

METHOD TO-12

METHOD FOR THE DETERMINATION OF NON-METHANE ORGANIC COMPOUNDS (NMOC) IN AMBIENT AIR USING CRYOGENIC PRECONCENTRATION AND DIRECT FLAME IONIZATION DETECTION (PDFID)

1. Scope

- 1.1 In recent years, the relationship between ambient concentrations of precursor organic compounds and subsequent downwind concentrations of ozone has been described by a variety of photochemical dispersion models. The most important application of such models is to determine the degree of control of precursor organic compounds that is necessary in an urban area to achieve compliance with applicable ambient air quality standards for ozone (1,2).
- 1.2 The more elaborate theoretical models generally require detailed organic species data obtained by multicomponent gas chromatography (3). The Empirical Kinetic Modeling Approach (EKMA), however, requires only the total non-methane organic compound (NMOC) concentration data; specifically, the average total NMOC concentration from 6 a.m. to 9 a.m. daily at the sampling location. The use of total NMOC concentration data in the EKMA substantially reduces the cost and complexity of the sampling and analysis system by not requiring qualitative and quantitative species identification.
- 1.3 Method T01, "Method for The Determination of Volatile Organic Compounds in Ambient Air Using Tenax® Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS)", employs collection of certain volatile organic compounds on Tenax® GC with subsequent analysis of thermal desorption/cryogenic preconcentration and GC/MS identification. This method (T012) combines the same type of cryogenic concentration techniques used in Method T01 for high sensitivity with the simple flame ionization detector (FID) of the GC for total NMOC measurements, without the GC columns and complex procedures necessary for species separation.
- 1.4 In a flame ionization detector, the sample is injected into a hydrogen-rich flame where the organic vapors burn producing ionized molecular fragments. The resulting ion fragments are then collected and detected. The FID is nearly a universal detector. However, the detector response varies with the species of [functional group in] the organic compound in an oxygen atmosphere. Because this method employs a helium or argon carrier

gas, the detector response is nearly one for all compounds. Thus, the historical short-coming of the FID involving varying detector response to different organic functional groups is minimized.

- 1.5 The method can be used either for direct, in situ ambient measurements or (more commonly) for analysis of integrated samples collected in specially treated stainless steel canisters. EKMA models generally require 3-hour integrated NMOC measurements over the 6 a.m. to 9 a.m. period and are used by State or local agencies to prepare State Implementation Plans (SIPs) for ozone control to achieve compliance with the National Ambient Air Quality Standards (NAAQS) for ozone. For direct, in situ ambient measurements, the analyst must be present during the 6 a.m. to 9 a.m. period, and repeat measurements (approximately six per hour) must be taken to obtain the 6 a.m. to 9 a.m. average NMOC concentration. The use of sample canisters allows the collection of integrated air samples over the 6 a.m. to 9 a.m. period by unattended, automated samplers. This method has incorporated both sampling approaches.

2. Applicable Documents

2.1 ASTM Standards

- D1356 - Definition of Terms Related to Atmospheric Sampling and Analysis
- E260 - Recommended Practice for General Gas Chromatography Procedures
- E355 - Practice for Gas Chromatography Terms and Relationships

2.2 Other Documents

- U. S. Environmental Protection Agency Technical Assistance Documents (4,5)
- Laboratory and Ambient Air Studies (6-10)

3. Summary of Method

- 3.1 A whole air sample is either extracted directly from the ambient air and analyzed on site by the GC system or collected into a precleaned sample canister and analyzed off site.
- 3.2 The analysis requires drawing a fixed-volume portion of the sample air at a low flow rate through a glass-bead filled trap that is cooled to approximately -186°C with liquid argon. The cryogenic trap simultaneously collects and concentrates the NMOC (either via condensation or adsorption) while allowing the methane, nitrogen, oxygen, etc. to pass through the trap without retention. The

system is dynamically calibrated so that the volume of sample passing through the trap does not have to be quantitatively measured, but must be precisely repeatable between the calibration and the analytical phases.

- 3.3 After the fixed-volume air sample has been drawn through the trap, a helium carrier gas flow is diverted to pass through the trap, in the opposite direction to the sample flow, and into an FID. When the residual air and methane have been flushed from the trap and the FID baseline restablizes, the cryogen is removed and the temperature of the trap is raised to approximately 90°C.
 - 3.4 The organic compounds previously collected in the trap revolatilize due to the increase in temperature and are carried into the FID, resulting in a response peak or peaks from the FID. The area of the peak or peaks is integrated, and the integrated value is translated to concentration units via a previously-obtained calibration curve relating integrated peak areas with known concentrations of propane.
 - 3.5 By convention, concentrations of NMOC are reported in units of parts per million carbon (ppmC), which, for a specified compound, is the concentration of volume (ppmV) multiplied by the number of carbon atoms in the compound.
 - 3.6 The cryogenic trap simultaneously concentrates the NMOC while separating and removing the methane from air samples. The technique is thus direct reading for NMOC and, because of the concentration step, is more sensitive than conventional continuous NMOC analyzers.
4. Significance
 - 4.1 Accurate measurements of ambient concentrations of NMOC are important for the control of photochemical smog because these organic compounds are primary precursors of atmospheric ozone and other oxidants. Achieving and maintaining compliance with the NAAQS for ozone thus depends largely on control of ambient levels of NMOC.
 - 4.2 The NMOC concentrations typically found at urban sites may range up to 5-7 ppmC or higher. In order to determine transport of precursors into an area, measurement of NMOC upwind of the area may be necessary. Upwind NMOC concentrations are likely to be less than a few tenths of 1 ppm.
 - 4.3 Conventional methods that depend on gas chromatography and qualitative and quantitative species evaluation are excessively difficult and expensive to operate and maintain when speciated

measurements are not needed. The method described here involves a simple, cryogenic preconcentration procedure with subsequent, direct, flame ionization detection. The method is sensitive and provides accurate measurements of ambient NMOC concentrations where speciated data are not required as applicable to the EKMA.

