

METHOD 204B--VOLATILE ORGANIC COMPOUNDS EMISSIONS IN CAPTURED STREAM

1. SCOPE AND APPLICATION

1.1 Applicability. This procedure is applicable for determining the volatile organic compounds (VOC) content of captured gas streams. It is intended to be used in the development of a gas/gas protocol for determining VOC capture efficiency (CE) for surface coating and printing operations. The procedure may not be acceptable in certain site-specific situations [e.g., when: (1) direct-fired heaters or other circumstances affect the quantity of VOC at the control device inlet; and (2) particulate organic aerosols are formed in the process and are present in the captured emissions].

1.2 Principle. The amount of VOC captured (G) is calculated as the sum of the products of the VOC content (C_{Gj}), the flow rate (Q_{Gj}), and the sample time (t_c) from each captured emissions point.

1.3 Sampling Requirements. A CE test shall consist of at least three sampling runs. Each run shall cover at least one complete production cycle, but shall be at least 3 hours long. The sampling time for each run need not exceed 8 hours, even if the production cycle has not been completed. Alternative sampling times may be used with the approval of the Administrator.

2. SUMMARY OF METHOD

A gas sample is extracted from the source through a heated sample line and, if necessary, a glass fiber filter to a flame ionization analyzer (FIA).

3. SAFETY

Because this procedure is often applied in highly explosive areas, caution and care should be exercised in choosing, installing, and using the appropriate equipment.

4. EQUIPMENT AND SUPPLIES

Mention of trade names or company products does not constitute endorsement. All gas concentrations (percent, ppm) are by volume, unless otherwise noted.

4.1 Gas VOC Concentration. A schematic of the measurement system is shown in Figure 204B-1. The main components are as follows:

4.1.1 Sample Probe. Stainless steel or equivalent. The probe shall be heated to prevent VOC condensation.

4.1.2 Calibration Valve Assembly. Three-way valve assembly at the outlet of the sample probe to direct the zero and calibration gases to the analyzer. Other methods, such as quick-connect lines, to route calibration gases to the outlet of the sample probe are acceptable.

4.1.3 Sample Line. Stainless steel or Teflon tubing to transport the sample gas to the analyzer. The sample line must be heated to prevent condensation.

4.1.4 Sample Pump. A leak-free pump, to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. The components of the pump that contact the gas stream shall be constructed of stainless steel or Teflon. The sample pump must be heated to prevent condensation.

4.1.5 Sample Flow Rate Control. A sample flow rate control valve and rotameter, or equivalent, to maintain a constant sampling rate within 10 percent. The flow rate control valve and rotameter must be heated to prevent condensation. A control valve may also be located on the sample pump bypass loop to assist in controlling the sample pressure and flow rate.

4.1.6 Organic Concentration Analyzer. An FIA with a span value of 1.5 times the expected concentration as propane; however, other span values may be used if it can be demonstrated to the Administrator's satisfaction that they would provide equally accurate measurements. The system shall be capable of meeting or exceeding the following specifications:

4.1.6.1 Zero Drift. Less than ± 3.0 percent of the span value.

4.1.6.2 Calibration Drift. Less than ± 3.0 percent of the span value.

4.1.6.3 Calibration Error. Less than ± 5.0 percent of the calibration gas value.

4.1.6.4 Response Time. Less than 30 seconds.

4.1.7 Integrator/Data Acquisition System. An analog or digital device, or computerized data acquisition system used to integrate the FIA response or compute the average response and record measurement data. The minimum data sampling frequency for computing average or integrated values is one measurement value every 5 seconds. The device shall be capable of recording average values at least once per minute.

4.2 Captured Emissions Volumetric Flow Rate.

4.2.1 Method 2 or 2A Apparatus. For determining volumetric flow rate.

4.2.2 Method 3 Apparatus and Reagents. For determining molecular weight of the gas stream. An estimate of the molecular weight of the gas stream may be used if approved by the Administrator.

4.2.3 Method 4 Apparatus and Reagents. For determining moisture content, if necessary.

5. REAGENTS AND STANDARDS

5.1 Calibration and Other Gases. Gases used for calibration, fuel, and combustion air (if required) are contained in compressed gas cylinders. All calibration gases shall be traceable to National Institute of Standards and Technology standards and shall be certified by the manufacturer to ± 1 percent of the tag value. Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not

change more than ± 2 percent from the certified value. For calibration gas values not generally available, dilution systems calibrated using Method 205 may be used. Alternative methods for preparing calibration gas mixtures may be used with the approval of the Administrator.

