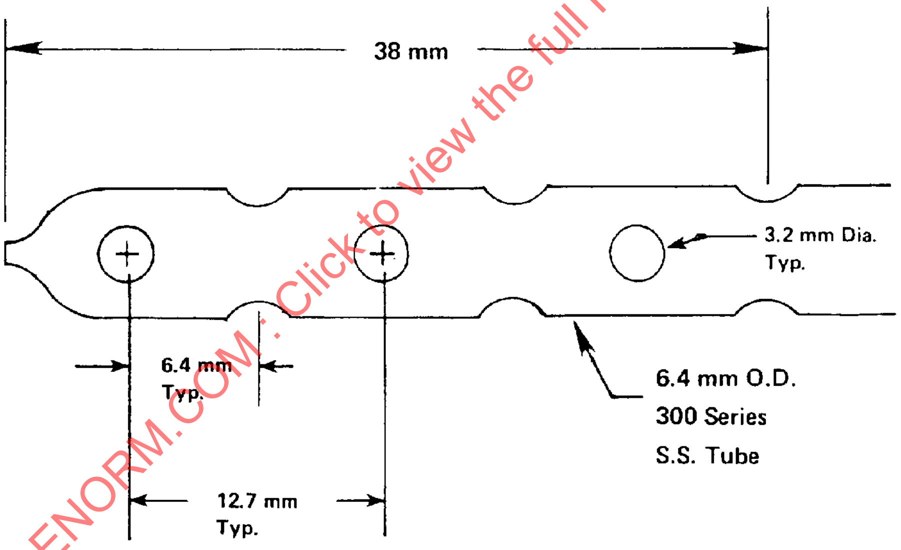

FIGURE 1—SAMPLE PROBE, UNDILUTED EXHAUST

5.1.2 DILUTED EXHAUST

5.1.2.1 Dynamically Diluted Exhaust—A common method of handling the exhaust of a vehicle operated in any cycle (for example, the S-7 Sulfate Cycle) in such a manner as to provide for the taking of a representative sample for analysis, is often designated the Constant Volume Sampling (CVS) system. In the CVS system all of the vehicle exhaust is mixed with an excess of relatively cooler air in the dynamic flow system, and the total flow of diluted exhaust pumped at a constant rate. A sample withdrawn at a uniform rate for the entire test cycle will be representative of the total emission from the vehicle in the cycle. Such a CVS system is utilized in the Federal Test Procedure (Ref. Federal Register). The method is also applicable to the determination of fine particulate matter, including sulfuric acid mist, in vehicle exhaust. However, with sulfuric acid mist, the diluted exhaust must be cool enough to avoid loss of acid as vapor and dry enough to avoid loss of acid by condensation of a water phase.

Exhaust from the car is conducted, via an extension of the tailpipe, into the dynamic dilution tube. The tailpipe extension is preferably short and of low mass so as to heat quickly and thus not act as a condenser for sulfuric acid once the vehicle exhaust system is hot. The diameter of the dilution tube appears not to be critical. Tubes of 95 mm to 584 mm diameter are in use. Mixing of exhaust with dilution air should be accomplished without directing the exhaust against any surface. The length of the dilution tube should be sufficient to provide complete mixing of exhaust and air. It is common for the distance from exhaust injection to sampling point to be a minimum of eight times the diameter of the dilution tube. In any case, the completeness of mixing should be verified by experiment.

5.1.2.1.1 System A—(Figure 2) This dynamic dilution system is designed to collect sulfates and other particulate material at essentially constant temperature during driving cycles such as the 1975 Federal Test Procedure, and during moderate speed conditions. It is capable of frequent operation and is compatible with CVS of auto exhaust. Compatibility is obtained because the collection system requires only a small portion of the diluted exhaust: the major portion of the sample is available to the CVS system for measurement of gaseous emissions.

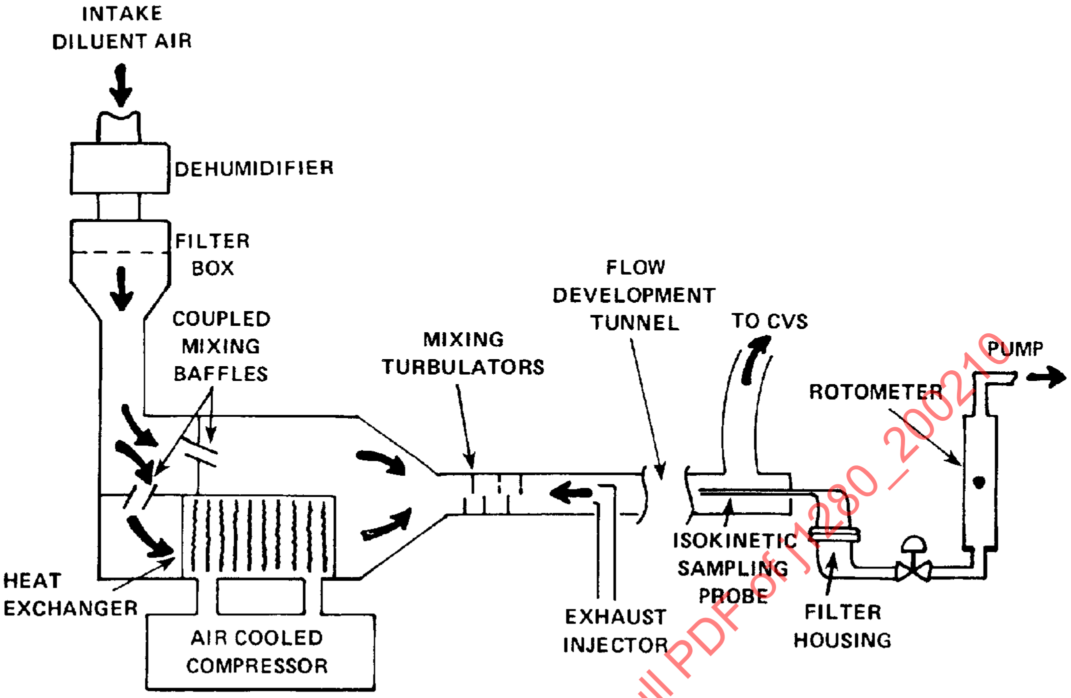

FIGURE 2—DYNAMIC DILUTION SYSTEM A

The system uses a relatively small tunnel which means that low dilution ratios are used, allowing gaseous emission such as CO, hydrocarbons, NO_X, and SO_2 to be measured accurately. While low dilution ratios are desirable from the standpoint of CVS gaseous emission measurements, the collection of the proportional sample of particulate matter at constant temperature near 32 °C from a sample stream having a high dew point without causing condensation of water, requires a humidity and temperature control system.

Linear velocities are higher in smaller tunnels. An analysis of turbulent diffusion losses in both small and large tunnels has shown the following:

a. For 10 µm particles, the turbulent diffusion loss would be about 20%, whereas, larger tunnels could handle particles up to 300 µm without internal turbulent diffusion losses.
b. The longer residence times in the larger tunnels result in much greater settling losses of dense large particles.
c. In practice, these two effects compensate each other so that ignoring entry losses, small and large dilution tunnels have an effective cut-off particle diameter of about 10 µm.

Since the H_2SO_4 aerosol size is well below 1 µm, acid aerosol losses in both tunnel types should be equivalent and negligible. This has been substantiated by experiment in which it was shown that sulfate aerosol losses in either tunnel system were about 1%. Therefore, both size tunnels are effective aerosol samplers.

5.1.2.1.1.1 Diluent Air Preparation—This subsystem consists of a dehumidifier filter, coupled mixing baffles, a cooling system, and mixing turbulators.

The dehumidifier shown schematically in Figure 3 minimizes the possibility of condensation occurring in the system during a run, and is an integral part of the temperature control system. Diluent air is dried by passage through a filter and a slowly rotating desiccant wheel containing laminated flat and corrugated asbestos, impregnated with a regenerable desiccant, LiCl. Dehumidification of diluent air and desiccant reactivation are concurrent processes, so that dehumidification can be carried out on a continuous basis.

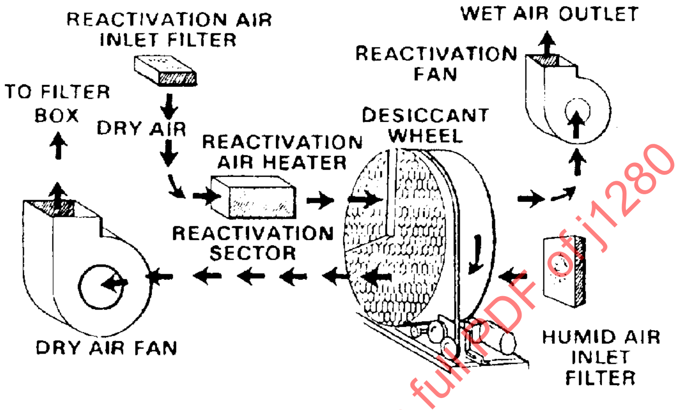

FIGURE 3—DEHUMIDIFIER, SYSTEM A

Dehumidified inlet air passes from the dehumidifier to a filter box containing a paper filter, a bed of activated charcoal, and a second paper filter. This assembly can be the standard filter box assembly for a CVS unit. The filter assembly removes the particulate matter present in the diluent air and reduces and stabilizes the background hydrocarbon content of the diluent air. Because regeneration of the desiccant is accomplished by heating, the dehumidified air emerging from the drum is above ambient temperature. A precooler situated between the dehumidifier and the CVS filter cools the dehumidified airstream down to ambient temperature to remove the additional cooling load imposed by the dehumidification step from the final cooling system. The precooler consists of several rows of coils through which chilled city water is passed.

The coupled mixing baffles continuously divide the dehumidified, filtered air into two portions, one of which passes through the cooling system, and the second of which bypasses the cooling system. The position of the mixing baffles is controlled by a rapid response, deviation-type controller operating on an input signal from a thermocouple in the filter housing.

The controller operates by comparing an input signal from a thermocouple in the filter housing with a set point signal, and takes corrective action to either raise or lower the output signal until the set point and thermocouple input are equal. The output signal from the controller is fed to an electropneumatic transducer which in turn activates a pneumatic controller which operates the coupled baffles. The cooling system is an air cooled condensing evaporator. Maximum flow through the diluent air preparation system is determined by the cooling capacity of the chiller, and the desired sampling temperature. The mixing turbulators insure that chilled air is thoroughly mixed with the portion of air bypassing the cooling system before the stream is used to dilute the vehicle exhaust. The turbulators consist of six semicircular perforated plates attached to a 12.7 mm diameter thickwall tube at their centers, arranged in a helical series sequence along the tunnel axis. This arrangement allows both longitudinal and latitudinal mixing.

5.1.2.1.1.2 Dilution Tube—Exhaust and diluent air are mixed and a uniform velocity profile is developed in the flow development tunnel. The flow development tunnel is a 2.29 m (7.5 ft) long section of a nominal 102 mm (4 in) diameter Schedule 5 stainless steel pipe (109 mm actual diameter). Neither the length nor the diameter of the flow development tunnel have been optimized, but a dilution tunnel of these dimensions is satisfactory. The probe is located at the end of the tunnel, ahead of the connection leading to the CVS unit.

An important factor in choosing the diameter of the flow development tunnel is its effect on the length of the tunnel and the diameter of the probes. As a general rule, eight to ten pipe diameters are usually sufficient to develop a fully turbulent velocity profile. The larger the diameter, the longer the tunnel required and the longer the residence time in the flow development section.

Longer residence time may lead to higher particulate settling which may cause errors in the measurements. Therefore, the tunnel diameter should be minimized. However, as tunnel diameter decreases, the pressure drop through the tunnel increases and the size of the probes needed for isokinetic sampling decreases. The problems caused by high pressure drop are obvious. Smaller diameter probes should be avoided since they provide higher surface to volume ratios and result in more loss of particulate by impaction. The 109 mm diameter pipe in use offers a reasonable compromise between these various factors.

5.1.2.1.1.3 Exhaust Injection System—Raw exhaust is mixed with the diluent air normally used in the CVS in such a way as to completely mix the two in as short a time interval as possible. This is accomplished by injecting the exhaust in a direction countercurrent to the diluent airstream. Experiments have shown this to be the most efficient way of obtaining a rapidly mixed, uniformly distributed diluted exhaust sample stream. Figure 4 shows a schematic of the exhaust injector in the countercurrent position.

5.1.2.1.1.4 Dilution Tube Losses—Particulate deposition in the flow development section is measured by introducing an artificially produced monodisperse (3.5 µm diameter) methylene blue aerosol into the exhaust injector in the same manner as for auto exhaust. The system is disassembled after the run, the tube surface washed with methanol, and the washing analyzed spectrophotometrically. The sensitivity of the method for methylene blue is in ppb range. Analysis has shown that tube losses are small, amounting to less than 1% of the total aerosol introduced. No dye was detected in the tube section housing the exhaust injector. About 0.1% of the aerosol was deposited in the tube midsection, and about 0.3% was deposited in the tube section housing the probes. Tests with a tube of similar dimensions have confirmed the results regarding sampling losses.

5.1.2.1.1.5 Temperature Capabilities and Effects—A typical installation of System A had a 9.8 kW cooling capacity and a total flow rate of 12.8 m^3/min. Under these conditions a temperature between 32 and 38 °C usually was maintained at the sample collection point throughout a 1975 FTP cycle with a catalyst-equipped car. If temperature at the collection point is not to exceed 32 °C, it may be necessary to add a finned-tube cooler (Figure 5) between the exhaust pipe and the exhaust ejector. This cooler also is useful in controlling temperature during high-speed cruise tests. Sulfates and other exhaust particulate matter can also be collected at set temperatures above 32 °C. In these cases the finned-tube cooler may not be needed.

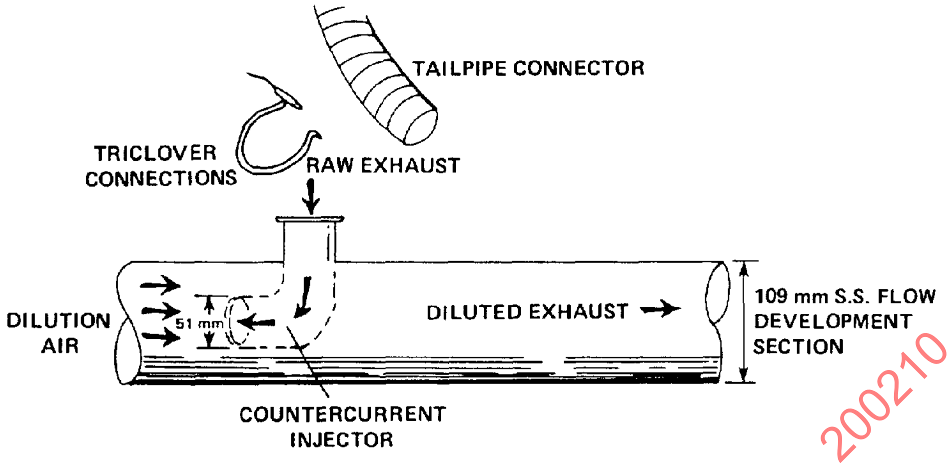

FIGURE 4—EXHAUST INJECTOR SYSTEM A

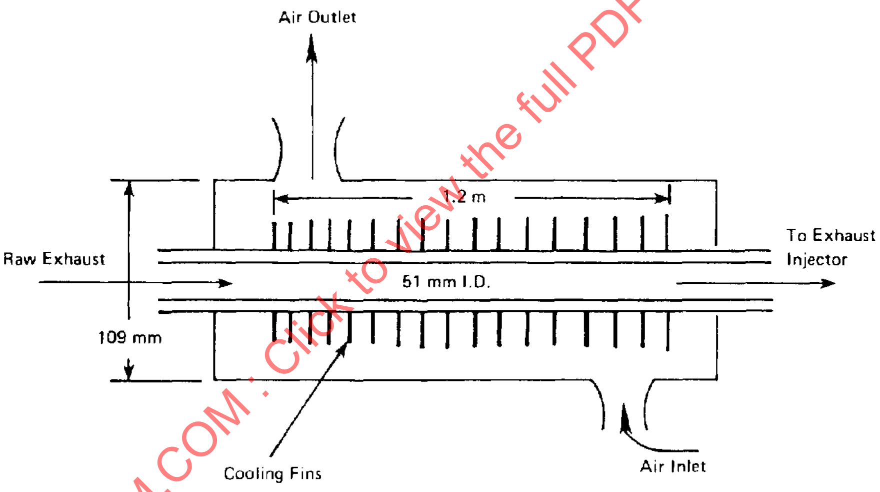

FIGURE 5—FINNED-TUBE COOLER

The set-point temperature is essentially determined by the fraction of the dehumidified air that is cooled. If collection at a higher temperature is desired, the fraction of dehumidified air that goes through the heat exchanger is decreased. This fraction is determined by the set-point temperature and the actual instantaneous temperature of the exhaust-dilution air mixture in the filter housing. Thus a range of particulate collection temperatures is possible, the lower limit being the dew point of the air exhaust mixture at the lowest dilution ratios, and the upper limit the minimum amount of cooled-dehumidified air required to prevent temperature increases at low dilution ratios.