5. Definitions

[Note: Definitions used in this document and in any user-prepared Standard Operating Procedures (SOPs) should be consistent with ASTM Methods D1356 and E355. All abbreviations and symbols are defined within this document at point of use.]

- 5.1 Absolute pressure - Pressure measured with reference to absolute zero pressure (as opposed to atmospheric pressure), usually expressed as pounds-force per square inch absolute (psia).
- 5.2 Cryogen - A substance used to obtain very low trap temperatures in the NMOC analysis system. Typical cryogens are liquid argon (bp-185.7) and liquid oxygen (bp-183.0).
- 5.3 Dynamic calibration - Calibration of an analytical system with pollutant concentrations that are generated in a dynamic, flowing system, such as by quantitative, flow-rate dilution of a high concentration gas standard with zero gas.
- 5.4 EKMA - Empirical Kinetics Modeling Approach; an empirical model that attempts to relate morning ambient concentrations of non-methane organic compounds (NMOC) and NO_x with subsequent peak, downwind ambient ozone concentrations; used by pollution control agencies to estimate the degree of hydrocarbon emission reduction needed to achieve compliance with national ambient air quality standards for ozone.
- 5.5 Gauge pressure - Pressure measured with reference to atmospheric pressure (as opposed to absolute pressure). Zero gauge pressure (0 psig) is equal to atmospheric pressure, or 14.7 psia (101 kPa).
- 5.6 In situ - In place; In situ measurements are obtained by direct, on-the-spot analysis, as opposed to subsequent, remote analysis of a collected sample.
- 5.7 Integrated sample - A sample obtained uniformly over a specified time period and representative of the average levels of pollutants during the time period.
- 5.8 NMOC - Nonmethane organic compounds; total organic compounds as measured by a flame ionization detector, excluding methane.
- 5.9 ppmC - Concentration unit of parts per million carbon; for a specific compound, ppmC is equivalent to parts per million by

volume (ppmv) multiplied by the number of carbon atoms in the compound.

5.10 Sampling - The process of withdrawing or isolating a representative portion of an ambient atmosphere, with or without the simultaneous isolation of selected components for subsequent analysis.

6. Interferences

6.1 In field and laboratory evaluation, water was found to cause a positive shift in the FID baseline. The effect of this shift is minimized by carefully selecting the integration termination point and adjusted baseline used for calculating the area of the NMOC peak(s).

6.2 When using helium as a carrier gas, FID response is quite uniform for most hydrocarbon compounds, but the response can vary considerably for other types of organic compounds.

7. Apparatus

7.1 Direct Air Sampling (Figure 1)

7.1.1 Sample manifold or sample inlet line - to bring sample air into the analytical system.

7.1.2 Vacuum pump or blower - to draw sample air through a sample manifold or long inlet line to reduce inlet residence time. Maximum residence time should be no greater than 1 minute.

7.2 Remote Sample Collection in Pressurized Canisters (Figure 2)

7.2.1 Sample canister(s) - stainless steel, Summa[®]-polished vessel(s) of 4-6 L capacity (Scientific Instrumentation Specialists, Inc., P.O. Box 8941, Moscow, ID 83843), used for automatic collection of 3-hour integrated field air samples. Each canister should have a unique identification number stamped on its frame.

7.2.2 Sample pump - stainless steel, metal bellows type (Model MB-151, Metal Bellows Corp., 1075 Providence Highway, Sharon, MA 02067) capable of 2 atmospheres minimum output pressure. Pump must be free of leaks, clean, and uncontaminated by oil or organic compounds.

7.2.3 Pressure gauge - 0-30 psig (0-240 kPa).

7.2.4 Solenoid valve - special electrically-operated, bistable solenoid valve (Skinner Magnelatch Valve, New Britain, CT), to control sample flow to the canister with negligible temperature rise (Figure 3). The use

of the Skinner Magnelatch valve avoids any substantial temperature rise that would occur with a conventional, normally closed solenoid valve, which would have to be energized during the entire sample period. This temperature rise in the valve could cause outgassing of organics from the Viton valve seat material. The Skinner Magnelatch valve requires only a brief electrical pulse to open or close at the appropriate start and stop times and therefore experiences no temperature increase. The pulses may be obtained with an electronic timer that can be programmed for short (5 to 60 seconds) ON periods or with a conventional mechanical timer and a special pulse circuit. Figure 3[a] illustrates a simple electrical pulse circuit for operating the Skinner Magnelatch solenoid valve with a conventional mechanical timer. However, with this simple circuit, the valve may operate unpredictably during brief power interruptions or if the time is manually switched on and off too fast. A better circuit incorporating a time-delay relay to provide more reliable valve operation is shown in Figure 3[b].