5.1.1 Fuel. The FIA manufacturer's recommended fuel should be used. A 40 percent H₂/60 percent He or 40 percent H₂/60 percent N₂ gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value. Other mixtures may be used provided the tester can demonstrate to the Administrator that there is no oxygen synergism effect

5.1.2 Carrier Gas. High purity air with less than 1 ppm of organic material (as propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

5.1.3 FIA Linearity Calibration Gases. Low-, mid-, and high-range gas mixture standards with nominal propane concentrations of 20-30, 45-55, and 70-80 percent of the span value in air, respectively. Other calibration values and other span values may be used if it can be shown to the Administrator's satisfaction that equally accurate measurements would be achieved.

5.2 Particulate Filter. An in-stack or an out-of-stack glass fiber filter is recommended if exhaust gas particulate loading is significant. An out-of-stack filter must be heated to

prevent any condensation unless it can be demonstrated that no condensation occurs.

6. QUALITY CONTROL

6.1 Required instrument quality control parameters are found in the following sections:

6.1.1 The FIA system must be calibrated as specified in section 7.1.

6.1.2 The system drift check must be performed as specified in section 7.2.

6.1.3 The system check must be conducted as specified in section 7.3.

6.2 Audits.

6.2.1 Analysis Audit Procedure. Immediately before each test, analyze an audit cylinder as described in section 7.2. The analysis audit must agree with the audit cylinder concentration within 10 percent.

6.2.2 Audit Samples and Audit Sample Availability. Audit samples will be supplied only to enforcement agencies for compliance tests. The availability of audit samples may be obtained by writing:

Source Test Audit Coordinator (STAC) (MD-77B)
Quality Assurance Division
Atmospheric Research and Exposure Assessment Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

or by calling the STAC at (919) 541-7834. The request for the

audit sample must be made at least 30 days prior to the scheduled compliance sample analysis.

6.2.3 Audit Results. Calculate the audit sample concentration according to the calculation procedure described in the audit instructions included with the audit sample. Fill in the audit sample concentration and the analyst's name on the audit response form included with the audit instructions. Send one copy to the EPA Regional Office or the appropriate enforcement agency, and a second copy to the STAC. The EPA Regional Office or the appropriate enforcement agency will report the results of the audit to the laboratory being audited. Include this response with the results of the compliance samples in relevant reports to the EPA Regional Office or the appropriate enforcement agency.

7. CALIBRATION AND STANDARDIZATION

7.1 FIA Calibration and Linearity Check. Make necessary adjustments to the air and fuel supplies for the FIA and ignite the burner. Allow the FIA to warm up for the period recommended by the manufacturer. Inject a calibration gas into the measurement system and adjust the back-pressure regulator to the value required to achieve the flow rates specified by the manufacturer. Inject the zero- and the high-range calibration gases and adjust the analyzer calibration to provide the proper responses. Inject the low- and mid-range gases and record the responses of the measurement system. The calibration and

linearity of the system are acceptable if the responses for all four gases are within 5 percent of the respective gas values. If the performance of the system is not acceptable, repair or adjust the system and repeat the linearity check. Conduct a calibration and linearity check after assembling the analysis system and after a major change is made to the system.

7.2 Systems Drift Checks. Select the calibration gas that most closely approximates the concentration of the captured emissions for conducting the drift checks. Introduce the zero and calibration gases at the calibration valve assembly and verify that the appropriate gas flow rate and pressure are present at the FIA. Record the measurement system responses to the zero and calibration gases. The performance of the system is acceptable if the difference between the drift check measurement and the value obtained in section 7.1 is less than 3 percent of the span value. Alternatively, recalibrate the FIA as in section 7.1 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period). The data that results in the lowest CE value shall be reported as the results for the test run. Conduct the system drift checks at the end of each run.

7.3 System Check. Inject the high-range calibration gas at the inlet of the sampling probe and record the response. The performance of the system is acceptable if the measurement system response is within 5 percent of the value obtained in section 7.1

for the high-range calibration gas. Conduct a system check before and after each test run.

8. PROCEDURE

8.1. Determination of Volumetric Flow Rate of Captured Emissions

8.1.1 Locate all points where emissions are captured from the affected facility. Using Method 1, determine the sampling points. Be sure to check each site for cyclonic or swirling flow.