The dehumidifier is a key component of the temperature control system, particularly since the exhaust handling system is one in which the air/exhaust dilution ratios are low. This means that the relative humidity of the diluent air is a key parameter. For example, during the rapid acceleration portion of the FTP, the exhaust volume flow rate from a vehicle equipped with a 5.7 L V-8 engine may be as high as 3.4 m^3/min. Thus, with a 12.8 m^3/min flow limit, the dilution ratio would drop below 3 in the sampling tunnel. If the relative humidity of the diluent air were high, attempts to control the collection temperature to a level of 32 °C would result in condensation of water vapor, with the associated loss of particulate matter.

If the relative humidity of the diluent air is low, for example, below 50%, it should be possible to maintain a 32 °C collection temperature without condensation occurring. In the absence of the dehumidifier, on humid days, the dew point of the mixture would exceed 32 °C at dilution ratios as high as four, so that condensation would invariably occur during the acceleration portions on FTP driving cycle.

Attempts to control collection temperatures by omitting the dehumidification step and chilling the diluent air would be difficult to accomplish since water condensing on the coils would feed back latent heat, decreasing the efficiency of the cooler. Continued running would probably result in the condensed water freezing on the heat-exchangers, rendering them inoperative. The collection of sulfuric acid aerosol should be independent of temperature as long as the collection temperature is below sulfuric acid dew point. Thus, if the collection temperature does not exceed about 90 °C, all of the acid exists as aerosol. Although the dilution tube residence time is small (0.1 s), the formation of aerosol droplets is virtually instantaneous.

5.1.2.1.2 System B—(Figure 6) This system uses a relatively large dilution tube and also can be used to examine particulates other than sulfates. The exhaust handling system includes a dilution air filter, a clear polyacrylate dilution tube, and a blower to induce flow. Exhaust gas is introduced into the tube upstream near the dilution air filter and diluted samples are collected downstream near the blower.

5.1.2.1.2.1 Dilution Air Preparation—Before mixing with automobile exhaust, the dilution air is filtered through a 610 x 610 x 292 mm pleated filter of approximately 23 m^2, rated 95% efficient for 0.3 µm particles by a DOP test and 99% efficient by a NBS color test. A pressure drop less than 12 mm (118 Pa) water, at the flow of dilution air used, is desirable.

5.1.2.1.2.2 Dilution Tube—The dilution tube portion of the system is built in sections and has two different diameters. The first group of sections, near the entrance, is 2.3 m long and 216 mm in diameter. The second group is 3.6 m long and 333 mm in diameter. The sections are joined with O-ring seals and, except for the short entrance and transition sections, is fabricated of clear polyacrylate having 6.4 mm wall thickness. The overall length of the exhaust handling system is approximately 12 m including dilution air filter and blower. The distance between the exhaust inlet and sample probes is 5.7 m. It is in this 5.7 m section that mixing of exhaust with dilution air and the development of a relatively flatfront velocity profile take place. The relatively large nonairborne particles settle from the main stream during the approximately 2 s required for the exhaust to travel this distance.

The dilution tube is located parallel with the vehicle and as close as feasible (about 1 m clearance).

The blower for pumping diluted exhaust through the dilution tube is equipped with a variable sheave pulley drive for adjusting the fan speed between approximately 700 and 1400 rpm, corresponding to flow rates of between about 17 and 33 m^3/min.

Velocity profiles and volumetric flow rates are measured in the exhaust dilution tube at the 333 mm diameter sampling section with a Pitot tube, and the volumetric flow is determined by the tube.

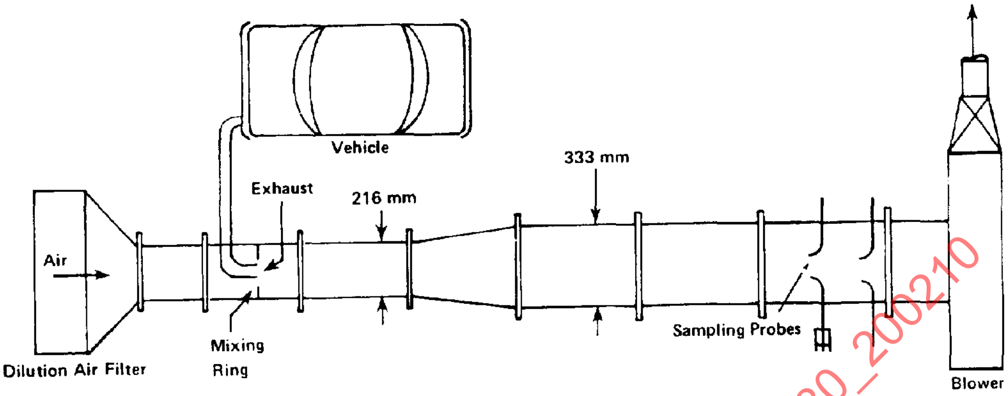

FIGURE 6—DYNAMIC DILUTION SYSTEM B

The Pitot tube is inserted through glands in the flange at the downstream edge of the sampling section. The tip of the Pitot tube projects forward about 254 mm so that the velocity is measured near the cross section of the particle sampling probes (the probes are removed for the velocity measurement).

Velocity profiles are illustrated in Figure 7 for maximum and minimum fan speeds. For the practical purpose of integration, velocity at the tube wall is assumed to be one-half the centerline velocity, as recommended. Velocity is symmetrical with respect to the tube centerline and reasonably uniform over the central 216 mm diameter section.

Volumetric flow rates are calculated from the velocity profiles integrated using 12.7 mm annular radius segments and velocities are read from Figure 7. Typical volumetric flow rates are shown in Table 1:

TABLE 1—VOLUMETRIC FLOW

Blower rpm	Total Flow, m^3/min Exh. In. Closed	Total Flow, m^3/min Exh. In. Open
730 Min	16.22	17.24
1385 Max	31.57	34.00

Because the exhaust inlet is downstream of the dilution air filter, air admitted at the exhaust inlet reduces the pressure drop of the system slightly, with a resulting slight increased flow. To the degree that the capacity of the blower depends on the ΔP across the blower, the exhaust dilution system is not a true Constant Volume Sampling system. The sampling probes are located on a circle of approximately 102 mm diameter with respect to the tube axis and are, therefore, in the area of nearly maximum and uniform velocity.

A standard size vehicle, operating through the 1972 FTP driving cycle, produces an average of approximately 1.22 m^3/min exhaust gas (at 21 °C), including water vapor. At low fan speed, the addition of 1.13 m^3/min gas at the exhaust inlet is equivalent to the measured flow with the exhaust inlet open. Therefore, for operation on the 1972 FTP driving cycle with the fan at 730 rpm, the average total flow is taken as 17.27 m^3/min. For operation on the FTP at high fan rpm, the average flow is takenas 32.84 m^3/min.

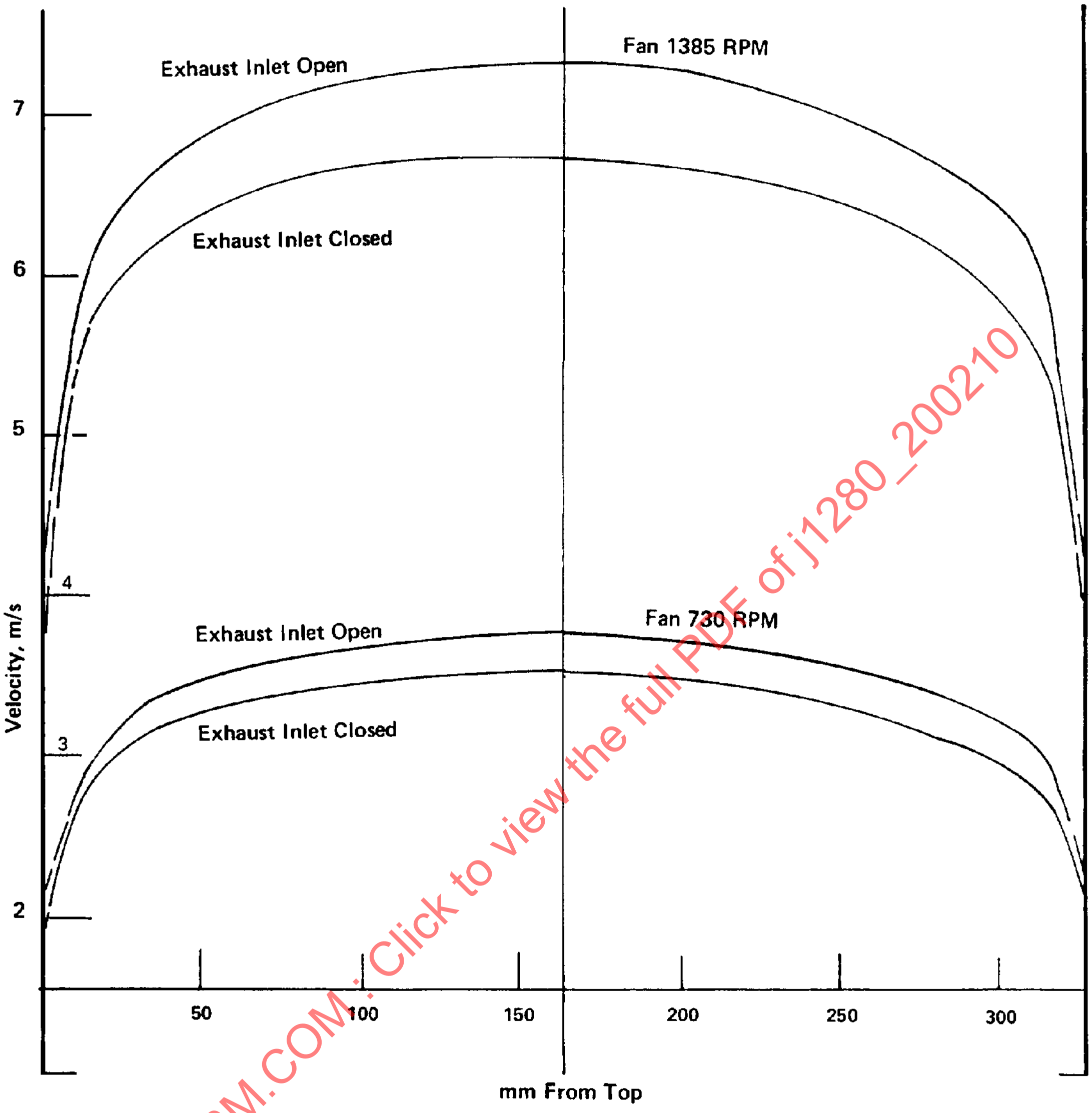

FIGURE 7—VELOCITY PROFILES AT SAMPLING SECTION

Reynolds numbers at the sampling section are shown in Table 2.

TABLE 2—REYNOLDS NUMBER

	Re
32.84 m^3/min	130 000
17.27 m^3/min	70 000

Thus, the flow is turbulent.

Temperature at the sampling section during the 1972 FTP driving cycle, at 17.27 m^3/min total flow, ranges from 27 to 54 °C.

5.1.2.1.2.3 Exhaust Injection System—All of the exhaust from a vehicle operated on a chassis dynamometer is fed via a 51 mm diameter tailpipe extension to the dilution tube, and is directed into the dilution tube on the centerline of the second 216 mm diameter section. The exhaust pipe discharges downstream. An annular ring, 216 mm OD x 165 mm ID is located coplanar with the discharge end of the exhaust pipe extension. This annular orifice produces relatively greater local turbulence at the area of exhaust introduction, resulting in rapid mixing of exhaust and dilution air.

5.1.2.1.2.4 Mixing of Auto Exhaust and Dilution Air—It is important for representative sampling that the exhaust be uniformly mixed with dilution air. Because inertial and gravitational effects are greater for discrete particles (depending on size and density) than for gases, uniform mixing of particles with dilution air may be more difficult. Nevertheless, a minimum requirement of the exhaust dilution system would be for exhaust gas to be uniformly mixed with dilution air. Should this requirement not be met, then uniform distribution of sulfates would certainly not occur.

The system is tested for mixing effectiveness by introducing propane at the exhaust inlet port and monitoring the propane concentration at the sampling section with a flame-ionization hydrocarbon analyzer. Propane flow is adjusted to give a calculated of –50 ppm at 32.84 m^3/min. The results obtained in such a test are illustrated in Figure 8.

Mixing of propane was found to be very uniform at a fan speed of 1385 rpm. At a fan speed of 730 rpm, propane concentration was found to be very uniform horizontally, and nearly uniform vertically except for a slightly low concentration at the bottom of the tube. Overall, uniformity of mixing was considered very good and satisfactory.

Uniformity of mixing of a gas does not necessarily guarantee uniformity of mixing of particulate matter. However, the mean particle size of freshly generated sulfate particulate matter derived from combustion is so small (less than 0.1 µm) that the particles behave very much like a gas. Therefore, the mixing effectiveness determined with propane will also apply to these particles.

5.1.2.1.2.5 Loss of Sulfate in the Dilution Tube—The transparent 6.4 mm wall clear polyacrylate dilution tube allows visual inspection of the mixing of the exhaust and dilution air. The blowing-in of liquid water with every cold start as well as the gradual deposition of film and sediment on the walls can be seen. The film-type deposit, distributed throughout the length of the tube, indicates the loss of some small particles, and a few much larger particles accumulate along the bottom of the tube. Characteristically, a portion of the sediment is rust-like material and accumulates in the first 216 mm diameter section near the exhaust inlet, where it is streaked along the bottom of the tube. This is the area in which the blow-in water first accumulates and then evaporates to leave a rusty residue.

The sulfate losses in the tube have been measured by disassembling it after several emission tests, wiping the inside with a damp cellulose filter, and analyzing the filter for sulfate. The large particles were brushed out beforehand. This procedure maximizes the calculated loss because the wipings include some material blown in with the condensed water. The sulfate losses in the tube ranged from 1 to 5% of the measured sulfate emissions.