- 7.2.5 Stainless steel orifice (or short capillary) - capable of maintaining a substantially constant flow over the sampling period (see Figure 4).
- 7.2.6 Particulate matter filter - 2 micron stainless steel sintered in-line type (see Figure 4).
- 7.2.7 Timer - used for unattended sample collection. Capable of controlling pump(s) and solenoid valve.
- 7.3 Sample Canister Cleaning (Figure 5)
 - 7.3.1 Vacuum pump - capable of evacuating sample canister(s) to an absolute pressure of <5 mm Hg.
 - 7.3.2 Manifold - stainless steel manifold with connections for simultaneously cleaning several canisters.
 - 7.3.3 Shut off valve(s) - seven required.
 - 7.3.4 Vacuum gauge - capable of measuring vacuum in the manifold to an absolute pressure of 5 mm Hg or less.
 - 7.3.5 Cryogenic trap (2 required) - U-shaped open tubular trap cooled with liquid nitrogen or argon used to prevent contamination from back diffusion of oil from vacuum pump, and to provide clean, zero air to sample canister(s).

- 7.3.6 Pressure gauge - 0-50 psig (0-345 kPa), to monitor zero air pressure.
 - 7.3.7 Flow control valve - to regulate flow of zero air into canister(s).
 - 7.3.8 Humidifier - water bubbler or other system capable of providing moisture to the zero air supply.
- 7.4 Analytical System (Figure 1)
- 7.4.1 FID detector system - including flow controls for the FID fuel and air, temperature control for the FID, and signal processing electronics. The FID burner air, hydrogen, and helium carrier flow rates should be set according to the manufacturer's instructions to obtain an adequate FID response while maintaining as stable a flame as possible throughout all phases of the analytical cycle.
 - 7.4.2 Chart recorder - compatible with the FID output signal, to record FID response.
 - 7.4.3 Electronic integrator - capable of integrating the area of one or more FID response peaks and calculating peak area corrected for baseline drift. If a separate integrator and chart recorder are used, care must be exercised to be sure that these components do not interfere with each other electrically. Range selector controls on both the integrator and the FID analyzer may not provide accurate range ratios, so individual calibration curves should be prepared for each range to be used. The integrator should be capable of marking the beginning and ending of peaks, constructing the appropriate baseline between the start and end of the integration period, and calculating the peak area.
- Note: The FID (7.4.1), chart recorder (7.4.2), integrator (7.4.3), valve heater (7.4.5), and a trap heating system are conveniently provided by a standard laboratory chromatograph and associated integrator. EPA has adapted two such systems for the PDFID method: a Hewlett-Packard model 5880 (Hewlett-Packard Corp., Avondale, PA) and a Shimadzu model GC8APF (Shimadzu Scientific Instruments Inc., Columbia, MD; see Reference 5). Other similar systems may also be applicable.

- 7.4.4 Trap - the trap should be carefully constructed from a single piece of chromatographic-grade stainless steel tubing (0.32 cm O.D, 0.21 cm I.D.) as shown in Figure 6. The central portion of the trap (7-10 cm) is packed with 60/80 mesh glass beads, with small glass wool (dimethyldichlorosilane-treated) plugs to retain the beads. The trap must fit conveniently into the Dewar flask (7.4.9), and the arms must be of an appropriate length to allow the beaded portion of the trap to be submerged below the level of liquid cryogen in the Dewar. The trap should connect directly to the six-port valve, if possible, to minimize line length between the trap and the FID. The trap must be mounted to allow the Dewar to be slipped conveniently on and off the trap and also to facilitate heating of the trap (see 7.4.13).
- 7.4.5 Six-port chromatographic valve - Seiscor Model VIII (Seismograph Service Corp., Tulsa, OK), Valco Model 9110 (Valco Instruments Co., Houston, TX), or equivalent. The six-port valve and as much of the interconnecting tubing as practical should be located inside an oven or otherwise heated to 80 - 90°C to minimize wall losses or adsorption/desorption in the connecting tubing. All lines should be as short as practical.
- 7.4.6 Multistage pressure regulators - standard two-stage, stainless steel diaphragm regulators with pressure gauges, for helium, air, and hydrogen cylinders.
- 7.4.7 Pressure regulators - optional single stage, stainless steel, with pressure gauge, if needed, to maintain constant helium carrier and hydrogen flow rates.
- 7.4.8 Fine needle valve - to adjust sample flow rate through trap.
- 7.4.9 Dewar flask - to hold liquid cryogen to cool the trap, sized to contain submerged portion of trap.
- 7.4.10 Absolute pressure gauge - 0-450 mm Hg, (2 mm Hg [scale divisions indicating units]), to monitor repeatable volumes of sample air through cryogenic trap (Wallace and Tiernan, Model 61C-ID-0410, 25 Main Street, Belleville, NJ).
- 7.4.11 Vacuum reservoir - 1-2 L capacity, typically 1 L.

- 7.4.12 Gas purifiers - gas scrubbers containing Drierite® or silica gel and 5A molecular sieve to remove moisture and organic impurities in the helium, air, and hydrogen gas flows (Alltech Associates, Deerfield, IL). Note: Check purity of gas purifiers prior to use by passing zero-air through the unit and analyzing according to Section 11.4. Gas purifiers are clean if produce [contain] less than 0.02 ppmC hydrocarbons.
 - 7.4.13 Trap heating system - chromatographic oven, hot water, or other means to heat the trap to 80° to 90°C. A simple heating source for the trap is a beaker or Dewar filled with water maintained at 80-90°C. More repeatable types of heat sources are recommended, including a temperature-programmed chromatograph oven, electrical heating of the trap itself, or any type of heater that brings the temperature of the trap up to 80-90°C in 1-2 minutes.
 - 7.4.14 Toggle shut-off valves (2) - leak free, for vacuum valve and sample valve.
 - 7.4.15 Vacuum pump - general purpose laboratory pump capable of evacuating the vacuum reservoir to an appropriate vacuum that allows the desired sample volume to be drawn through the trap.
 - 7.4.16 Vent - to keep the trap at atmospheric pressure during trapping when using pressurized canisters.
 - 7.4.17 Rotameter - to verify vent flow.
 - 7.4.18 Fine needle valve (optional) - to adjust flow rate of sample from canister during analysis.
 - 7.4.19 Chromatographic-grade stainless steel tubing (Alltech Applied Science, 2051 Waukegan Road, Deerfield, IL, 60015, (312) 948-8600) and stainless steel plumbing fittings - for interconnections. All such materials in contact with the sample, analyte, or support gases prior to analysis should be stainless steel or other inert metal. Do not use plastic or Teflon® tubing or fittings.
- 7.5 Commercially Available PDFID System (5)
- 7.5.1 A convenient and cost-effective modular PDFID system suitable for use with a conventional laboratory chromatograph is commercially available (NuTech