8.1.2 Measure the velocity at each sampling site at least once every hour during each sampling run using Method 2 or 2A.

8.2 Determination of VOC Content of Captured Emissions

8.2.1 Analysis Duration. Measure the VOC responses at each captured emissions point during the entire test run or, if applicable, while the process is operating. If there are multiple captured emission locations, design a sampling system to allow a single FIA to be used to determine the VOC responses at all sampling locations.

8.2.2 Gas VOC Concentration.

8.2.2.1 Assemble the sample train as shown in Figure 204B-1. Calibrate the FIA according to the procedure in section 7.1.

8.2.2.2 Conduct a system check according to the procedure in section 7.3.

8.2.2.3 Install the sample probe so that the probe is centrally located in the stack, pipe, or duct, and is sealed tightly at the stack port connection.

8.2.2.4 Inject zero gas at the calibration valve assembly. Allow the measurement system response to reach zero. Measure the system response time as the time required for the system to reach the effluent concentration after the calibration valve has been returned to the effluent sampling position.

8.2.2.5 Conduct a system check before, and a system drift check after, each sampling run according to the procedures in sections 7.2 and 7.3. If the drift check following a run indicates unacceptable performance (see section 7.3), the run is not valid. Alternatively, recalibrate the FIA as in section 7.1 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period). The data that results in the lowest CE value shall be reported as the results for the test run. The tester may elect to perform system drift checks during the run not to exceed one drift check per hour.

8.2.2.6 Verify that the sample lines, filter, and pump temperatures are $120 \pm 5^{\circ}\text{C}$.

8.2.2.7 Begin sampling at the start of the test period and continue to sample during the entire run. Record the starting and ending times and any required process information as

appropriate. If multiple captured emission locations are sampled using a single FIA, sample at each location for the same amount of time (e.g., 2 minutes) and continue to switch from one location to another for the entire test run. Be sure that total sampling time at each location is the same at the end of the test run. Collect at least four separate measurements from each sample point during each hour of testing. Disregard the measurements at each sampling location until two times the response time of the measurement system has elapsed. Continue sampling for at least 1 minute and record the concentration measurements.

8.2.3 Background Concentration. NOTE: Not applicable when the building is used as the temporary total enclosure (TTE).

8.2.3.1 Locate all natural draft openings (NDO's) of the TTE. A sampling point shall be at the center of each NDO, unless otherwise specified by the Administrator. If there are more than six NDO's, choose six sampling points evenly spaced among the NDO's.

8.2.3.2 Assemble the sample train as shown in Figure 204B-2. Calibrate the FIA and conduct a system check according to the procedures in sections 7.1 and 7.3.

NOTE: This sample train shall be separate from the sample train used to measure the captured emissions.

8.2.3.3 Position the probe at the sampling location.

8.2.3.4 Determine the response time, conduct the system check, and sample according to the procedures described in sections 8.2.2.4 through 8.2.2.7.

8.2.4 Alternative Procedure. The direct interface sampling and analysis procedure described in section 7.2 of Method 18 may be used to determine the gas VOC concentration. The system must be designed to collect and analyze at least one sample every 10 minutes. If the alternative procedure is used to determine the VOC concentration of the captured emissions, it must also be used to determine the VOC concentration of the uncaptured emissions.

9. DATA ANALYSIS AND CALCULATIONS

9.1 Nomenclature

A_i = area of NDO i , ft^2 .

A_N = total area of all NDO's in the enclosure, ft^2 .

C_{Bi} = corrected average VOC concentration of background emissions at point i , ppm propane.

C_B = average background concentration, ppm propane.

C_{Gj} = corrected average VOC concentration of captured emissions at point j , ppm propane.

C_{DH} = average measured concentration for the drift check calibration gas, ppm propane.

C_{D0} = average system drift check concentration for zero concentration gas, ppm propane.

C_H = actual concentration of the drift check calibration gas, ppm propane.

C_i = uncorrected average background VOC concentration measured

at point i , ppm propane.

C_j = uncorrected average VOC concentration measured at point j , ppm propane.

emissions, kg.

$$K_1 = 1.830 \times 10^{-6} \text{ kg}/(\text{m}^3\text{-ppm}).$$

ement points.

Q_{Gj} = average effluent volumetric flow rate corrected to standard conditions at captured emissions point j , m^3/min .

z_c = total duration of captured emissions.