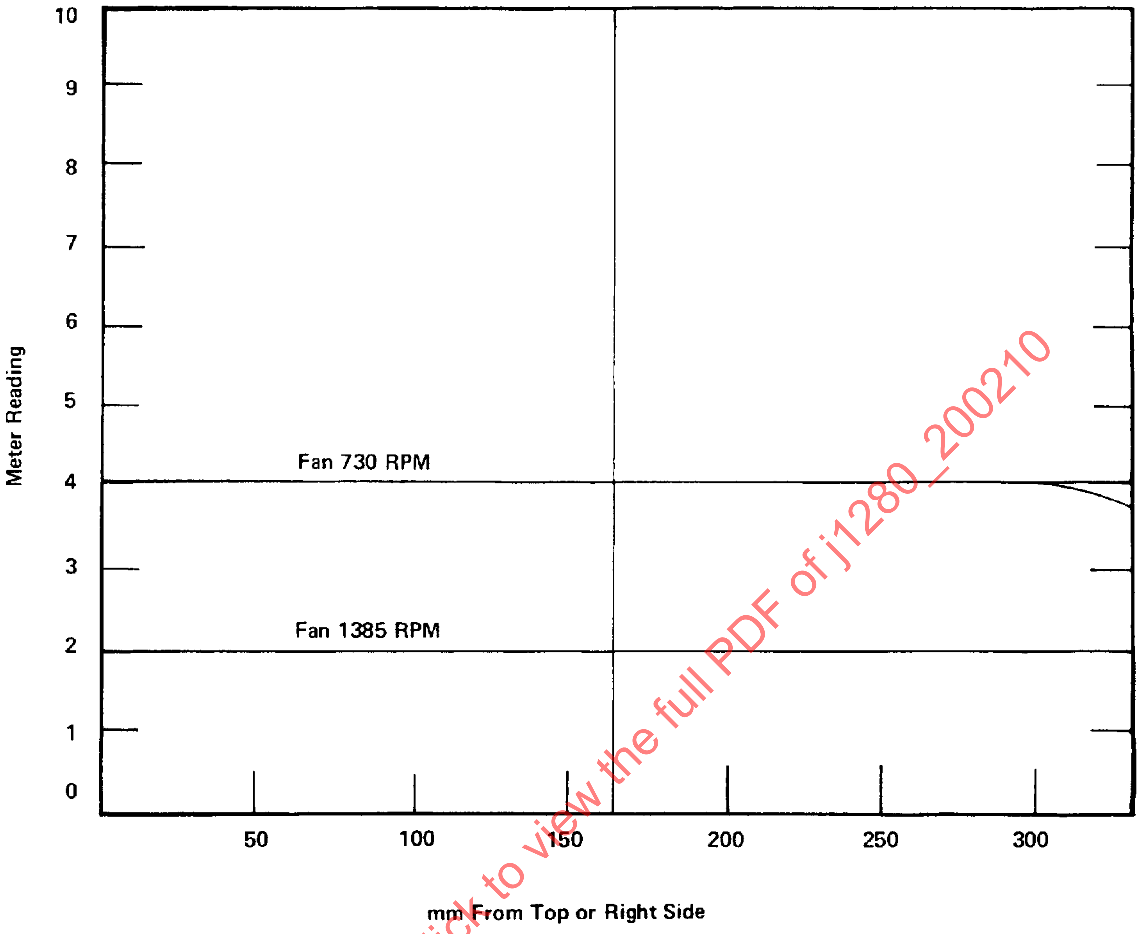

FIGURE 8—PROPANE CONCENTRATION PROFILES AT SAMPLING SECTION

5.1.2.1.3 System C—(Figure 9) This dynamic dilution system is a relatively large exhaust handling system designed to permit general particulate sampling as well as sulfate measurements. In this system the blower is upstream from the filter element and produces a positive pressure at the downstream sampling section.

5.1.2.1.3.1 Dilution Air Preparation—Dilution air is passed through two 0.1 m^3 High Efficiency Particulate Air (HEPA) filters contained in a 0.4 m^3 box fore it combines with engine exhaust at the mixing orifice. Typical filter material has an efficiency of 95% at 0.3 µm particle size and serves to minimize the contribution of background particulate matter to the test sample.

The blower used has sufficient capacity to supply up to 34 m^3/min of dilution air flow at 25 mm H_2O positive pressure; however, normal delivery is in the range of 25 to 28 m^3/min for use with driving patterns similar to that of the Federal Test Procedure.

5.1.2.1.3.2 Dilution Tube—The dilution tube is 11 m long x 584 mm diameter. Each 1.8 m section is formed from a 1.8 x 1.8 m sheet of 16-gage stainless steel by rolling it into a cylinder and welding the longitudinal seam. Mild steel flanges 32 mm wide are welded to each end of the tunnel sections for bolting them together. Dilution air and exhaust gases are mixed by means of turbulence created by a 203 mm diameter orifice at the dilution tube entrance. Dilution air flow rate through the tube is controlled by adjustment of three dampers, one at the blower inlet, one at the blower outlet, and one at a spill port between the blower and the filter box. Nominal dilution ratios between 10:1 and 30:1 are typical for this system. The sample point is about 10 m downstream from the exhaust gas-dilution air mixing orifice.

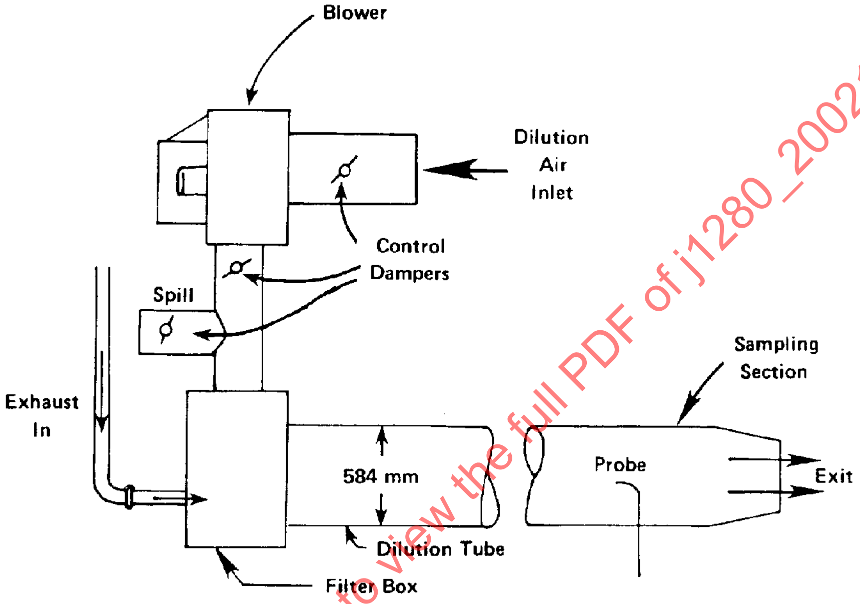

FIGURE 9—DYNAMIC DILUTION SYSTEM C

5.1.2.1.3.3 Exhaust Injection System—The vehicle exhaust enters the system downstream from the dilution air filter box and at the entrance to the dilution tube as described in 5.1.2.1.3.2.

5.1.2.1.3.4 Velocity and Gas Mixing—Velocity profiles in the dilution tube are measured at various sampling stations at two total flow rates and two exhaust-gas flow rates, using shop air to simulate exhaust gas flow. Velocity measurements are made with an anemometer using a hot-film sensor projecting into the airstream. Mixing profiles are determined at 176.8 m/min using CO as a tracer gas added to the simulated exhaust gases and an NDIR CO analyzer to measure the CO concentrations in the tube.

Both velocity and mixing profiles are measured by traverses of probes in vertical and horizontal planes. In each traverse, 14 positions are measured for the velocity profiles and 15 positions for the mixing profiles. Tests are run separately for horizontal and vertical velocity traverses, without attempting to adjust flow to exactly the same value in each test. Velocity and mixing profiles show whether mixing of exhaust gases and dilution are good and whether velocity profiles are satisfactorily flat in the cross section up to 203 mm from the centerline of the tube. The velocity and mixing profiles are not affected by changes of exhaust-gas flow rate.

5.1.2.1.3.5 Aerosol Mixing—Mixing analyses are repeated with an aerosol at the high flow velocity used in the gas mixing studies above, in order to determine the variation in concentration of the aerosol particles across the vertical and horizontal tube profiles. A sample probe assembly is bolted between two tube sections about 9 m downstream to hold 13 fixed sampling tubes, 9.5 mm in diameter, at the center and on vertical and horizontal axes at 127, 203, and 267 mm radii. The exit ends of the tubes are connected to absolute filter holders. Each holder contains a critical flow orifice which is designed for 0.0142 m^3 ± 0.0003 m^3 min and is connected to a vacuum line.

During these profile studies, the air velocity in the duct is adjusted to 176.8 m/min, a velocity intermediate between high and low flow. The test aerosol, a fluorescent dye dissolved in Freon-12 and toluene, is introduced while exhaust from an auto running at 56 km/h and with power output equivalent to 2.2 kW was flowing into the assembly. The particle size of the aerosol is determined with a cascade impactor for each run and is varied from run to run between 0.87 to 5.9 µm mass-mean equivalent diameter by varying the dye concentration. The amounts of dye collected on each impaction stage and on the absolute filter are determined with a fluorophotometer.

The variations in uniformity of distribution of the aerosol on the filters are generally found to be minor and the exhaust is mixed essentially completely throughout the cross section of the tube. Nonuniform dispersion of particles within the tube is not believed to be a major source of sampling error.

5.1.2.1.4 System D—(Figure 10) This dynamic dilution system is shown schematically in Figure 10.

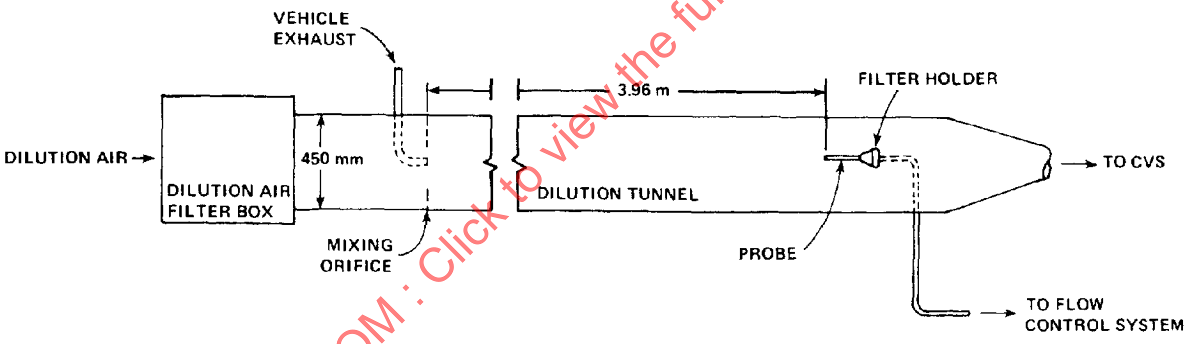

FIGURE 10—DYNAMIC DILUTION SYSTEM D

5.1.2.1.4.1 Dilution Air Preparation—There is no special preparation of dilution air for this system. Dilution air is drawn directly from the test area.

5.1.2.1.4.2 Dilution Tube—This system is of intermediate size, using a stainless steel (Type 304) tube of about 450 mm outside diameter with a 1.5 mm wall. Overall length of the cylindrical segment is 5.5 m while the tapered end is 0.6 m long. Distance from exhaust inlet to sample probe is about 4 m with the exhaust inlet mixing orifice 0.9 m downstream from the dilution air filter box. The sample probe centerline is on the centerline of the tube.

5.1.2.1.4.3 Exhaust Injection System—Exhaust gas entering the tube is mixed with dilution air by an orifice one-half the tube diameter. This system is compatible with the CVS system and uses the CVS to draw exhaust and dilution air through the tube. The dilution air filter is a standard high efficiency particulate air filter from a CVS unit. Normal flow rate is 24.53 m^3/s which provides 2.5 s mixing time between the orifice and the probe. Reynolds number is about 40 000.

5.1.2.1.4.4 Mixing of Exhaust Gas with Diluent Air—Turbulent flow profile 200 mm on either side of the probe centerline has been determined to be essentially flat with a 3% deviation from maximum flow. Mixing has been evaluated with propane injection and has been found satisfactory.

Under most conditions, tube flow rate is sufficient to permit sulfuric acid condensation yet prevent the condensation of water. At the same time it provides a sample stream concentrated enough to permit good particulate collection. However, during the cold start portion of an FTP, some condensation can be formed in the tube. If condensation does occur, it is rapidly evaporated back into the flowing stream by exhaust heat. While it is assumed that the condensate is primarily water, it contains some sulfate. Upon evaporation, part of the sulfate could be left on the tube walls. Analysis of tube sweepings indicate that a small amount of sulfate does accumulate. This could be due to both the above phenomenon and particle impaction.

During very hot vehicle operation, such as with certain types of catalyst vehicles at 96 km/h steady state cruise, probe area temperatures of up to 120 °C have been recorded. Although this is below the 140 °C H_2SO_4 nominal dew point, it is above the 90 °C point considered to be the upper limit for reliable sulfuric acid collection.

5.1.2.2 Static Diluted Exhaust (Dilution Chamber) (System E)—This technique dilutes engine exhaust gas with ambient air and then introduces the mixture into a suspended 100 m^3 black polyethylene bag. The bag is 5.8 m long, 4.6 m wide, and 3.7 m high, made of 152 μm (6 mil) black industrial-grade polyethylene with all seams heat-sealed and corner seams double heat-sealed. A door built into the bag provides access and special ports are installed for attaching sample probes and for introducing the gas mixture. The inside of the bag is sprayed with Merix Anti-Static No. 79.

The bag is equipped with a means for introducing exhaust at a point well into the chamber and with ports for both gaseous and particulate samples. The connector between the bag and the engine exhaust pipe is designated to eliminate sulfate losses to the walls of the connector and to the floor of the bag. All surfaces of the connector that are exposed to exhaust gas are heated to 250 °C. Additionally, the exhaust is partially diluted with ambient air prior to its entry into the chamber. Under these conditions sulfates have been found to remain gaseous until diluted and dispersed with only about 2% of the fuel sulfur lost in the connector. Data indicate that both heat and dilution are often needed to insure effective dispersion of sulfates. Figure 11 is a schematic drawing of the connector.

The system provides a static and stable sample and when combined with sensitive analytical methods has proved satisfactory for both steady-state and cycling operational tests. Bag volume limits exhaust sample collection to 12 to 15 min, especially at high exhaust flow rates. The bag may be somewhat more inconvenient than dynamic dilution tubes since it must be cleaned and prepared for each new sample. Normally five to six runs can be made in an 8 h shift.

5.1.2.2.1 Test Procedure—If engine warm-up is desired the exhaust can be bypassed to the vent (Figure 11). When sampling is to begin, the air-dilution system is activated, the bypass valve closed and the bag valve opened. Exhaust mixture is then introduced into the bag for a predetermined length of time. The test is ended by reversing the connector valving sequence.

5.1.2.2.2 Cleaning Procedure—A circulating system is provided to purge the exhaust gas mixture in the bag and replace it with fresh air. One of the circulating blowers draws air in and the other vents it, the flow rates balanced. The bag is partially collapsed during the purge period. After a minimum of 1/2 h of purging, the blowers are stopped and rerouted to recirculate the air in the bag through a Drierite drum and filter. This recirculation is allowed to continue for another 1/2 h, and reduces the relative humidity to about 15%. All blowers, pumps, and dehumidifiers are turned off during the introduction of exhaust mixture and when withdrawing samples.

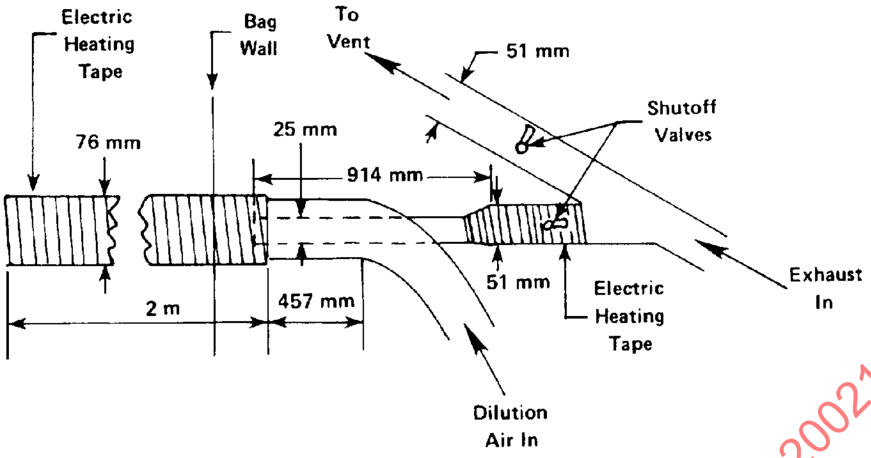

FIGURE 11—SCHEMATIC OF CONNECTOR

5.1.2.2.3 Verification of System—Deposition of sulfates on the walls of the connector has been found to be on the order of 2% of total sulfur handled. Rate of decay for both SO_2 and sulfates during the first 30 min after introduction of the exhaust sample into the chamber has been determined to be less than the analytical variation. Also, traverses of the bag have shown variations in gaseous composition (SO_2 sulfates, and CO_2) and temperature no greater than the analytical variability. Exhaust gas introduction increases chamber temperature 2 to 5 °C above ambient. All studies to date indicate that good mixing occurs in this collection system.