Corporation, Model 8548, 2806 Cheek Road, Durham, NC, 27704, (919) 682-0402).

7.5.2 This modular system contains almost all of the apparatus items needed to convert the chromatograph into a PDFID analytical system and has been designed to be readily available and easy to assemble.

8. Reagents and Materials

8.1 Gas cylinders of helium and hydrogen - ultrahigh purity grade.

8.2 Combustion air - cylinder containing less than 0.02 ppm hydrocarbons, or equivalent air source.

8.3 Propane calibration standard - cylinder containing 1-100 ppm (3-300 ppmC) propane in air. The cylinder assay should be traceable to a National Bureau of Standards (NBS) Standard Reference Material (SRM) or to a NBS/EPA-approved Certified Reference Material (CRM).

8.4 Zero air - cylinder containing less than 0.02 ppmC hydrocarbons. Zero air may be obtained from a cylinder of zero-grade compressed air scrubbed with Drierite® or silica gel and 5A molecular sieve or activated charcoal, or by catalytic cleanup of ambient air. All zero air should be passed through a liquid argon cold trap for final cleanup, then passed through a hydrocarbon-free water bubbler (or other device) for humidification.

8.5 Liquid cryogen - liquid argon (bp -185.7°C) or liquid oxygen, (bp -183°C) may be used as the cryogen. Experiments have shown no differences in trapping efficiency between liquid argon and liquid oxygen. However, appropriate safety precautions must be taken if liquid oxygen is used. Liquid nitrogen (bp -195°C) should not be used because it causes condensation of oxygen and methane in the trap.

9. Direct Sampling

9.1 For direct ambient air sampling, the cryogenic trapping system draws the air sample directly from a pump-ventilated distribution manifold or sample line (see Figure 1). The connecting line should be of small diameter (1/8" O.D.) stainless steel tubing and as short as possible to minimize its dead volume.

9.2 Multiple analyses over the sampling period must be made to establish hourly or 3-hour NMOC concentration averages.

10. Sample Collection in Pressurized Canister(s)

For integrated pressurized canister sampling, ambient air is sampled by a metal bellows pump through a critical orifice (to maintain constant flow), and pressurized into a clean, evacuated, Summa®-polished sample

canister. The critical orifice size is chosen so that the canister is pressurized to approximately one atmosphere above ambient pressure, at a constant flow rate over the desired sample period. Two canisters are connected in parallel for duplicate samples. The canister(s) are then returned to the laboratory for analysis, using the PDFID analytical system. Collection of ambient air samples in pressurized canisters provides the following advantages:

- ! Convenient integration of ambient samples over a specific time period
- ! Capability of remote sampling with subsequent central laboratory analysis
- ! Ability to ship and store samples, if necessary
- ! Unattended sample collection
- ! Analysis of samples from multiple sites with one analytical system
- ! Collection of replicate samples for assessment of measurement precision

With canister sampling, however, great care must be exercised in selecting, cleaning, and handling the sample canister(s) and sampling apparatus to avoid losses or contamination of the samples.

10.1 Canister Cleanup and Preparation

- 10.1.1 All canisters must be clean and free of any contaminants before sample collection.
- 10.1.2 Leak test all canisters by pressurizing them to approximately 30 psig [200 kPa (gauge)] with zero air. The use of the canister cleaning system (see Figure 5) may be adequate for this task. Measure the final pressure - close the canister valve, then check the pressure after 24 hours. If leak tight, the pressure should not vary more than ± 2 psig over the 24-hour period. Note leak check result on sampling data sheet, Figure 7.
- 10.1.3 Assemble a canister cleaning system, as illustrated in Figure 5. Add cryogen to both the vacuum pump and zero air supply traps. Connect the canister(s) to the manifold. Open the vent shut off valve and the canister valve(s) to release any remaining pressure in the canister. Now close the vent shut off valve and open the vacuum shut off valve. Start the vacuum pump and evacuate the canister(s) to ≤ 5.0 mm Hg (for at least one hour). [Note: On a daily basis or more often if necessary, blow-out the cryogenic traps with zero air to remove any trapped water from previous canister cleaning cycles.]