9.2 Calculations

9.2.1 Total VOC Captured Emissions.

$$G = \sum_{j=1}^n (C_{Gj} - C_B) Q_{Gj} \theta_C K_1 \quad \text{Eq. 204B-1}$$

9.2.2 VOC Concentration of the Captured Emissions at Point j .

$$C_{Gj} = (C_j - C_{DO}) \frac{C_H}{C_{DH} - C_{DO}} \quad \text{Eq. 204B-2}$$

9.2.3 Background VOC Concentration at Point i .

$$C_{Bi} = (C_i - C_{DO}) \frac{C_H}{C_{DH} - C_{DO}} \quad \text{Eq. 204B-3}$$

9.2.4 Average Background Concentration.

$$C_B = \frac{\sum_{i=1}^n C_{Bi} A_i}{A_N} \quad \text{Eq. 204B-4}$$

NOTE: If the concentration at each point is within 20 percent of the average concentration of all points, then use the arithmetic average.

10. METHOD PERFORMANCE.

The measurement uncertainties are estimated for each captured or uncaptured emissions point as follows:

$Q_{Gj} = \pm 5.5$ percent and $C_{Gj} = \pm 5.0$ percent. Based on these numbers, the probable uncertainty for G is estimated at about ± 7.4 percent.

11. DIAGRAMS

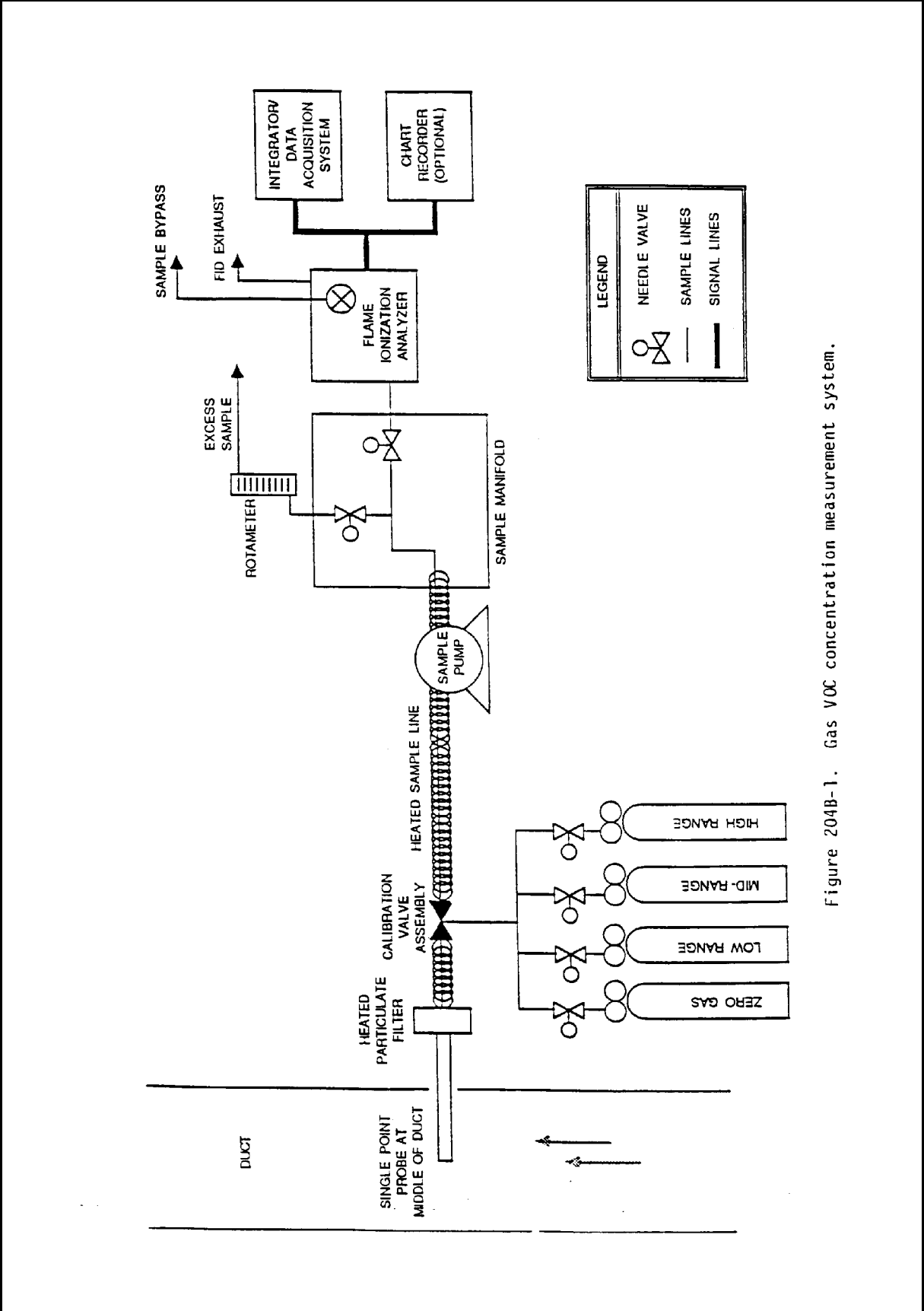


Figure 204B-1. Gas VOC concentration measurement system.