5.2 Sampling and Collection Procedures—Isokinetic sampling, probe and filter housing designs, probe installations, and filtering media are discussed. Filters, controlled condensation coils, and impingers-bubblers are the three systems commonly used to collect sulfates. Typical examples of each are described in detail as follows:

5.2.1 ISOKINETIC SAMPLING, PROBE, AND FILTER HOUSING DESIGNS—Isokinetic sampling is desirable to insure that the particulate sampled is representative of the particulate in the main stream; that is, the particulate concentration and size distribution in the probe sample should correspond to that of the main stream. (See Equation 1.) Probes for isokinetic sampling are designed so that the sample stream is divided into two parts with a volume ratio equal to the ratio of the cross-sectional areas of the openings of the sample probes and the dilution tube cross-sectional area.

$$\text{Thus: } \frac{\text{Area (probe)}}{\text{Area (tube)}} = \frac{\text{Volume Flow (probe)}}{\text{Volume Flow (tube)}} \qquad \text{(Eq. 1)}$$

However, studies have shown that for fine particles, less than 10 µm mass mean equivalent diameter, the error introduced by deviations from isokinetic sampling that are less than 20% are negligible. In addition, for particles smaller than about 4 µm diameter isokinetic sampling is relatively unimportant over a range of at least 250% higher than the isokinetic velocity, where the velocity is not over about 15 m/s. Since sulfate particles are normally of submicron size, isokinetic sampling is considered to be of minor importance. Another item to be considered in probe design is minimizing sample deposition in the probe. When suspended particulate matter leaves the dilution tube and enters the sampling probe, it is leaving a low surface to volume region and entering a high surface to volume region. Relative sample losses by impaction should be greater in the probe than in the tube. Therefore, the probe should be as short and direct as possible to minimize the residence time of the particulate matter in the probe. The filter housing connected to the probe is flared out as soon as physically possible to minimize the surface to volume ratio of the housing and thereby reduce sampling losses by impaction in this portion of the sampling system.

5.2.2 FILTERS AND FILTER COLLECTION SYSTEMS

5.2.2.1 Filters—The selection of a filter for any application is a compromise, generally arrived at by rejecting those with features which are least tolerable. For automobile exhaust particulate matter several types have been used. The choice in a particular experiment depends mainly on the analytical information desired. Table 3 summarizes the principal characteristics of several filters. All of the filters are considered absolute, that is, they are rated at >99% efficient for particles 0.3 µm diameter. This feature is a requirement for the quantitative sampling of auto exhaust particulate matter which is of relatively small particle size.

5.2.2.1.1 Glass Fiber Filters—Glass fiber filters are generally satisfactory for sulfate collection if handled very carefully so as to avoid the loss of tiny fibers from the edge. Glass fiber filters can be weighed with an average loss per cycle (tare weighing, insertion in and removal from the holder, and gross weighing) of about 100 µg per 142 mm filter. Their humidity sensitivity is relatively low. Pressure drop is also low. Impurities can be relatively high in some cases; however, an unidentified extractable colored component (probably organic) tends to interfere with the sulfate determination unless the filters are pretreated as described later in this paragraph. Glass fiber filters are especially useful for the capture of liquid aerosols, including sulfate aerosol. High surface-to-volume ratio of this type filter permits the absorption of much more liquid than permitted by a membrane filter.

5.2.2.1.1.1 Glass Fiber Filter Pretreating—Glass fiber filters have been pretreated successfully by the following procedure: A few filters, 4 to 6, are loosely stacked alternately on a piece of heavy aluminum foil (freezer wrap). The sides are folded over loosely, and the package placed in a muffle furnace at about 200 °C. In perhaps two steps over a period of about an hour, the temperature is raised to 450 °C and held for several hours. The exact times are not critical. Near the end of the day shift, the muffle furnace control is set to 200 °C, which allows the temperature to drop slowly during the night.

The next day the filters are soaked in 20% HCl in a large borosilicite glass baking dish on a warm hot plate. After about an hour, the HCl is poured off, and the filters rinsed in flowing deionized water. Each filter is further rinsed in a large Buchner funnel until the washing shows no Cl with the $AgNO_3$ test. The washed filters are air dried for several hours, then gradually heated to 450 °C and cooled overnight as in the preheating step described previously. The washed and dried filters are then equilibrated at least 24 h in controlled temperature-humidity room before weighing.

5.2.2.1.1.2 Precautions—Two adverse factors mentioned earlier must be recognized when weighing glass fiber filters—the effect of moisture and of fiber loss. Both can be offset to some degree by weighing a control filter. However, to the extent that fiber loss is random, the precision of the correction is low. If this technique is to be used, a control filter of the type and size of the filters to be weighed is selected at random. This filter is weighed before each group of not more than three sample filters. The change, either positive or negative, of the weight of the control filter during the interval between the tare weighing and the gross weighing, should be subtracted algebraically from the weight change following collection of the particulate sample. Positive control-filter weight changes have been noted frequently when the gross weighing was made at a higher relative humidity than that during the tare weighing. This weighing method presumably corrects for moisture absorption difference by the filter (not by the sample, for example $H_2SO_4 \times H_2O$), if the control and the sample filter respond similarly to humidity. On the average, the method corrects for fiber loss with the exception that the control sample is not clamped in the holder. Experiments have shown that the clamping loss, if a fluorocarbon washer is used (see 5.2.2.2.2), is less than the loss caused by handling in placing a filter on and off the balance pan.

TABLE 3—CHARACTERISTICS OF CANDIDATE FILTER FOR AUTO EXHAUST PARTICULATE MATTER

Filter	Composition	ΔP cm Hg 10 L/min/cm^2	ΔWt ΔRH	Loading Capacity	Electrostatic Effect	Handling Charac-teristics	C/H Analysis
Dexiglas No. 225	glass fiber	24	rel. low	rel. high	low	fair	fair
Gelman—A	glass fiber	24	rel. low	rel. high	low	fair	fair
Millipore HA 0.45	cellulose triacetate	100	rel. high	rel. low	rel. high	good	un. sat.
Nuclepore N040 10200	polycarbonate	50	low	low	high	poor	un. sat.
Selas metal membrane	silver	100	vy. low	low	nil	vy. good	good
Gelman DM-450	copolymer polyvinylchloride and polyacrylonitrile	100	fair	low	moderate	good	un. sat.
Gelman AN-450 Acropor	copolymer polyvinylchloride and polyacrylonitrile	100	fair	low	moderate	poor	un. sat.
Tissue quartz(1)	quartz fibers	—	good	good	good	vy. poor	good

Filter	Impurities S	Impurities Pb	Impurities Fe	Impurities Ca	Impurities P	Impurities Zn	Impurities Al
Dexiglas No. 225	med.	low	low	high	low	low	med.
Gelman—A	med.	low	low	high	low	low	med.
Millipore HA 0.45	low	low	low	low	low	low	low
Nuclepore N040 10200	low	low	low	low	low	low	low
Selas metal membrane	low	not satisfactory	not satisfactory	not satisfactory	not satisfactory	not satisfactory	not satisfactory
Gelman DM-450	high	low	low	low	low	low	low
Gelman AN-450 Acropor	high	low	low	low	low	low	low
Tissue quartz (1)	good	no information	no information	no information	no information	no information	no information

1. May not qualify as an "absolute" filter.

5.2.2.1.2 Quartz Fiber Filters—Quartz fiber filters have quite low concentrations of most impurities but they are extremely fragile. Handling quartz fiber filters causes weight loss from ablation, making weight measurements unreliable in the submilligram range. Furthermore, they are extremely sensitive to humidity variations, causing additional weighing problems. Metal membrane filters have very high pressure drop and are quite expensive. The copolymer filters have a high sulfur background and are therefore not satisfactory for the measurement of sulfate aerosols. The polycarbonate filter has a moderate pressure drop and low sulfur impurity and can be used if care is exercised in handling.

5.2.2.1.3 Fluorocarbon Filters—The State of California Air Resources Board and the Environmental Protection Agency recommends the use of Millipore Corp., Fluorocarbon Type FA, 1 µ pore, 90 mm diameter filter for reasons presented in SAE Paper 770166. “Automotive Sulfate Emission—A Baseline Study,” Somers, Garbe, Lawrence, and Baines.

5.2.2.2 Filter Collection Systems—When using filters, a dilute sample should be hot enough to prevent premature water condensation in the probe assembly and cold enough to contain particulate sulfates at the filter. Under these conditions, sulfates will be deposited on the filter media for subsequent analysis. Filter media should have low pressure drop and high strength. They should not contain impurities that will interfere with analytical methods. Filter diameter depends upon sample flow rate and desired face velocity. Sample flow rate should be high enough to collect an adequate mass in a reasonable length of time and may be eliminated by filter pressure drop. Some in-use systems attempt to maintain isokinetic conditions in the probe assembly while others permit limited deviation.

Three filter collection systems used successfully are described as follows:

5.2.2.2.1 System F—(Figure 12) This system is associated with Dynamic Dilution System B (5.1.2.1.2). However, it is representative of those in use with other diluted-exhaust handling systems. The probe is made of 30 mm I.D. x 32 mm O.D. stainless steel tubing 230 mm long bent through a 90 degree angle on a 90 mm radius. The open end is inserted through the dilution tube wall and oriented to point upstream with the tip about 120 mm in from the wall. The probe is connected to a stainless steel filter holder which is one of two sizes:

a. For 102 mm diameter (90 mm effective) filters; or
b. For 142 mm diameter (127 mm effective) filters (see Figure 12).

The complete collection system includes a vane-type vacuum pump and flow meter as illustrated in Figure 12. Vane pumps generate a smooth flow so that no ballast plus resistance is required for correct flow indication by a Rotameter flow meter. However, because the Rotameter in these collection systems must be ahead of the pump, the pressure at the Rotameter will be subatmospheric. The indicated flow rate must therefore be corrected according to the relationship (see Equation 2):

$$\text{Flow rate at ambient pressure} = \text{indicated rate}\left(\frac{P_1}{P_2}\right)^{1/2} \qquad \text{(Eq. 2)}$$

where:

P_1 = pressure at Rotameter exit
P_2 = ambient pressure (for which Rotameter calibration applies)

Gelman A glass fiber filters, pretreated by heating at 530 °C to destroy organic material, are used most frequently. Nuclepore polycarbonate filters, 0.4 µm diameter pore size, and Selas silver membrane filters are also used. All filters are rated as >99% efficient for particles 0.3 µm.

The normal filter sample flow rates, corrected to atmospheric pressure are 0.0047 m^3/s for glass fiber filters and approximately 0.0014 m^3/s for the more restrictive Nuclepore and silver filters. The filter samples constitute approximately 0.3 to 2% of the total exhaust. The dilution tube flow rate is generally 17.27 m^3/min for the FTP and for 48 km/h cruise and 32.84 m^3/min for 64 and 96 km/h cruise. Thus, sampling is not always isokinetic, but the departures from isokinetic flow are assumed inconsequential in view of the apparent submicron-size of the sulfate aerosol.

5.2.2.2.2 System G—(Figure 13) Two versions of System G have been used with the exhaust handling tube of Dynamic Dilution System C. However, either can be used with other types of dilution systems.

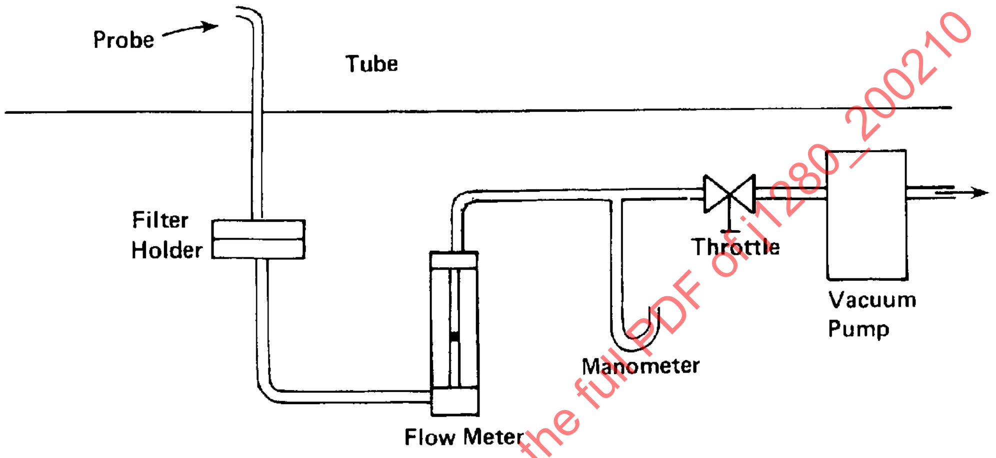

FIGURE 12—FILTER SAMPLE COLLECTION SYSTEM F

In the Type I system, filter sample probes are 19 mm ID x 350 mm long Teflon tubes with a 30 degree bend inside the dilution tube. The probe tip is also Teflon, 56 mm in diameter, tapering to probe diameter. Sample flow rate is about 0.1 m^3/min which, when using a nominal 13.3 m^3/min dilution tube flow rate, results in collection at about 93% of isokinetic conditions. This is considered more than adequate for the submicron sulfate particles. The filter holder is stainless steel containing a 142 mm flat filter. A short conical transition piece connects the probe to the holder. The particulate path from tube to filter is short and free of severe bends or other restrictions.

In a Type II system, particulate samples are collected on 142 mm diameter filters held in Millipore Model YY22 142 99 stainless steel holders. The holders are modified by the addition of straight stainless steel tubes and a conical entrance to the inlets, and the insertion of flat fluorocarbon gaskets (3 mm thick x 130 mm ID and 147 mm OD), between the mating surfaces. The inlet tubes facilitate connection to the dilution-tube sampling ports, and the gaskets minimize filter cutting and fiber loss when the holder parts are clamped together. The filter holders are connected by machined PVC adapters to 50 mm stainless steel tubing inserted into the dilution tube at the 10 m point. The inlets of the stainless steel probes are fitted with PVC nozzles machined to an entrance cross section to give isokinetic flow at the tip. Different nozzles are used for each steady speed test, and for FTP tests. O-rings are used to seal the adaptors to the probe tubes and the filter holders to the adaptor. This permits a quick connect-disconnect operation, which is essential for cyclic tests.

Both glass fiber and quartz fiber filters have been used in this system. Filters are stored in opened packages in a controlled temperature-humidity room with a nominal ambient of 22 °C and 45% relative humidity. Within 24 h preceding a test, the filter holders are loaded with the proper filters. Before loading, glass fiber filters (not quartz fiber filters) are weighed. The weighing procedure is critical if reproducible weights are to be obtained.

With either Type I or Type II versions, the filter holders with weighed filters are connected to the sampling probes on the dilution tube. At the exit of each holder a critical flow orifice with a nominal flow of 0.1 m^3/min at 100 kPa is installed. Downstream from each critical flow orifice there is a Bourdon vacuum gauge backed by a full-flow throttle valve. The valves are connected to a manifold held at 55.8 kPa vacuum by a 0.8 m^3/min carbon vane vacuum pump. Filter holders are calibrated by a dry gas meter using the 55.8 kPa vacuum. Each filter is operated at a downstream pressure established by calibration tests to be below the critical flow pressure, that is, the flow is critical through each orifice during all tests. Before every test (or after the test in the case of reloaded filters in a cycle), the actual flow through each filter at the vacuum gauge setting is measured using a calibrated dry test meter. Small but measurable differences in the flow have been observed from one filter to the next. The actual flows are used to calculate the volume of each sample.