- 10.1.4 Close the vacuum and vacuum gauge shut off valves and open the zero air shut off valve to pressurize the canister(s) with moist zero air to approximately 30 psig [200 kPa (gauge)]. If a zero gas generator systems is used, the flow rate may need to be limited to maintain the zero air quality.
- 10.1.5 Close the zero shut off valve and allow canister(s) to vent down to atmospheric pressure through the vent shut off valve. Close the vent shut off valve. Repeat steps 10.1.3 through 10.1.5 two additional times for a total of three (3) evacuation/pressurization cycles for each set of canisters.
- 10.1.6 As a "blank" check of the canister(s) and cleanup procedure, analyze the final zero-air fill of 100% of the canisters until the cleanup system and canisters are proven reliable. The check can then be reduced to a lower percentage of canisters. Any canister that does not test clean (compared to direct analysis of humidified zero air of less than 0.02 ppmC) should not be utilized.
- 10.1.7 The canister is then re-evacuated to ≤ 5.0 mm Hg, using the canister cleaning system, and remains in this condition until use. Close the canister valve, remove the canister from the canister cleaning system and cap canister connection with a stainless steel fitting. The canister is now ready for collection of an air sample. Attach an identification tag to the neck of each canister for field notes and chain-of-custody purposes.
- 10.2 Collection of Integrated Whole-Air Samples
- 10.2.1 Assemble the sampling apparatus as shown in Figure 2. The connecting lines between the sample pump and the canister(s) should be as short as possible to minimize their volume. A second canister is used when a duplicate sample is desired for quality assurance (QA) purposes (see Section 12.2.4). The small auxiliary vacuum pump purges the inlet manifold or lines with a flow of several L/min to minimize the sample residence time. The larger metal bellows pump takes a small portion of this sample to fill and pressurize the sample canister(s). Both pumps should be shock-

mounted to minimize vibration. Prior to field use, each sampling system should be leak tested. The outlet side of the metal bellows pump can be checked for leaks by attaching the 0-30 psig pressure gauge to the canister(s) inlet via connecting tubing and pressurizing to 2 atmospheres or approximately 29.4 psig. If pump and connecting lines are leak free pressure should remain at ± 2 psig for 15 minutes. To check the inlet side, plug the sample inlet and insure that there is no flow at the outlet of the pump.

- 10.2.2 Calculate the flow rate needed so that the canister(s) are pressurized to approximately one atmosphere above ambient pressure (2 atmospheres absolute pressure) over the desired sample period, utilizing the following equation:

$$F = \frac{(P)(V)(N)}{(T)(60)}$$

where:

- F = flow rate (cm³/min)
 P = final canister pressure (atmospheres absolute)
 = (Pg/Pa) + 1
 V = volume of the canister (cm³)
 N = number of canisters connected together for simultaneous sample collection
 T = sample period (hours)
 Pg = gauge pressure in canister, psig (kPa)
 Pa = standard atmospheric pressure, 14.7 psig (101 kPa)

For example, if one 6-L canister is to be filled to 2 atmospheres absolute pressure (14.7 psig) in 3 hours, the flow rate would be calculated as follows:

$$F = \frac{2 \times 6000 \times 1}{3 \times 60} = 67 \text{ cm}^3/\text{min}$$

- 10.2.3 Select a critical orifice or hypodermic needle suitable to maintain a substantially constant flow at the calculated flow rate into the canister(s) over the desired sample period. A 30-gauge hypodermic needle,

2.5 cm long, provides a flow of approximately 65 cm³/min with the Metal Bellows Model MBV-151 pump (see Figure 4). Such a needle will maintain approximately constant flow up to a canister pressure of about 10 psig (71 kPa), after which the flow drops with increasing pressure. At 14.7 psig (2 atmospheres absolute pressure), the flow is about 10% below the original flow.

- 10.2.4 Assemble the 2.0 micron stainless steel in-line particulate filter and position it in front of the critical orifice. A suggested filter-hypodermic needle assembly can be fabricated as illustrated in Figure 4.
- 10.2.5 Check the sampling system for contamination by filling two evacuated, cleaned canister(s) (See Section 10.1) with humidified zero air through the sampling system. Analyze the canisters according to Section 11.4. The sampling system is free of contamination if the canisters contain less than 0.02 ppmC hydrocarbons, similar to that of humidified zero air.
- 10.2.6 During the system contamination check procedure, check the critical orifice flow rate on the sampling system to insure that sample flow rate remains relatively constant ($\pm 10\%$) up to about 2 atmospheres absolute pressure (101 kpa). Note: A drop in the flow rate may occur near the end of the sampling period as the canister pressure approaches two atmospheres.
- 10.2.7 Reassemble the sampling system. If the inlet sample line is longer than 3 meters, install an auxiliary pump to ventilate the sample line, as illustrated in Figure 2.
- 10.2.8 Verify that the timer, pump(s) and solenoid valve are connected and operating properly.
- 10.2.9 Verify that the timer is correctly set for the desired sample period, and that the solenoid valve is closed.
- 10.2.10 Connect a cleaned, evacuated canister(s) (Section 10.1) to the non-contaminated sampling system, by way of the solenoid valve, for sample collection.
- 10.2.11 Make sure the solenoid valve is closed. Open the canister valve(s). Temporarily connect a small rotameter to the sample inlet to verify that there is

no flow. Note: Flow detection would indicate a leaking (or open) solenoid valve. Remove the rotameter after leak detection procedure.

- 10.2.12 Fill out the necessary information on the Field Data Sheet (Figure 7).
- 10.2.13 Set the automatic timer to start and stop the pump or pumps to open and close the solenoid valve at the appropriate time for the intended sample period. Sampling will begin at the pre-determined time.
- 10.2.14 After the sample period, close the canister valve(s) and disconnect the canister(s) from the sampling system. Connect a pressure gauge to the canister(s) and briefly open and close the canister valve. Note the canister pressure on the Field Data Sheet (see Figure 7). The canister pressure should be approximately 2 atmospheres absolute [1 atmosphere or 101 kPa (gauge)]. Note: If the canister pressure is not approximately 2 atmospheres absolute (14.7 psig), determine and correct the cause before next sample. Re-cap canister valve.
- 10.2.15 Fill out the identification tag on the sample canister(s) and complete the Field Data Sheet as necessary. Note any activities or special conditions in the area (rain, smoke, etc.) that may affect the sample contents on the sampling data sheet.
- 10.2.16 Return the canister(s) to the analytical system for analysis.