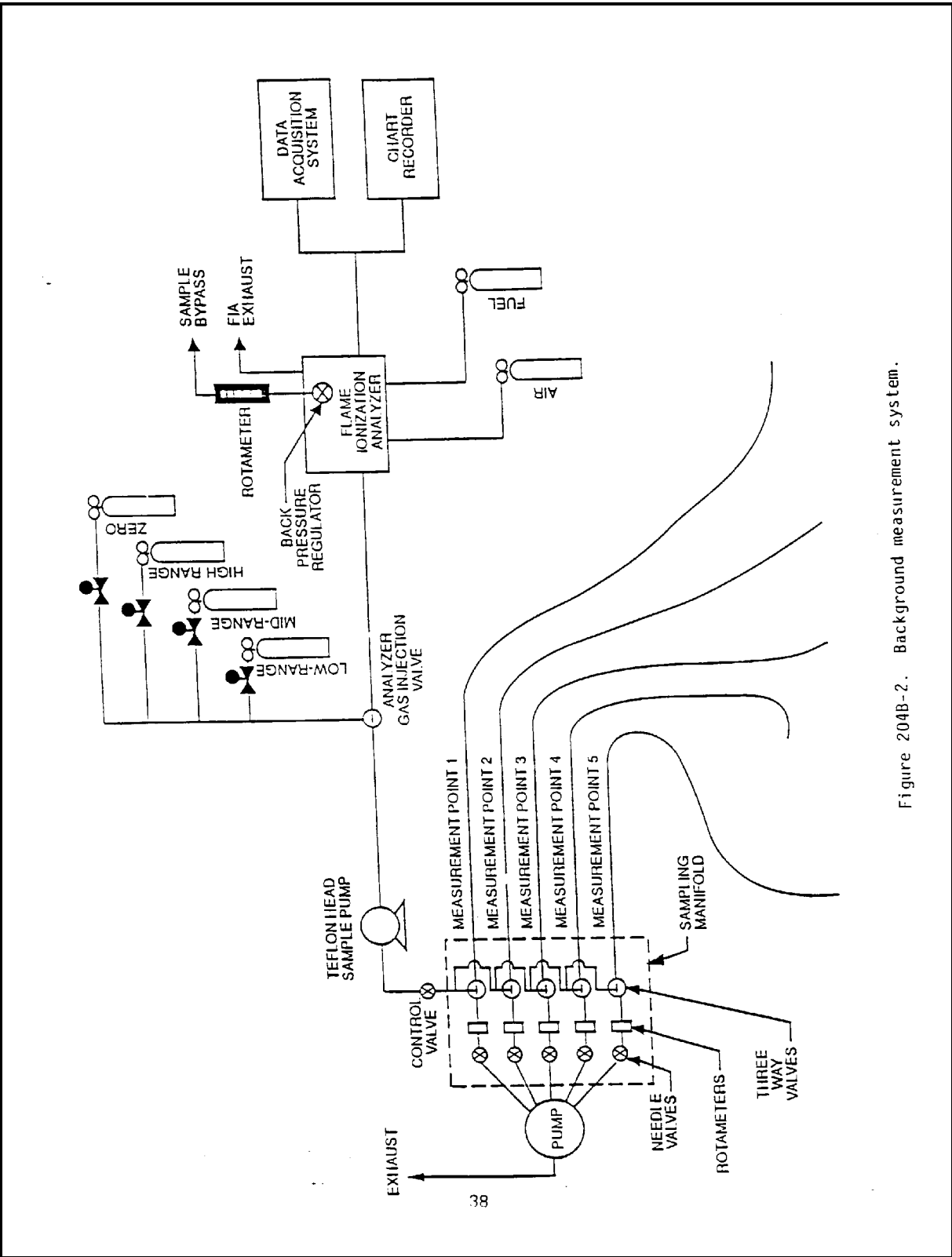


Figure 204B-2. Background measurement system.