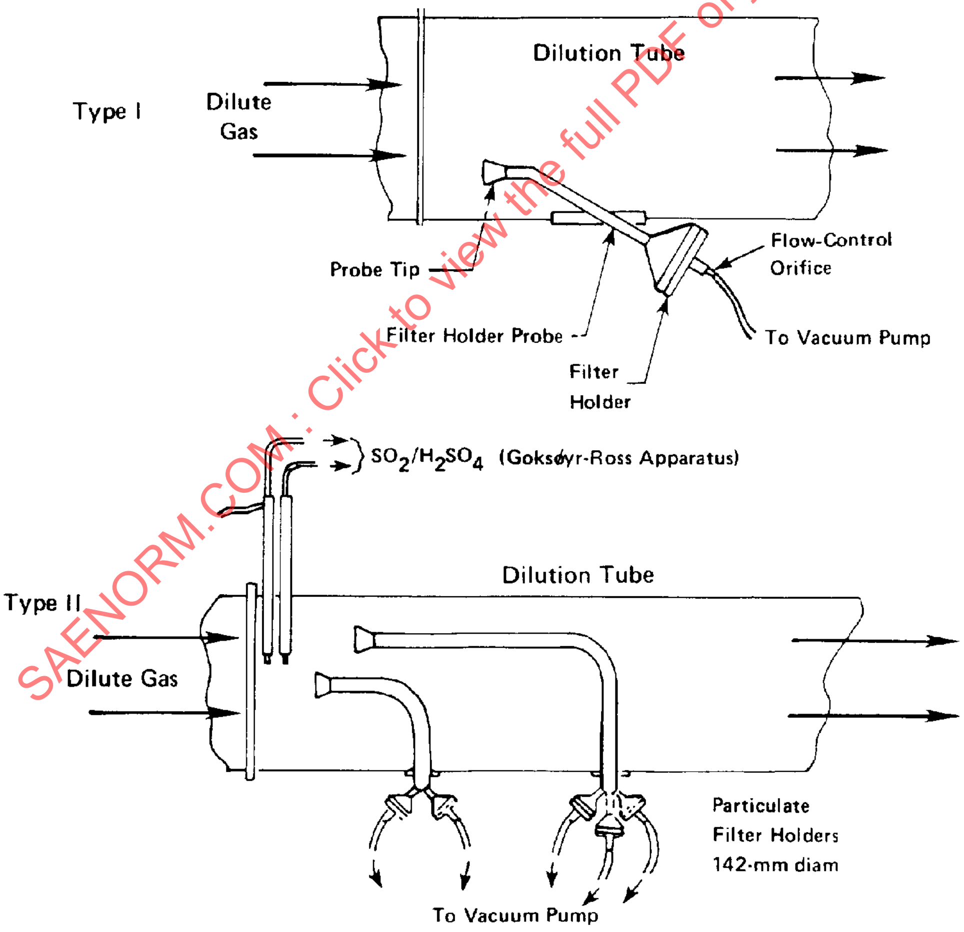

FIGURE 13—FILTER COLLECTION SYSTEM G

At the beginning of each test, the throttle valves for each filter are quickly adjusted to the desired gauge setting. Because flow is critical, the exact gauge setting is relatively unimportant; however, it is normally reproduced for each test. In cycle tests, some filters are used during one portion or phase of the complete cycle, others during other portions. After sampling is completed, the filter holders are returned to the controlled temperature-humidity weighing room, where the sample filters are removed and placed in partially covered plastic petri dishes. After a minimum 16 h equilibration period in the weighing room, the glass fiber filters are weighed versus a control filter as described in 5.2.2.1.1.2. The net weight of particulate matter is obtained by subtraction of gross-tare weight, with corrections being made based on the change in the control filter weight.

5.2.2.2.3 System H—(Figure 14) This system is normally used with a static dilution chamber such as the one described in 5.1.2.2.

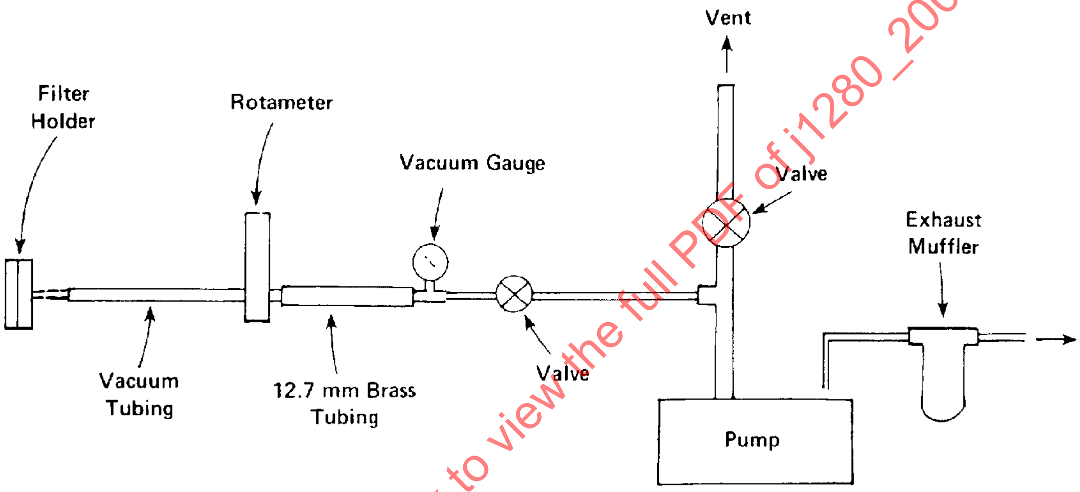

FIGURE 14—COLLECTION SYSTEM H

The sample train consists of a filter holder, Rotameter (0 to 2.83 m^3/h range), vacuum gauge, pump, plus associated valves and tubing. If sampling is done from a static dilution chamber, mount the filter holder in a horizontal position so that the filter is positioned inside the bag 63.5 mm from the wall.

It is convenient to mount the filter holder on a metal plate attached to the wall of the chamber. The metal plate has a circular hole cut in to receive a No. 13 one-hole neoprene stopper. Attach a metal tube to the exit of the filter holder, and mount the holder by passing the tube through the stopper.

Place a glass fiber filter inside the filter holder and lock it in place. Attach the filter holder to the sampling train. Start the pump and adjust the line valve and the bleed valve to give a gas sampling rate of 2.72 m^3/h. Pump ambient air through the filter for 5 min (equivalent to a gas sample of 0.23 m^3). Record the sampling time and the temperature of the ambient air.

If the iodate method of analysis is used refer to 5.3.1.3.3 for filter preparation and handling precautions.

5.2.3 Controlled Condensation System—(Figure 15) In the controlled condensation/hydrogen peroxide method, sulfuric acid is collected by condensation in a coil, often referred to as a Goksoyr-Ross (G-R) condenser-absorber. Downstream of the apparatus SO_2 may be collected by oxidation with aqueous H_2O_2 to $SO_4^{=}$. A typical system, illustrated in Figure 15, consists of a heated quartz or Vycor sampling probe, a quartz wool plug filter, a condenser coil with exit frit, and H_2O_2 bubblers, plus drying tube, pump, and dry gas displacement meter. A typical sample probe arrangement is shown in Figure 8. Isokinetic conditions are deliberately avoided so that large particles, such as flakes from the exhaust system, are suppressed. The probe is wrapped with heating tape and enclosed in 16 mm ID stainless steel tubing. The exterior end is connected via 12/5 spherical joints to a 25/15 spherical unit containing quartz-wool as a particulate fiber. This filter unit, which is wrapped with heater tape before each run is connected to the entrance end of the G-R coil, followed by three bubblers in series. The G-R gas sampling units have three distinct sampling functions:

a. The probe, quartz wool filter, and associated glassware should remove only particulate matter but no sulfuric acid mist because they are maintained at temperatures above the SO_3 dewpoint;
b. The coil should retain all and only the condensed H_2SO_4; and
c. The bubblers should retain all and only the SO_2 as $SO_4^{=}$.

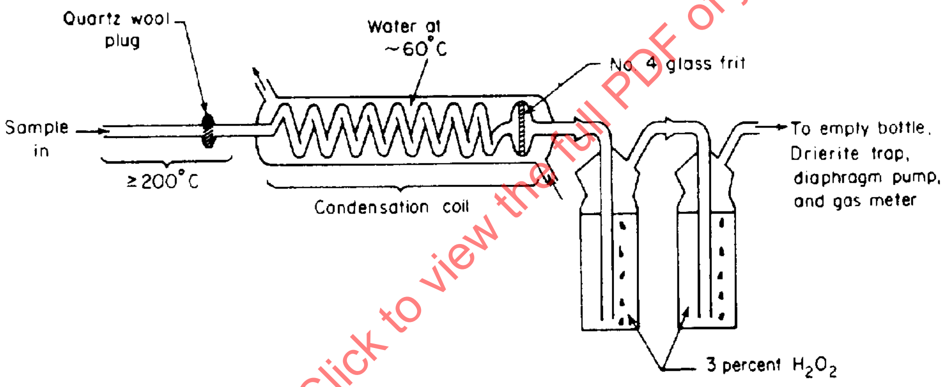

FIGURE 15—CONTROLLED CONDENSATION COLLECTION SYSTEM FOR SULFATE AND SULFUR DIOXIDE

The first two bubblers are loaded with 50 mL ± 2 mL of 3% H_2O_2; the third is empty. All connections are made via unlubricated 12/5 spherical joints. The last bubbler is connected by Tygon® tubing to a 50 mm borosilicite glass (Pyrex® or equivalent) drying tower containing about 340 g silica gel. The sample gas is pulled through the system and exhausted through a dry-gas-test meter by means of a sealed bellows pump with a throttling valve. Each dry test meter is calibrated against a standard meter that has been calibrated against an instrument laboratory standard. The probe assembly and quartz wool filter are kept hot during the sampling period by heater tape. In one G-R unit, a mercury thermometer is inserted in a tee between the quartz filter and the G-R coil. The thermometer bulb is directly in the gas flow path; during a test the indicated temperature is normally 170 to 210 °C, depending primarily on how the tape has been wrapped. In all tests this temperature should be maintained higher than the condensation point of the H_2SO_4 x H_2O mixture (about 140 °C). The G-R condenser coil is maintained at 60 to 70 °C by a water jacket surrounding the coil and frit of the G-R unit through which heated water at 70 °C is circulated from a thermostatted supply vessel.

Before a test, two bubblers are loaded with H_2O_2, the drying tower filled with silica gel, and the train installed in position at the sampling point. Each train is then disconnected from the probe and capped for leak test. Polyvinyl chloride (Tygon® or equivalent) tubing connections are made from the empty bubbler through the drying tower to the pump. Connections in the pumping unit to the needle valve, vacuum gauge, and dry-test meter are checked. When all are in order, the pump is started and the needle valve controlling the air flow from the train to the pump slowly opened. Initially the bubblers should bubble as air is emptied from the system. If there are no leaks, the bubbling soon stops and no gas flow is indicated on the dry-test meter. If leaks are present, they often can be repaired by merely flexing a leaking spherical joint. When shutting down, either to repair a leak or to reconnect the unit to the probe, the system should be slowly vented from the coil end while simultaneously closing the sampling needle valve. Failure to observe this procedure will cause the bubbler solutions to suck back into the coil. If that occurs, the coil must be removed, rinsed, and dried, then reinstalled in the unit and rechecked for leaks. When ready, the coil jacket is connected to the hot water circulating system maintained at 60 to 70 °C.

When the units are ready, the sampling needle valve is quickly opened and adjusted to approximately 5 to 6 L/min. No further adjustments should be necessary during a test to maintain this flow. About every 15 min, readings should be taken of the coil jacket water temperature, the dry-test meter (gas) temperature, and its cumulative volume reading. Periodically, the temperature of the thermometer in the sampling line should be noted. At the end of a sampling period, each unit is shut down by closing the sampling needle valve, noting the final cumulative sample volume reading, and disconnecting the unit from both sample probe and pump.

Refer to 5.3.3.1 for a typical procedure used to analyze downstream bubblers for SO_2.

As a result of several experiments, a number of characteristics of the system have been established:

a. Most of the sulfuric acid is trapped in the coil and not ahead of it in the heated probe or quartz wool plug.
b. Virtually no sulfuric acid can be condensed in a second condenser coil in series, indicating the efficient capture of H_2SO_4 by a single coil.
c. Most of the H_2SO_4 condenses in the coil walls, though some of it (up to about one-third) does condense in the gas stream and hence requires the exit frit.
d. The first of two H_2O_2 bubblers in series captures about 90% of the SO_2, the second bubbler about 10%, and a third empty bubbler less than 1%, confirming the ample SO_2 absorbing capacity of the bubbler train.

Permeation tube experiments, in which SO_2 was introduced at a known rate into a carrier airstream have established that:

a. The controlled condensation technique recovers quantitatively the SO_2 in the carrier gas, as $SO_4^{=}$ in the H_2O_2 bubblers.
b. The system created no H_2SO_4.

5.2.4 BUBBLER/IMPINGER COLLECTION SYSTEMS—This collection system is similar to that of EPA Method 8 for determining sulfur-related species in effluent stacks. Systems tested to date are modifications of the previous method and must be classed as highly experimental when applied to engine exhaust. Due to the many inconsistencies and other difficulties that have arisen with data obtained by this collection system, the user is cautioned to exercise extreme care, both in equipment operation and interpretation of results. There is an indication that impurities in various batches of reagent grade isopropanol may be responsible for some of the problems encountered. Three typical systems that have been used are described, briefly, as follows:

5.2.4.1 System—(Figure 16) In this bubbler system the gas sample is passed through a sample train in which a sampling bubbler containing isopropanol acidified with a known amount of weak sulfuric acid is connected in series with a sampling bubbler containing hydrogen peroxide solution. Sulfur trioxide and sulfuric acid mist are absorbed in the isopropanol solution and sulfur dioxide is absorbed in the hydrogen peroxide solution. The volume of gas passed through the absorbers is measured with a wet-test gas meter.

5.2.4.2 *System K*—This bubbler collection system is used principally to determine sulfur trioxide in engine exhaust and is a modification of a method proposed by Seidman.[1]

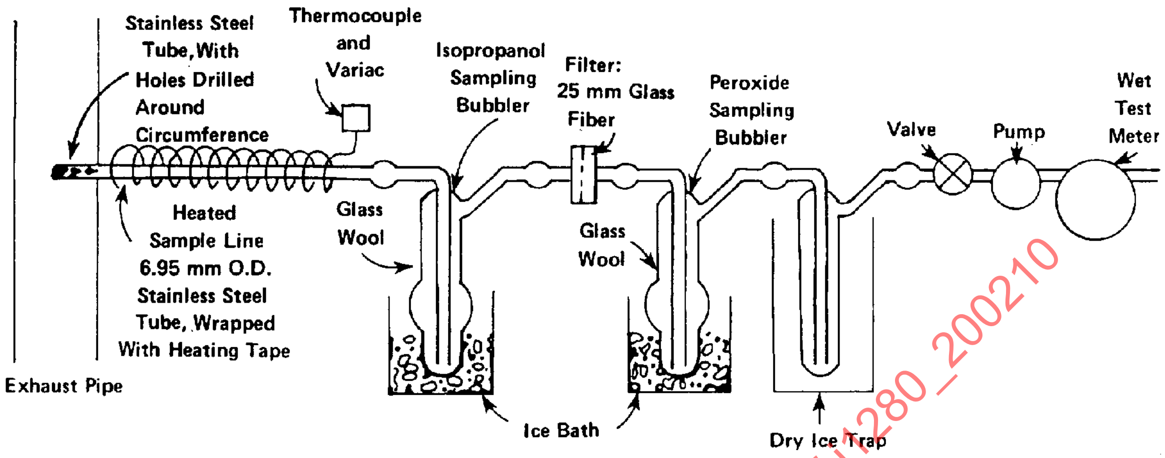

FIGURE 16—BUBBLER COLLECTION SYSTEM J

Four midget impingers, three with orifice stems and one with a fritted glass stem, are used to collect the sulfur trioxide emissions. The first three absorbers, having orifice stems, are filled with 15 mL of 80% reagent grade isopropyl alcohol. A small amount (2 to 3 mL) of 80% isopropyl alcohol is added to the fourth absorber which has a fritted glass stem. This small amount of solution in the fourth absorber is sufficient to keep the fritted glass moist and to aid in retaining any solution or sulfur trioxide which may escape from the first impingers. All of the impingers are immersed in an ice water-salt solution.