11. Sample Analysis

11.1 Analytical System Leak Check

- 11.1.1 Before sample analysis, the analytical system is assembled (see Figure 1) and leak checked.
- 11.1.2 To leak check the analytical system, place the six-port gas valve in the trapping position. Disconnect and cap the absolute pressure gauge. Insert a pressure gauge capable of recording up to 60 psig at the vacuum valve outlet.
- 11.1.3 Attach a valve and a zero air supply to the sample inlet port. Pressurize the system to about 50 psig (350 kPa) and close the valve.

- 11.1.4 Wait approximately 3 hrs. and re-check pressure. If the pressure did not vary more than ± 2 psig, the system is considered leak tight.
- 11.1.5 If the system is leak free, de-pressurize and reconnect absolute pressure gauge.
- 11.1.6 The analytical system leak check procedure needs to be performed during the system checkout, during a series of analysis or if leaks are suspected. This should be part of the user-prepared SOP manual (see Section 12.1).

11.2 Sample Volume Determination

11.2.1 The vacuum reservoir and absolute pressure gauge are used to meter a precisely repeatable volume of sample air through the cryogenically-cooled trap, as follows: With the sample valve closed and the vacuum valve open, the reservoir is first evacuated with the vacuum pump to a predetermined pressure (e.g., 100 mm Hg). Then the vacuum valve is closed and the sample valve is opened to allow sample air to be drawn through the cryogenic trap and into the evacuated reservoir until a second predetermined reservoir pressure is reached (e.g., 300 mm Hg). The (fixed) volume of air thus sampled is determined by the pressure rise in the vacuum reservoir (difference between the predetermined pressures) as measured by the absolute pressure gauge (see Section 12.2.1).

11.2.2 The sample volume can be calculated by:

$$V_s = \frac{(\Delta P)(V_r)}{P_s}$$

where:

- V_s = volume of air sampled (standard cm^3)
- ΔP = pressure difference measured by gauge (mm Hg)
- V_r = volume of vacuum reservoir (cm^3)
usually 1 L
- P_s = standard pressure (760 mm Hg)

For example, with a vacuum reservoir of 1000 cm^3 and a pressure change of 200 mm Hg (100 to 300 mm Hg), the volume sampled would be 263 cm^3 . [Note: Typical sample volume using this procedure is between 200-300 cm^3 .]

- 11.2.3 The sample volume determination need only be performed once during the system check-out and shall be part of the user-prepared SOP Manual (see Section 12.1).
- 11.3 Analytical System Dynamic Calibration
- 11.3.1 Before sample analysis, a complete dynamic calibration of the analytical system should be carried out at five or more concentrations on each range to define the calibration curve. This should be carried out initially and periodically thereafter [may be done only once during a series of analyses]. This should be part of the user-prepared SOP Manual (See Section 12.1). The calibration should be verified with two or three-point calibration checks (including zero) each day the analytical system is used to analyze samples.
- 11.3.2 Concentration standards of propane are used to calibrate the analytical system. Propane calibration standards may be obtained directly from low concentration cylinder standards or by dilution of high concentration cylinder standards with zero air (see Section 8.3). Dilution flow rates must be measured accurately, and the combined gas stream must be mixed thoroughly for successful calibration of the analyzer. Calibration standards should be sampled directly from a vented manifold or tee. Note: Remember that a propane NMOC concentration in ppmC is three times the volumetric concentration in ppm.
- 11.3.3 Select one or more combinations of the following parameters to provide the desired range or ranges (e.g., 0-1.0 ppmC or 0-5.0 ppmC): FID attenuator setting, output voltage setting, integrator resolution (if applicable), and sample volume. Each individual range should be calibrated separately and should have a separate calibration curve. Note: Modern GC integrators may provide automatic ranging such that several decades of concentration may be covered in a single range. The user-prepared SOP manual should address variations applicable to a specific system design (see Section 12.1).
- 11.3.4 Analyze each calibration standard three times according to the procedure in Section 11.4. Insure that flow rates, pressure gauge start and stop

readings, initial cryogen liquid level in the Dewar, timing, heating, integrator settings, and other variables are the same as those that will be used during analysis of ambient samples. Typical flow rates for the gases are: hydrogen, 30 cm³/minute; helium carrier, 30 cm³/minute; burner air, 400 cm³/minute.

- 11.3.5 Average the three analyses for each concentration standard and plot the calibration curve(s) as average integrated peak area reading versus concentration in ppmC. The relative standard deviation for the three analyses should be less than 3% (except for zero concentration). Linearity should be expected; points that appear to deviate abnormally should be repeated. Response has been shown to be linear over a wide range (0-10,000 ppbC). If nonlinearity is observed, an effort should be made to identify and correct the problem. If the problem cannot be corrected, additional points in the nonlinear region may be needed to define the calibration curve adequately.