The gas sample is drawn into the impingers by a pump operating at a flow rate of less than 0.28 m^3/h of gaseous sample through the system. When possible, at least 0.14 m^3 of sample is used.

Due to the high temperatures of actual engine exhausts, it is necessary to use a stainless steel probe inserted into the exhaust pipe. The probe is connected directly to the first impinger with fluorocarbon (Teflon ® or equivalent) tubing. The sampling system is shown as follows:

Exhaust → Probe → Impingers → Flowmeter → Pump → Outlet

5.2.4.3 *System L*—This bubbler collection system is based on EPA Method 8 but is modified to adapt it to engine exhaust testing. A sampling pipe, 57 mm in diameter and 1.2 m long is connected to the exhaust pipe with a flexible metal hose. The sampling nozzle, Pitot tube, and thermocouple are inserted to the centerline of the sampling pipe. The outlet of the sampling pipe is connected to a CVS system, in the usual manner. A standard Method 8 probe and sampling train is used (Lear-Siegler Model 100 Manual Stack Sampler or equivalent). In some cases, the second impinger contains 100 mL of 80% IPA solution rather than 100 mL hydrogen peroxide solution. The filter position is between the first and second impingers and the filter is added to the contents of the first impinger as called for in Method 8. Sampling time is 1/2 h per test. For sampling undiluted exhaust, isokinetic sampling is unnecessary because the sulfuric acid (H_2SO_4) is in vapor form. However, sampling is usually close to isokinetic.

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[1] E. B. Seidman, "Determination of Sulfur Oxides in Stack Gases." Anal. Chem. 30:1680 (1958).

5.3 Sample Preparation and Analysis—This section covers methods for determining sulfate and other sulfur-related compounds from the material trapped by the collection system.

5.3.1 METHODS SPECIFIC FOR SULFATES—Five known methods are discussed in the following paragraphs:

5.3.1.1 Barium Perchlorate Titration—$Ba(ClO_4)_2$.

5.3.1.1.1 Theory of Operation—This general technique is one of the most common methods in use. It is adaptable to analysis of samples obtained on filters, by controlled condensation, or in IPA bubblers. Various methods used with filter and controlled condensation samples are similar enough to be covered together. However, one method used in 5.3.1.1.5.2 in conjunction with IPA bubblers warrants separate treatment.

Experimental conditions for applying this method can be varied to measure sulfate at different levels. Both visual and instrumental methods are used to detect the endpoint of the titration. Two different indicators are employed for visual endpoint detection. The general titration procedure is described followed by specific instruction for sample preparation associated with each mode of endpoint detection.

5.3.1.1.2 Apparatus Required—The following apparatus is used in the titrations:

a. Ion exchange column, 10 x 250 mm
b. Burettes (at least 0.05 mL divisions)
c. Low range pH paper, pH 1.0 to 4.3
d. Colorimeter and probe for endpoint detection
e. Automatic titrator

5.3.1.1.3 Reagents Required

a. Barium perchlorate standard solution 0.01 N
b. Barium perchlorate standard solution 0.001 N
c. Hexamethylenetetramine (5% aqueous)
d. Sulfonazo III indicator (0.1 g/100 mL H_2O)
e. Ethyl alcohol, absolute
f. Acetone
g. Nitric acid (2% aqueous)
h. Dowex 50 W-X8 cation exchange resin (50 to 100 mesh)
i. Sulfonazo III indicator
j. Thorin
k. Methylene blue

5.3.1.1.4 Calibration Procedure—The barium perchlorate solution is standardized by titration against previously standardized 0.01 N sulfuric acid. Five mL 0.01 N sulfuric acid is pipetted into a 125 mL Erlenmeyer flask and 45 mL of deionized water and 2.5 mL 2% nitric acid are added. The solution is adjusted to pH 4 using 5% hexamethylenetetramine and titrated with barium perchlorate solution. Normality is calculated from Equation 3:

$$\text{N Ba(ClO)} = \frac{\text{mL } H_2SO_4 \times \text{N } H_2SO_4}{\text{mL Ba } (ClO_4)_2} \quad \text{(Eq. 3)}$$

5.3.1.1.5 Analytical Procedures

5.3.1.1.5.1 Sulfonazo III Method:

a. Procedure—In order to analyze the filter samples, cut and place one-quarter section of filter in 100 mL beaker. (One-half filter can be used for low levels of sulfate.) Add 3.0 mL of 2% nitric acid, wetting the filter section completely, then add 20 mL deionized water. Place a small glass stirring rod in the beaker and cover with watch glass. Digest the samples on hot plate and allow to boil for 5 min. Cool the beaker and filter the liquid through glass wool into the ion-exchange column containing 7.5 g of Dowex 50 W-X8 (or equivalent) cation exchange resin, collecting the sample in a 125 mL Erlenmeyer flask. Wash the beaker with three 5 mL portions of deionized water and add the washings to the column. After each washing, squeeze liquid from the filter by pressing it against the wall of the beaker with the stirring rod.

If the sample is obtained by controlled condensation, rinse the coil and glass frit with deionized water into a flask. At this point, for samples obtained by either method, place the flask on a hot plate and evaporate to approximately 5 mL. Adjust the pH of the remaining solution to pH 4 using 5% hexamethylenetetramine. Add 10 mL ethyl alcohol and 25 mL acetone to the flask, then add 3 drops Sulfonazo III indicator. Titrate with 0.01 N barium perchlorate solution (if sulfate content is low, use 0.001 N barium perchlorate). If the sample requires more than 10 mL of barium perchlorate to reach the endpoint, the results are unreliable and should be discarded. In this event, another section of the filter should be processed through the ion-exchange step. If a controlled condensation sample is involved, some should be saved against this eventuality. At this point, the solution is diluted to an appropriate level before proceeding with the remainder of the steps.

b. Interferences and Precautions—The preceding procedure was arrived at after experimental work identifying sources of error and the means to minimize or eliminate them. Reliable results from filter samples can be obtained if the following precautionary measures are taken:

1. Keep HNO_3 at minimum concentration
2. Keep water in sample at minimum
3. pH is very critical (4)
4. Use blank for color comparison of endpoint
5. Change Dowex frequently (approximately every 3 samples)
6. If sample is basic, adjust with nitric acid

In order to obtain a sharp endpoint, it has been found that ion-exchange is a necessary procedural step. Steps should not only be taken to insure that the ion-exchange bed capacity is not close to exhaustion, but also to use a new rather than regenerated batch of ion-exchange resin.

Positive deviations have been obtained when titrating the effluent from a regenerated ion-exchange bed.

c. Precision—Comparisons have been made between the titrimetric and gravimetric analytical procedures on particulate filters from actual vehicle runs. The titrimetric analysis was carried out on one-quarter sections of the filters, the gravimetric on an entire parallel filter. The particulate filters were generated from vehicles equipped with pelletized and monolithic catalysts, operating on fuels of sulfur levels ranging from 0.004 to 0.14 wt%. Both cyclic and steady-state modes were used. The results of regression analysis on 26 comparison sets are shown in Equation 4:

$$\text{Titrimetric } SO_4 = 1.029 \text{ Gravimetric } SO_4 + 0.00085 \quad \text{(Eq. 4)}$$

$$\text{Standard Deviation} = 0.01$$

5.3.1.1.5.2 Thorin Method

a. Procedure (Visual Endpoint)—Samples are recovered by rinsing controlled condensation coils with water, or by overnight leaching of filters with hot water on a steam bath. Sample volume is adjusted to 100 mL or other convenient volume by adding water, and the pH is measured for later reference. A known volume, usually 5 or 10 mL, is withdrawn from the sample, the pH adjusted to 3.0 to 3.5 with NaOH (NH_4OH may be preferable) or $HClO_4$ or HCl and four volumes of isopropanol (IPA) added (for example, for a 10 mL sample, 40 mL IPA). Two drops of the Na salt of Thorin (0.2 g/100 mL H_2O) are then added and the $SO_4^=$ titrated with standard 0.01 N or 0.001 N Ba $(ClO_4)_2$ in 80% isopropanol which has been standardized against standard H_2SO_4. Blanks are run with each set of samples. Endpoint detection of samples normally is by eye by color comparison with titrated standards. Titrations also have been performed with an automatic titrator interfaced with a probe colorimeter for photometric endpoint detection at a wavelength of 5200 A (520 nm). Samples determined by the two means as previously stated usually give good agreement. Interferences and vague endpoints are sometimes encountered in visual detection (though not in photometric detection) especially with glass fiber filter samples. These problems can be overcome by treating the sample with diluted H_2O_2 (to destroy colored organic interferences) and passing the solution through a cation exchange resin (to remove cationic interferences). As noted previously, automatic titration coupled with instrument detection of endpoint has been applied successfully to barium perchlorate titrations of both filters and controlled condensation collected samples. One such technique using commercial equipment is as follows:

For samples obtained from a controlled condensation coil, a 5 or 10 mL sample aliquot with its pH adjusted to 3.5 using either dilute HCl or CO_3^{-2} free NaOH, is transferred to the titration beaker. Forty mL of isopropanol are added (5 mL of deionized water are also added if a 5 mL sample aliquot was used) along with 3 drops of Thorin indicator. With filter samples, a filter is leached into 50 mL of deionized water on a steam bath. After cooling and filtering the pH is adjusted to 3.5 as previously stated and the sample diluted. In either case the solution is now ready to be titrated.

If the sample is expected to have high concentrations of salts, especially Ca, Sr, or Al, or if the titration break obtained is poor (a slope of less than 2, Figure 17) passage through an ion-exchange resin will greatly improve the results. The cation exchanger recommended is Amberlite CG-120 100 to 200 (or equivalent) mesh. The Amberlite should be well washed and in the H^+ form. A 50 x 8 mm column is filled with the resin, and the sample is passed through. The first 5 mL of the eluent is discarded. The second 5 mL fraction may be used for titration after adjusting its pH to 3.5 and diluting to 10 mL. Forty mL of isopropanol and 3 drops of Thorin indicator are added as in the preceding paragraph.

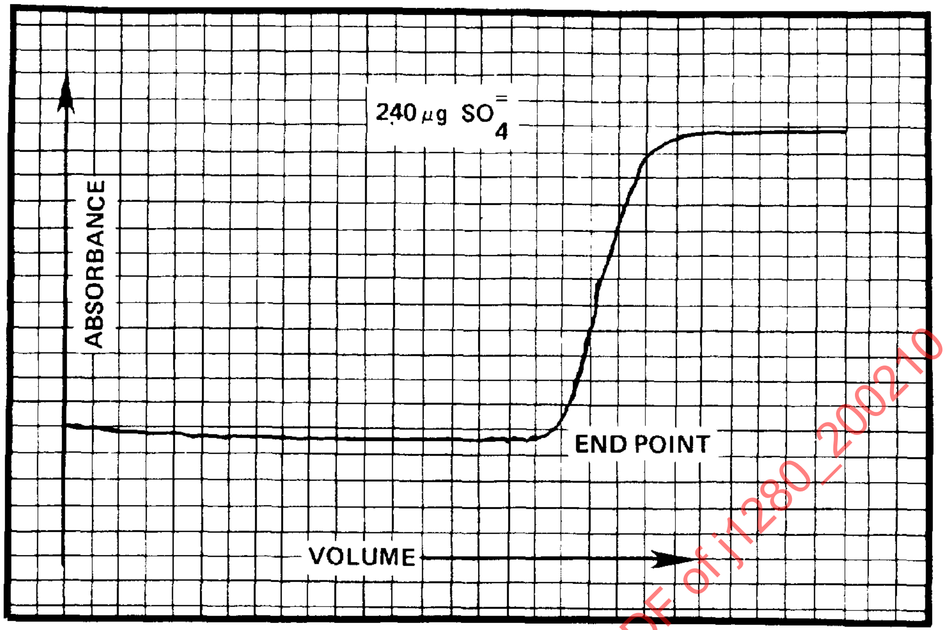


FIGURE 17—A TYPICAL ENDPOINT

b. Special Procedure for IPA Bubbler Samples—In order to determine the amount of sulfate collected in an IPA bubbler system, the absorber solutions are evaporated to a low volume. They are then passed through an ion-exchange resin to remove cations that would otherwise interfere by reacting with the indicator. The purified samples are titrated with standard barium perchlorate solution using Thorin and methylene blue as indicator. The titration is corrected for the amount of any sulfuric acid added. The sulfur content of each absorber solution is calculated and expressed as micrograms of sulfur per cubic meter of gas sampled.

c. Procedure (Automated)—Automated analysis of the sulfate samples solution is performed with an automatic titrator interfaced with a colorimeter equipped with a 20 mm pathlength photometric probe. A block diagram of the colorimeter and probe is shown in Figure 18. The probe colorimeter has the wavelength set to 520 nm and can monitor the appearance of the pink endpoint. The recorder output is 100 mV and is directly related to the 100 mV range of the calorimeter. The electronic agreement of the calorimeter and titrator should be checked as follows:

1. With mirror end off probe, set %T = 0 on colorimeter with transmittance zero, and adjust zero on titrator (selector in millivolt mode).
2. With mirror end in place and probe immersed in deionized water, set %T = 100 on colorimeter with absorbance zero. If the electronics are in good adjustment the pen of the titrator should be at full scale with selector switch in the millivolt mode.

For sample and standard titration, set titration rate at 7, temperature compensator at room temperature, attenuator at 50 mV full scale and mode switch in the pH/mV position. It is important that the position of the probe in the titration vessel be such that the solution can be stirred through the probe without producing bubbles which result in an unstable base line.

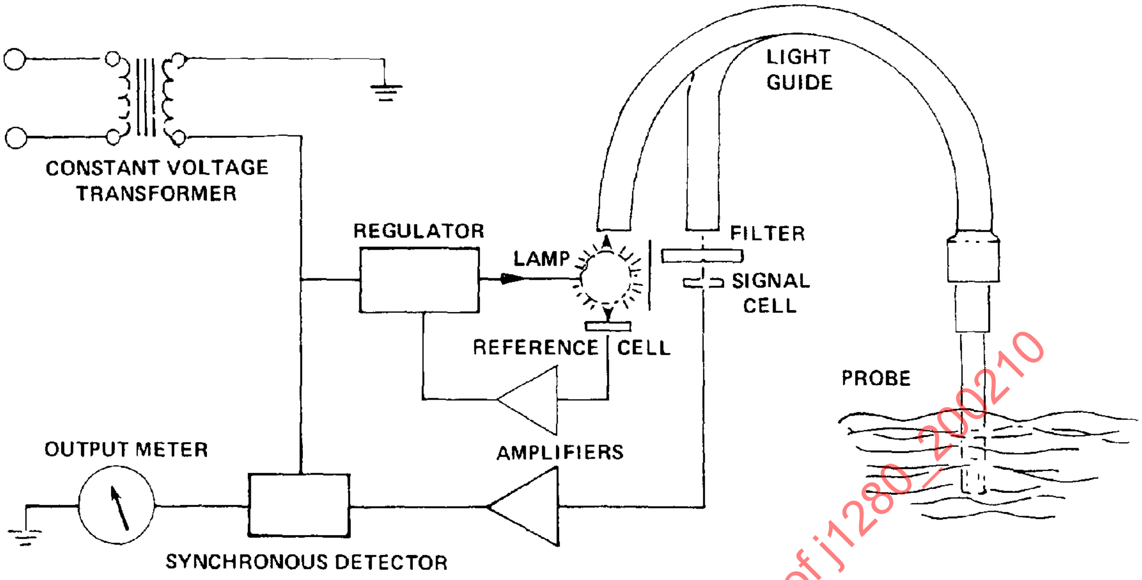


FIGURE 18—BLOCK DIAGRAM OF THE COLORIMETER AND PROBE

The titrant is 1×10^{-3} N Ba $(ClO_4)_2$ prepared by diluting a 1×10^{-2} N Ba $(ClO_4)_2$ stock solution 1:10 with deionized water and isopropanol. Thorin indicator is prepared by dissolving 200 mg of Thorin (ortho-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzene-arsonate disodium salt) in 100 mL of deionized water. Five mL of 1×10^{-3} N H_2SO_4 is added to 40 mL of isopropanol and 5 mL of deionized water added. The pH of this solution is 3.3 and does not require adjustment. Three drops of the indicator are added and the solution stirred until bubbles cease to form (approximately 3 min). The sample is then titrated and the endpoint determined from the chart such as that shown in Figure 17. The titer of this solution is approximately 50 µg $SO_4^{=}$/mL.

1. Precision—The detection limit of the method as described is 1.2 µg (detection limit is defined as twice the blank value). The reproducibility of the titration at the 50 µg level is 2.2% (for eight successive titrations of the same standard).

5.3.1.2 Automated Barium Chloranilate Method

5.3.1.2.1 Theory of Method—This method is for the determination of water-soluble sulfates from diluted automobile exhaust collected on fluoro-carbon (Teflon® or equivalent) filters. The method is general and may be used for trace sulfate analysis of any sample from which sulfates can be leached out with water or aqueous alcoholic solutions. It is applicable to sulfate analysis of exhaust emissions from cars run on nonleaded gasoline.

The filter is extracted with 60/40 isopropyl alcohol/water solution (that is, 60 mL isopropyl alcohol (IPA) + 40 mL water). This extract is fed by a high pressure liquid (chromatographic) pump, through a column of cation exchange resin to remove cationic interferences, and then through a column of solid barium chloranilate where $BaSO_1$ precipitates out. An equivalent amount of reddish color acid chloranilate ion is released and is measured colorimetrically at 310 nm. To use this method for aqueous sulfate solutions, four parts by volume of the solution are mixed with six parts of IPA before feeding through the columns. A manual method or an automatic analytical system can be used. The detailed descriptions that follow cover an automated method.

5.3.1.2.2 Apparatus Required—A schematic drawing of the principal components of the automated set-up is shown in Figure 19. Specific items are:

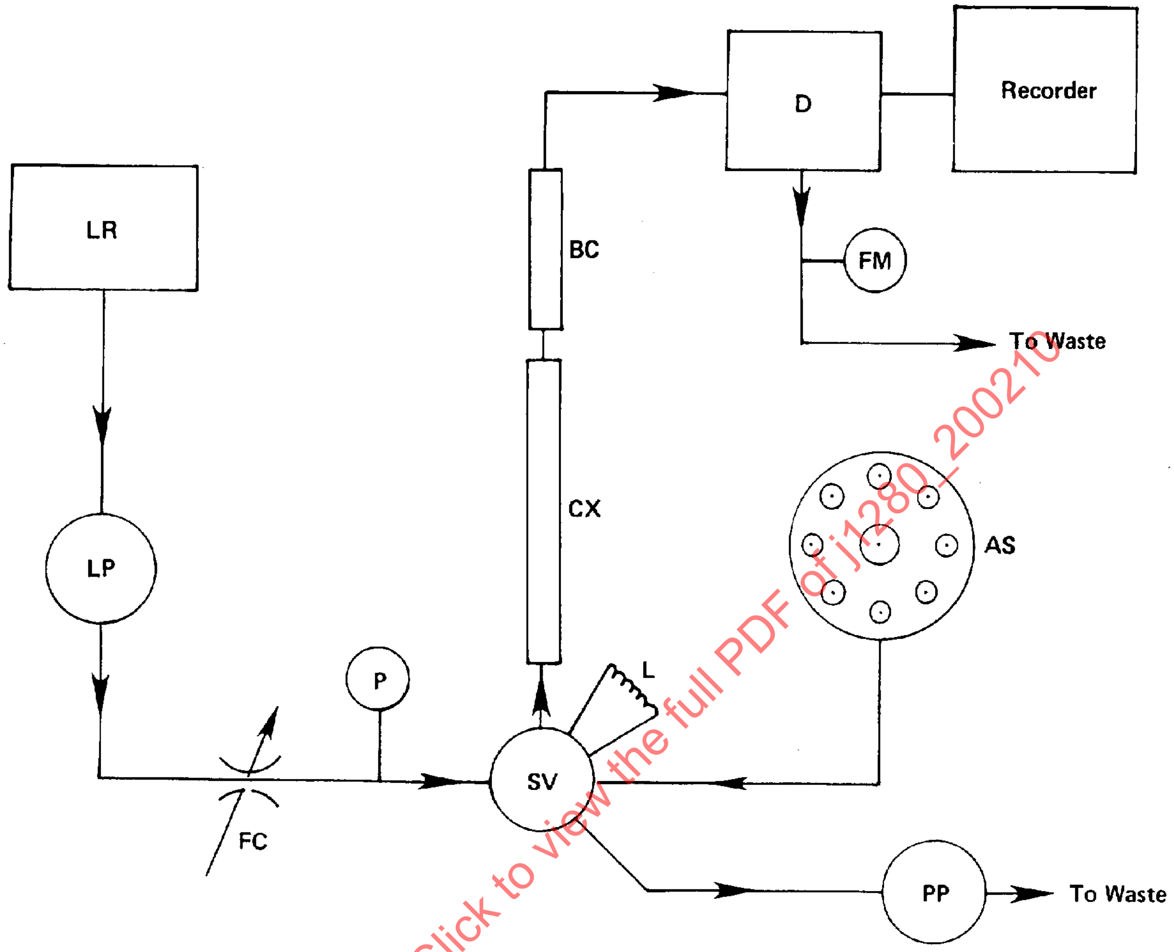
a. Reservoir (LR) for the solvent (60% IPA)
b. High pressure liquid pump (LP) capable of delivering liquids at flow rates of up to 3 mL/min at pressures as high as 6895 kPa. Most liquid pumps used in high pressure liquid chromatography should be satisfactory.
c. Flow or pressure controller (FC)
d. Six-port high pressure switching valve (SV) equipped with interchangeable external loop (L)
e. Ultraviolet detector (D) equipped with appropriate filters to isolate a narrow band of radiation centered at 310 mm. A microscope cover glass has been found to be satisfactory for this purpose.
f. Recorder to monitor detector response
g. Automatic sampler (AS), such as the one used for a Technicon Auto Analyzer
h. Peristaltic pump (PP) to draw sample into sampling loop
i. Cation exchange resin column (CS)—standard 6.35 mm OD × 254 mm stainless steel column packed with analytical grade Dowex 50W-X2 (or equivalent) cation exchange resin in hydrogen form
j. Barium chloranilate column (BC)—standard 6.35 mm OC × 127 mm stainless steel column packed with barium chloranilate

The sample is pumped from the columns through thermally insulated lines into the spectrophotometer.

In operation the solvent (60% IPA) in reservoir (LR) is continuously fed through the cation exchange and barium chloranilate columns at flow rates of about 3 mL/min by the high pressure liquid pump. Background absorbance is continuously measured by the UV detector at 310 nm and visually monitored on a strip chart recorder. The solenoid actuated air operated switching valve (SV) is used for filling the external sampling loop (L) with samples in conjunction with the automatic sampler and peristaltic pump and for injecting the sample into the columns.

At CX, cations are removed and at BC, color reaction takes place. The $BaSO_4$ precipitate is retained in the column while the acid chloranilate is carried by the solvent through the detector system for colorimetric measurement.

For an automated sampling system such as shown in Figure 19, both SV and PP are electrically coupled to AS by electric relays such that both are activated whenever AS is sampling (that is, L is being filled and mobile phase bypasses L). At the end of the sampling cycle, PP and AS stop and SV switches to the injection mode (that is, the mobile phase passes through L and carries sample through CX and BC columns). For manual operation, SV may be retained or replaced by a similar switching valve equipped with an extended handle for manual switching. Samples may be introduced into the sampling loop by syringe injection or peristaltic pump system similar to the one used in the automated system.



LR—LIQUID RESERVOIR
LP—HIGH PRESSURE LIQUID PUMP
FC—FLOW OR PRESSURE CONTROLLER
P—PRESSURE MONITOR
SV—HIGH PRESSURE SWITCHING VALVE
L—EXTERNAL SAMPLING LOOP
CX—CATION EXCHANGE RESIN COLUMN
BC—BARIUM CHLORANILATE COLUMN
D—UV DETECTOR
FM—FLOW METER
AS—AUTOMATIC SAMPLER
PP—PERISTALTIC PUMP

FIGURE 19—FLOW SCHEMATIC FOR AUTOMATED SULFATE INSTRUMENT

5.3.1.2.3 Reagents Required

a. Isopropyl alcohol (IPA) spectroquality grade or equivalent. Volatile solvent, safety class 1B
b. 60% IPA. Add four parts water to six parts IPA by volume. Store in tightly capped bottle. About 3 L are needed for a 12 h operation.
c. Barium chloranilate, suitable for sulfate analysis

d. Dowex 50W-X2 cation exchange resin (or equivalent), hydrogen form, 100 to 200 mesh
e. Hydrochloric acid (4 N). Add 30 mL concentrated hydrochloric acid to 60 mL deionized water. (Danger: strong acid.)
f. Standard sulfuric acid (1 N). Dilute to the mark 2.8 mL concentrated sulfuric acid with deionized distilled water in a liter volumetric flask which has been washed in 1:1 nitric acid and copiously rinsed with deionized distilled water, standardized against accurately weighed sodium carbonate to get exact normality, 0.1 N H_2SO_4 is equivalent to 4800 $\mu g/SO_4^=/mL$. (Danger: Strong acid.)
g. Standard sulfate solution (1000 μg $SO_4^=/mL$). Dissolve 1.4787 g sodium sulfate which has been heated up to 105 °C for 4 h and cooled in a desiccator and dilute to 1000 mL.

5.3.1.2.4 Barium Chloranilate and Cation Exchange Column Preparation

5.3.1.2.4.1 Barium Chloranilate Column—In order to prepare a full column with minimum dead volume, connect two lengths of standard 6.35 mm OD 1.47 mm wall, stainless steel tubing as shown in Figure 20, b = 51 mm, a = 127 mm. Connect a small funnel to the open end of B with a polyvinyl chloride (Tygon® or equivalent) tubing sleeve. Fill the funnel halfway with barium chloranilate and use a vibrator (that is, electric pencil engraver) to pack the solid in column. Continue operation until B is about half filled. Remove funnel, plug empty space with glass wool, and cap the end with a 6.35 to 1.59 mm reducer. Plumb column B directly to SV in Figure 19. Connect a Tygon tubing at A and direct tubing to waste reservoir. Activate liquid pump, set flow controller at pressure drop of about 4140 kPa. Let solvent flow for 20 min. Deactivate pump, disconnect column from SV. Disconnect column A from column B. Connect a glass wool plugged 6.35 to 1.59 mm reducer to uncapped end of column A.

It has been found that barium chloranilate of rather coarse crystals (approximately 200 × 15 μm) works much better than the fine BCA in that the coarser material contains fewer fines. The fines tend to plug the column and produce excessively high column back pressure.

The packing of the columns is very important, especially when height responses are used rather than peak areas. A column which is too tightly packed will plug resulting in a very high pressure buildup across the column. A column too loosely packed will give reduced peak height responses. Satisfactory operating pressures are in the 6200 to 6900 kPa range.

5.3.1.2.4.2 Cation Exchange Resin Column—Add cation exchange resin, 100 to 200 mesh. Dowex 50W-X2 (or equivalent) to 80 mL of 4 N HCl in a 150 mL beaker until a wet volume equivalent to 20 mL has settled at the bottom. Let soak for at least 3 h with occasional stirring using a glass rod. Decant the acid and add 100 mL of deionized distilled water. Stir and slowly decant the liquid as soon as most of the solid has settled down at the bottom. Repeat rinsing procedure several times until rinse liquid gives a neutral reaction to pH paper. Connect two pieces of standard 6.35 mm OD stainless steel tubing shown in Figure 20 with b = 127 mm and a = 254 mm. Connect a small funnel to the open end of B with a fluorocarbon (Teflon® or equivalent) or polyvinyl chloride (Tygon® or equivalent) tubing sleeve. Clamp the composite tube vertically and connect the open end of A to a vacuum line equipped with a liquid trap. Fill the funnel with deionized distilled water and turn on vacuum slowly until the composite tube is completely filled with water. Add water until the funnel is half filled. Stop the vacuum and add the slurry of freshly washed resin. Let the resin settle by gravity until resin top is seen above B. Turn on vacuum slowly, keep adding resin slurry until composite tube is completely filled. Proceed as in 5.3.1.2.4.1 beginning with the sentence: Remove funnel, plug empty space… Careful attention must be given to complete fine removal when acidifying and packaging the resin. An isopropanol/water solution should be pumped through the columns by the chromatographic pump before installing the column in the complete system. This operation purges the column of fines or other material that could affect the spectrophotometer cells.

5.3.1.2.5 Calibration—Chloranilic acid is an active absorber of UV at a wavelength of 310 nm. This absorption is nearly linear with concentration but still requires 6 to 10 standards to define a calibration curve from which peak height can be converted to sample concentration. Either sulfuric acid or sodium sulfate standards may be used. For a sulfuric acid standard, add 200 mL of 0.1 N H_2SO_4 aqueous stock solution to 300 mL 100% IPA in 500 mL volumetric flask.

NOTE—There is a volume decrease of about 2.7% when these proportions of water and IPA are mixed.

Dilute to the mark with 60% IPA. This is equivalent to 1920 µg $SO_4^=$/mL in 60% IPA. Prepare from this alcoholic stock solution calibration standards in the range 0.5 to 25 µg $SO_4^=$/mL by dilution of appropriate aliquots with 60% IPA. The 0.1 N H_2SO_4 is standardized by titration with sodium carbonate (Na_2CO_3) and methyl orange indicator. Proper standard laboratory procedures should be followed such as rinsing all glassware carefully with dilute nitric acid, followed by a copious rinse with deionized water.

5.3.1.2.6 Analytical Procedures

5.3.1.2.6.1 Sample Preparation—Filters are weighed both before and after the sample collection with a four-place chemical balance. Careful attention must be given to the humidity during these weighings as the hydrophilic nature of the H_2SO_4 can easily alter the resulting masses. It is important to stabilize the filters under equivalent humidity conditions to provide repeatable filter masses. This may take up to four days at 40% relative humidity and 20 °C. With the gross filter mass established, the filter is placed in a 3.0 mL polypropylene bottle which has been washed with dilute nitric acid and copiously rinsed several times and dried. The leaching solution is a 60% IPA, 40% deionized water mixture. If the filter is taken from a catalyst-car test, about one-half of the particulate weight on the filter can be assumed to be sulfate. Under this assumption it is possible to determine the quantity of 60/40 isopropanol/water in which to leach the filter so the resulting concentration will result in midrange analyzer response. For high-sulfate tests the original leach solution (usually 20 mL) can be re-diluted, and for low-sulfate tests a smaller (10 mL) leach volume may be used. The samples are mixed with a test tube vortex mixer for about 20 s. An ultrasonic bath also has been used to extract sulfate from the filter.

5.3.1.2.6.2 Priming System for Analytical Run—Connect the cation exchange and barium chloranilate columns with a 6.35 mm union packed with glass wool as shown in Figure 19. Fill the solvent reservoir (LR) with 60% IPA. Activate the liquid pump, detector, recorder switching valve, sampler, and peristaltic pump.