11.4 Analysis Procedure

- 11.4.1 Insure the analytical system has been assembled properly, leaked checked, and properly calibrated through a dynamic standard calibration. Light the FID detector and allow to stabilize.
- 11.4.2 Check and adjust the helium carrier pressure to provide the correct carrier flow rate for the system. Helium is used to purge residual air and methane from the trap at the end of the sampling phase and to carry the re-volatilized NMOC from the trap into the FID. A single-stage auxiliary regulator between the cylinder and the analyzer may not be necessary, but is recommended to regulate the helium pressure better than the multistage cylinder regulator. When an auxiliary regulator is used, the secondary stage of the two-stage regulator must be set at a pressure higher than the pressure setting of the single-stage regulator. Also check the FID hydrogen and burner air flow rates (see 11.3.4).

- 11.4.3 Close the sample valve and open the vacuum valve to evacuate the vacuum reservoir to a specific predetermined value (e.g., 100 mm Hg).
- 11.4.4 With the trap at room temperature, place the six-port valve in the inject position.
- 11.4.5 Open the sample valve and adjust the sample flow rate needle valve for an appropriate trap flow of 50-100 cm³/min. Note: The flow will be lower later, when the trap is cold.
- 11.4.6 Check the sample canister pressure before attaching it to the analytical system and record on Field Data Sheet (see Figure 7). Connect the sample canister or direct sample inlet to the six-port valve, as shown in Figure 1. For a canister, either the canister valve or an optional fine needle valve installed between the canister and the vent is used to adjust the canister flow rate to a value slightly higher than the trap flow rate set by the sample flow rate needle valve. The excess flow exhausts through the vent, which assures that the sample air flowing through the trap is at atmospheric pressure. The vent is connected to a flow indicator such as a rotameter as an indication of vent flow to assist in adjusting the flow control valve. Open the canister valve and adjust the canister valve or the sample flow needle valve to obtain a moderate vent flow as indicated by the rotameter. The sample flow rate will be lower (and hence the vent flow rate will be higher) when the trap is cold.
- 11.4.7 Close the sample valve and open the vacuum valve (if not already open) to evacuate the vacuum reservoir. With the six-port valve in the inject position and the vacuum valve open, open the sample valve for 2-3 minutes [with both valves open, the pressure reading won't change] to flush and condition the inlet lines.
- 11.4.8 Close the sample valve and evacuate the reservoir to the predetermined sample starting pressure (typically 100 mm Hg) as indicated by the absolute pressure gauge.
- 11.4.9 Switch the six-port valve to the sample position.

- 11.4.10 Submerge the trap in the cryogen. Allow a few minutes for the trap to cool completely (indicated when the cryogen stops boiling). Add cryogen to the initial level used during system dynamic calibration. The level of the cryogenic liquid should remain constant with respect to the trap and should completely cover the beaded portion of the trap.
- 11.4.11 Open the sample valve and observe the increasing pressure on the pressure gauge. When it reaches the specific predetermined pressure (typically 300 mm Hg) representative of the desired sample volume (Section 11.2), close the sample valve.
- 11.4.12 Add a little cryogen or elevate the Dewar to raise the liquid level to a point slightly higher (3-15 mm) than the initial level at the beginning of the trapping. Note: This insures that organics do not bleed from the trap and are counted as part of the NMOC peak(s).
- 11.4.13 Switch the 6-port valve to the inject position, keeping the cryogenic liquid on the trap until the methane and upset peaks have diminished (10-20 seconds). Now close the canister valve to conserve the remaining sample in the canister.
- 11.4.14 Start the integrator and remove the Dewar flask containing the cryogenic liquid from the trap.
- 11.4.15 Close the GC oven door and allow the GC oven (or alternate trap heating system) to heat the trap at a predetermined rate (typically, 30°C/min) to 90°. Heating the trap volatilizes the concentrated NMOC such that the FID produces integrated peaks. A uniform trap temperature rise rate (above 0°C) helps to reduce variability and facilitates more accurate correction for the moisture-shifted baseline. With a chromatograph oven to heat the trap, the following parameters have been found to be acceptable: initial temperature, 30°C; initial time, 0.20 minutes (following start of the integrator); heat rate, 30°/minute; final temperature, 90°C.
- 11.4.16 Use the same heating process and temperatures for both calibration and sample analysis. Heating the trap too quickly may cause an initial negative response that could hamper accurate integration. Some initial

experimentation may be necessary to determine the optimal heating procedure for each system. Once established, the procedure should be consistent for each analysis as outlined in the user-prepared SOP Manual.

- 11.4.17 Continue the integration (generally, in the range of 1-2 minutes is adequate) only long enough to include all of the organic compound peaks and to establish the end point FID baseline, as illustrated in Figure 8. The integrator should be capable of marking the beginning and ending of peaks, constructing the appropriate operational baseline between the start and end of the integration period, and calculating the resulting corrected peak area. This ability is necessary because the moisture in the sample, which is also concentrated in the trap, will cause a slight positive baseline shift. This baseline shift starts as the trap warms and continues until all of the moisture is swept from the trap, at which time the baseline returns to its normal level. The shift always continues longer than the ambient organic peak(s). The integrator should be programmed to correct for this shifted baseline by ending the integration at a point after the last NMOC peak and prior to the return of the shifted baseline to normal (see Figure 8) so that the calculated operational baseline effectively compensates for the water-shifted baseline. Electronic integrators either do this automatically or they should be programmed to make this correction. Alternatively, analyses of humidified zero air prior to sample analyses should be performed to determine the water envelope and the proper blank value for correcting the ambient air concentration measurements accordingly. Heating and flushing of the trap should continue after the integration period has ended to insure all water has been removed to prevent buildup of water in the trap. Therefore, be sure that the 6-port valve remains in the inject position until all moisture has purged from the trap (3 minutes or longer).