Allow the system to cycle normally to clean out all components. For this initial operation, dip the sampling probe in at least 100 mL of 60% IPA. Set the liquid flow rate at about 3 mL/min. Let the system run for at least 30 min. Then deactivate the switching valve, sampler, and peristaltic pump. Leave all other components in operating mode. When background is stable at attenuation of 0.01 absorbance units full scale, the system is ready for analysis.

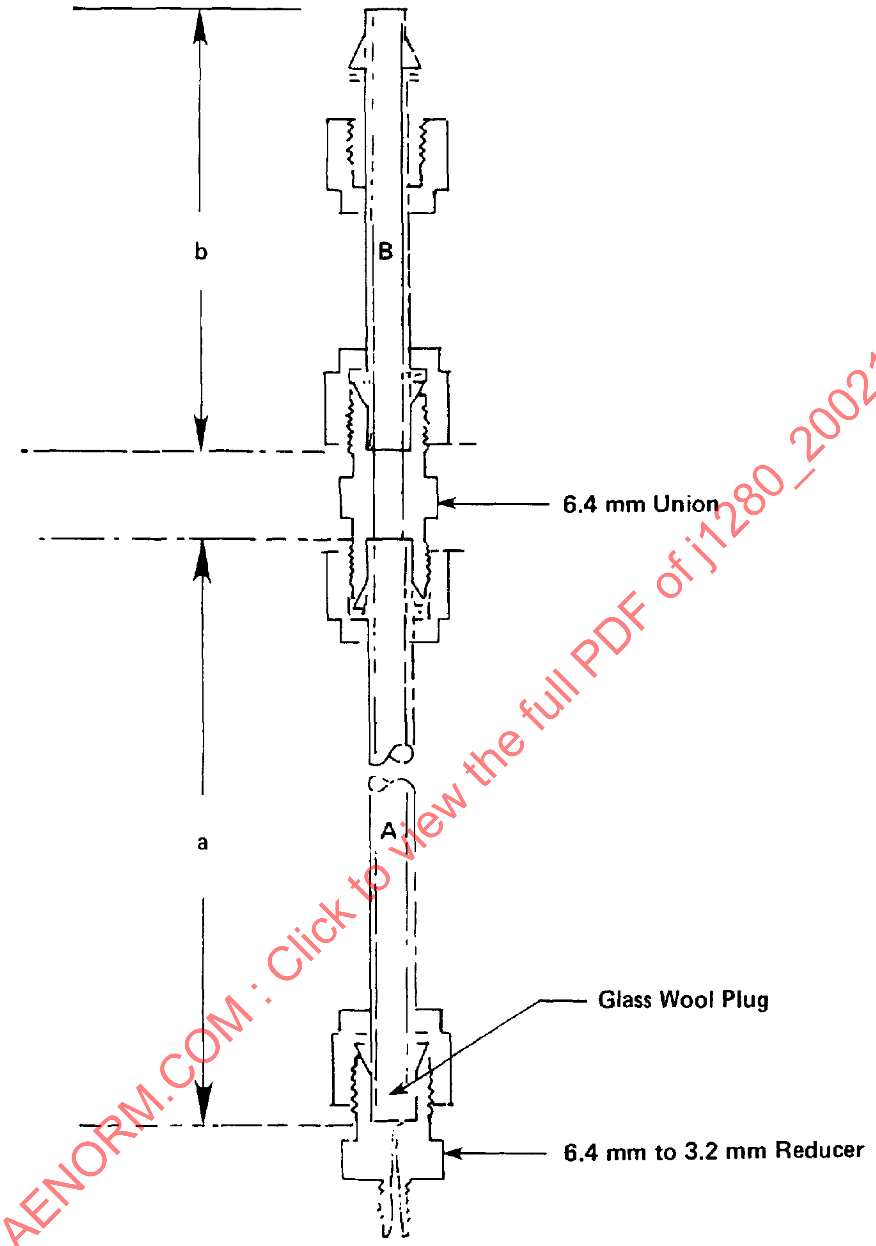


FIGURE 20—CONFIGURATION FOR LOADING COLUMN

5.3.1.2.6.3 Sulfate Analysis—Set the instrument in operating mode, remove the sampling probe from its holder, and dip it in 100 mL 60% IPA. Let it run at a flow rate of 3 mL/min until a stable background is obtained, then remount the sampling probe to the holder. In the meantime, pour about 5 mL of the leach solution into a polypropylene cuvette. Cover cuvette with a polyethylene film to help prevent changes in the isopropanol/water balance due to evaporation. Place the covered cuvette in the automatic sampler. The probe will easily puncture the polyethylene film when sampling begins. Sampling pattern is blank-sample-blank-sample at the rate of about 5 min per sample and blank. Blanks are used to wash out system between samples and minimize sample overlap. One blank between samples is adequate for dilute samples. A series of standards should be run, preferably before sample runs to develop a calibration curve of peak height versus concentration. A control standard may also be run after every ten samples as a quality check on the stability of the system. The plot of peak height (detector responses) versus concentration (µg $SO_4^=$/mL) is nonlinear in the low concentration end as would be expected from solubilities and kinetics consideration. Nonlinearity is also observed at the upper end of the curve.

5.3.1.2.7 Calculations—Calculate the concentration of sulfate as µg $SO_4^=$/mL using the calibration curve. Total soluble sulfates $(SO_4^=)_F$ in filter is given by Equation 5:

$$(SO_4=) = (\mu g\ SO_4=/mL) \times V_o \times d \qquad \text{(Eq. 5)}$$

where:

V_o = total volume of original sample extract
d = dilution factor

Example: Suppose 10 mL 60% IPA was used to extract the soluble sulfates in the filter and that 2 mL of this was diluted further to 6 mL with 60% IPA to bring detector response within calibration range. Suppose that the concentration of the diluted sample was found to be 5 µg/mL. Then, $(SO_4^=)_F$ = (5 µg/mL) × 10 mL × 6/2 = 150 µg.

5.3.1.2.8 Range and Sensitivity—Working concentration range and sensitivity depend on sample size. A sensitivity better than 0.5 µg ($SO_4^=$/mL) in 60% IPA and working range of 0 to 25 µg/mL have been obtained using a 0.5 mL external sampling loop injection system in conjunction with a liquid chromatograph UV detector. Sensitivity may be further increased by increasing the alcohol content of the solvent, as this would further decrease the solubility of $BaSO_4$ and barium chloranilate. This, however, requires a much tighter control of the water/IPA ratio in the sample and in the mobile phase. To minimize spurious results arising from water imbalance, it is recommended that all standards, the leaching solvent, and the mobile phase for analytical runs be taken from the same batch of IPA/water mixture. A sample size as large as 1.5 mL has been used successfully.

5.3.1.2.9 Interferences—Cations interfere negatively by reacting with the acid chloranilate to form insoluble salts. These, however, are conveniently removed by passing the sample through a cation exchange resin in the acid form. Some anions such as Cl^-, Br^-, F^-, $PO_4^=$ interfere positively by precipitating out as barium salts with subsequent release of acid chloranilate ions. Some buffer systems are reported to minimize anion interference. These systems are being investigated for possible inclusion in the procedure. Alternative clean-up methods are also under consideration. Fortunately, for nonleaded exhaust samples collected on filters, ionic interference is minimal. Interference from aromatic compounds is minimal and can be minimized by using a 333 nm cut-off filter in the optical path of the detector system.

5.3.1.2.10 Precision-Accuracy and Stability—With an external sampling loop of about 1.5 mL, and photometer attenuation set to read 0.04 absorbance units full scale, a standard deviation of 0.05 µg $SO_4^=$/mL has been obtained for a sample containing 4.0 µg $SO_4^=$/mL. Sulfuric acid standards containing 10 and 100 µg $SO_4^=$/mL in 60% IPA are stable for at least one month when stored in a tightly capped volumetric flask which has been cleaned with 1:1 nitric acid and copiously rinsed with deionized water. Special precautions must be taken to be certain the acid standards stored in glass have remained stable. If unusual results are obtained, fresh standards should be made to check stability of stored standards. Alternative storage containers are capped polyethylene reagent bottles. The cation exchange resin and the barium chloranilate columns as described in 5.3.1.2.4 last for over two months. For samples known to contain cations, it is advisable to remove these cations by external treatment with cation exchange resin prior to injection into the sampling loop. Since the barium chloranilate column is depleted each time sulfate samples are fed through, it is good practice to run sulfuric acid standards before and after the sample. Exposure of alcoholic samples, standards, and solvent to the atmosphere should be minimized since IPA solution picks up atmospheric water on standing.

5.3.1.2.11 System Variations—Several modifications of the preceding system and procedures have been used successfully. One such change is the ammoniation of filters and the use of ammonium sulfate $(NH_4)_2SO_4$ for standards. The ammoniation of filters involves placing the sample filters in a desiccator and drawing a partial vacuum on it. Air bubbled through ammonium hydroxide is used to bring the desiccator up to atmospheric pressure. Sufficient ammonia is then present to react with the sulfuric acid on the filter to form ammonium sulfate. About 1 h of ammoniation has been found sufficient for this process. Ammoniation has been found to be very effective in permitting rapid, stable filter weight determination. This is because the ammonium sulfate is less hygroscopic than H_2SO_4. Therefore, ammoniated filters come to equilibrium in 12 h rather than up to four days required for nonammoniated filters. While filter weights are being obtained, the room in which the filters are handled and stabilized is maintained at 40% relative humidity. If filter weight is not required, the sample can be analyzed as soon as the 1 h ammoniation is complete.

Other advantages of using ammonium sulfate include greater sensitivity due to sharper peak response. This is because of lower absorption of the ammonium sulfate on the stainless steel lines. Also, using ammonium sulfate for standards preparation is more accurate and much faster. The increased accuracy is due to the use of gravimetric rather than titration procedures. Finally, if the net weight of the material on the filter after ammoniation is compared with the amount of sulfate found, a very repeatable ratio is observed. Most catalyst cars tested have very little particulate emissions that are not sulfate and, therefore, nearly all the weight gain on the filter is ammonium sulfate.

Another modification that has been made is the elimination of almost all of the glassware in the system. The only exposure to glass currently is during the primary mixing of standards and in the burettes for measuring the leaching solution. Everything else is polypropylene or polyethylene. This includes the standard bottles, the isopropanol/water carboy, sample bottles, and cuvettes. The reason for this is that glassware use has been observed to yield erratic UV detector results, especially negative peak responses. Other changes that have been made include the use of distilled, deionized water instead of simply deionized water, the integration of peak area rather than using peak heights, and the use of a Sartorious six-place microgram balance for weighing the filters and the ammonium sulfate used in standard preparation.

5.3.1.3 Iodate Method—(This method is applicable in the presence of lead particulate.)

5.3.1.3.1 Theory of Method—This technique is a procedure for determining airborne particulate sulfate that is collected on glass fiber filters. The particulate matter is leached from the filter with a warm aqueous solution containing a small amount of ammonium carbonate to eliminate lead ion interference. An aliquot of this aqueous solution is placed in an ethanolic matrix containing formaldehyde which eliminates sulfite ion interference. To this solution, barium iodate is added. Two iodate ions are released for each sulfate ion. In an acid medium, 12 iodine atoms are released by iodate reaction with potassium iodide as follows:

$$\begin{gathered} H_2SO_4 + Ba(IO_3)_2 \rightarrow BaSO_4 + 2HIO_3 \\ 2HIO_3 + 10HCl + 10KI \rightarrow 10\ KCl + 6H_2O + 6I_2 \end{gathered} \tag{Eq. 6}$$

Starch is added to produce the characteristic starch-iodine color which is measured spectrophotometrically. The concentration of sulfate is calculated from the optical absorbance of the solution and the measured volume of air sampled.

5.3.1.3.2 Apparatus Required

a. Spectrophotometer, capable of measuring absorbance at 590 nm. Beckman Model B or equivalent
b. Absorption cell 50 mm path length
c. Erlenmeyer flask, ground glass neck, 500 mL capacity fitted with a 5 mL pipet

d. Volumetric flasks, 25, 100, 500, and 1000 mL capacity
e. Pipets, Mohr-type, 0.1, 0.2, 0.3, 0.4, and 0.5 mL capacity
f. Pipets, volumetric, 2.5, and 25 mL capacity
g. Beakers, 150 mL capacity
h. Disposable bottles, with caps, 30 mL capacity (polyethylene bottles are convenient)

NOTE—All glassware should be rinsed with methanol or ethanol before use. Acetone and/or IPA, if present, will destroy the starch-iodine color.

5.3.1.3.3 Reagents and Required Materials

a. Ammonium carbonate solution—6 mg/mL—dissolve 1.2 g of $(NH_4)_2\ CO_3$ into 200 mL of deionized water and mix well.
b. Barium iodate $(Ba(IO_3)_2 \cdot H_2O)$. If unavailable from a commercial source, this compound may be prepared as follows: Dissolve 21.4 g of potassium iodate (KIO_3) in 100 mL of distilled water. Dissolve 11 g of barium chloride $BaCl_2 \cdot 2H_2O$ in water and add this solution to the potassium iodate solution. Stir the precipitate well for about 1 h. Filter it through Whatman No. 1 filter paper and wash it several times with distilled water. Wash it twice with 95% ethanol and dry it in an oven at 110 °C for about 1 h. Store it in a tightly capped jar out of direct sunlight.
c. Ethanol-formaldehyde matrix. Mix 180 mL of 95% ethanol with 60 mL of distilled water and add 0.5 mL of formaldehyde. Prepare the solution fresh daily. Dispense it from a 500 mL Erlenmeyer flask fitted with a 5 mL pipet. Do not substitute isopropanol for ethanol. The starch-iodine color will fade rapidly in isopropanol solution.
d. Ethanol diluting solution. To 240 mL of pure anhydrous ethanol add 0.5 mL of formaldehyde and mix well.
e. Hydrochloric acid, 5% solution. Mix one volume of hydrochloric acid (sp. gr. 1.19) with nineteen volumes of deionized water.
f. Hydrochloric acid 2.5 N solution. Add 200 mL of hydrochloric acid (sp. gr. 1.19) to 600 mL of deionized water. Dilute the solution to 100 mL with deionized water.
g. Potassium iodide, 10% solution. Dissolve 5 g of potassium iodide (KI) in 45 mL of deionized water. Store the solution in actinic glassware out of direct sunlight.
h. Starch solution. To 180 mL of boiling deionized water containing 1.0 g of glycerine, add 1.5 g of soluble starch powder which has been dissolved in 20 mL of deionized water. Add a few crystals of CdI_2. Cool and store in a brown bottle out of the light. Should be checked daily with a standard sulfate solution for stability.
i. Sulfuric acid, 0.005 N solution. Pipet 25 mL of 0.1 N standardized sulfuric acid solution into a 500 mL volumetric flask and dilute it to volume with deionized water. Purchase standard 0.1 N sulfuric solution.
j. Filter paper, Whatman No. 40 or equivalent. If glass fiber filters are used with this analytical method, they require special preparation as follows: Wash the filter with 5% hydrochloric acid solution. Rinse each filter thoroughly with deionized water until the rinse is no longer acid to methyl red indicator. Then rinse with methanol twice and dry the filters in an oven at 110 °C for at least 1 h. Store in a clean covered glass container.

5.3.1.3.4 Calibration—Calibration curves for this method are developed in the following way:

Into successive 100 mL volumetric flasks, each containing about 20 mL of H_2O, pipet 1, 2, 3, 4, 5, and 6 mL of 0.005 N sulfuric acid solution, respectively. Add 0.5 mL of ammonium carbonate solution and mix well. Dilute to the mark with deionized water and mix again. Into 25 mL volumetric flasks, aliquot 7 mL of each of the above solutions, respectively, and dilute to the mark with the ethanol diluting solution. This creates standards containing 17.2, 34.3, 51.5, 68.6, 85.8, and 102.9 µg of $SO_4^=$, respectively. Prepare a blank by filling a 25 mL volumetric flask with the ethanol-formaldehyde matrix. Add 30 mg of barium iodate to each flask. Shake each flask well to mix the contents and let it stand for 30 min. Filter each standard and the blank through No. 40 filter paper as follows: Prior to filtering, rinse the filter paper with