- 11.4.18 Use the dynamic calibration curve (see Section 11.3) to convert the integrated peak area reading into concentration units (ppmC). Note that the NMOC peak shape may not be precisely reproducible due to variations in heating the trap, but the total NMOC peak area should be reproducible.
- 11.4.19 Analyze each canister sample at least twice and report the average NMOC concentration. Problems during an analysis occasionally will cause erratic or inconsistent results. If the first two analyses do not agree within $\pm 5\%$ relative standard deviation (RSD), additional analyses should be made to identify inaccurate measurements and produce a more accurate average (see also Section 12.2).

12. Performance Criteria and Quality Assurance

This section summarizes required quality assurance measures and provides guidance concerning performance criteria that should be achieved within each laboratory.

12.1 Standard Operating Procedures (SOPs)

- 12.1.1 Users should generate SOPs describing and documenting the following activities in their laboratory: (1) assembly, calibration, leak check, and operation of the specific sampling system and equipment used; (2) preparation, storage, shipment, and handling of samples; (3) assembly, leak check, calibration, and operation of the analytical system, addressing the specific equipment used; (4) canister storage and cleaning; and (5) all aspects of data recording and processing, including lists of computer hardware and software used.
- 12.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by, the laboratory personnel conducting the work.

12.2 Method Sensitivity, Accuracy, Precision and Linearity

- 12.2.1 The sensitivity and precision of the method is proportional to the sample volume. However, ice formation in the trap may reduce or stop the sample flow during trapping if the sample volume exceeds 500 cm³. Sample volumes below about 100-150 cm³ may cause increased measurement variability due to dead volume in lines and valves. For most typical ambient NMOC

concentrations, sample volumes in the range of 200-400 cm³ appear to be appropriate. If a response peak obtained with a 400 cm³ sample is off scale or exceeds the calibration range, a second analysis can be carried out with a smaller volume. The actual sample volume used need not be accurately known if it is precisely repeatable during both calibration and analysis. Similarly, the actual volume of the vacuum reservoir need not be accurately known. But the reservoir volume should be matched to the pressure range and resolution of the absolute pressure gauge so that the measurement of the pressure change in the reservoir, hence the sample volume, is repeatable within 1%. A 1000 cm³ vacuum reservoir and a pressure change of 200 mm Hg, measured with the specified pressure gauge, have provided a sampling precision of ± 1.31 cm³. A smaller volume reservoir may be used with a greater pressure change to accommodate absolute pressure gauges with lower resolution, and vice versa.

12.2.2

Some FID detector systems associated with laboratory chromatographs may have autoranging. Others may provide attenuator control and internal full-scale output voltage selectors. An appropriate combination should be chosen so that an adequate output level for accurate integration is obtained down to the detection limit; however, the electrometer or integrator must not be driven into saturation at the upper end of the calibration. Saturation of the electrometer may be indicated by flattening of the calibration curve at high concentrations. Additional adjustments of range and sensitivity can be provided by adjusting the sample volume use, as discussed in Section 12.2.1.

12.2.3

System linearity has been documented (6) from 0 to 10,000 ppbC.

12.2.4

Some organic compounds contained in ambient air are "sticky" and may require repeated analyses before they fully appear in the FID output. Also, some adjustment may have to be made in the integrator off time setting to accommodate compounds that reach the FID late in the analysis cycle. Similarly, "sticky" compounds from ambient samples or from contaminated propane

standards may temporarily contaminate the analytical system and can affect subsequent analyses. Such temporary contamination can usually be removed by repeated analyses of humidified zero air.

- 12.2.5 Simultaneous collection of duplicate samples decreases the possibility of lost measurement data from samples lost due to leakage or contamination in either of the canisters. Two (or more) canisters can be filled simultaneously by connecting them in parallel (see Figure 2(a)) and selecting an appropriate flow rate to accommodate the number of canisters (Section 10.2.2). Duplicate (or replicate) samples also allow assessment of measurement precision based on the differences between duplicate samples (or the standard deviations among replicate samples).

13. Method Modification

13.1 Sample Metering System

- 13.1.1 Although the vacuum reservoir and absolute pressure gauge technique for metering the sample volume during analysis is efficient and convenient, other techniques should work also.

- 13.1.2 A constant sample flow could be established with a vacuum pump and a critical orifice, with the six-port valve being switched to the sample position for a measured time period. A gas volume meter, such as a wet test meter, could also be used to measure the total volume of sample air drawn through the trap. These alternative techniques should be tested and evaluated as part of a user-prepared SOP manual.

13.2 FID Detector System

- 13.2.1 A variety of FID detector systems should be adaptable to the method.

- 13.2.2 The specific flow rates and necessary modifications for the helium carrier for any alternative FID instrument should be evaluated prior to use as apart of the user-prepared SOP manual.

13.3 Range

- 13.3.1 It may be possible to increase the sensitivity of the method by increasing the sample volume. However, limitations may arise such as plugging of the trap by ice.

- 13.3.2 Any attempt to increase sensitivity should be evaluated as part of the user-prepared SOP manual.
- 13.4 Sub-Atmospheric Pressure Canister Sampling
 - 13.4.1 Collection and analysis of canister air samples at sub-atmospheric pressure is also possible with minor modifications to the sampling and analytical procedures.
 - 13.4.2 Method TO-14, "Integrated Canister Sampling for Selective Organics: Pressurized and Sub-atmospheric Collection Mechanism," addresses sub-atmospheric pressure canister sampling. Additional information can be found in the literature (11-17).

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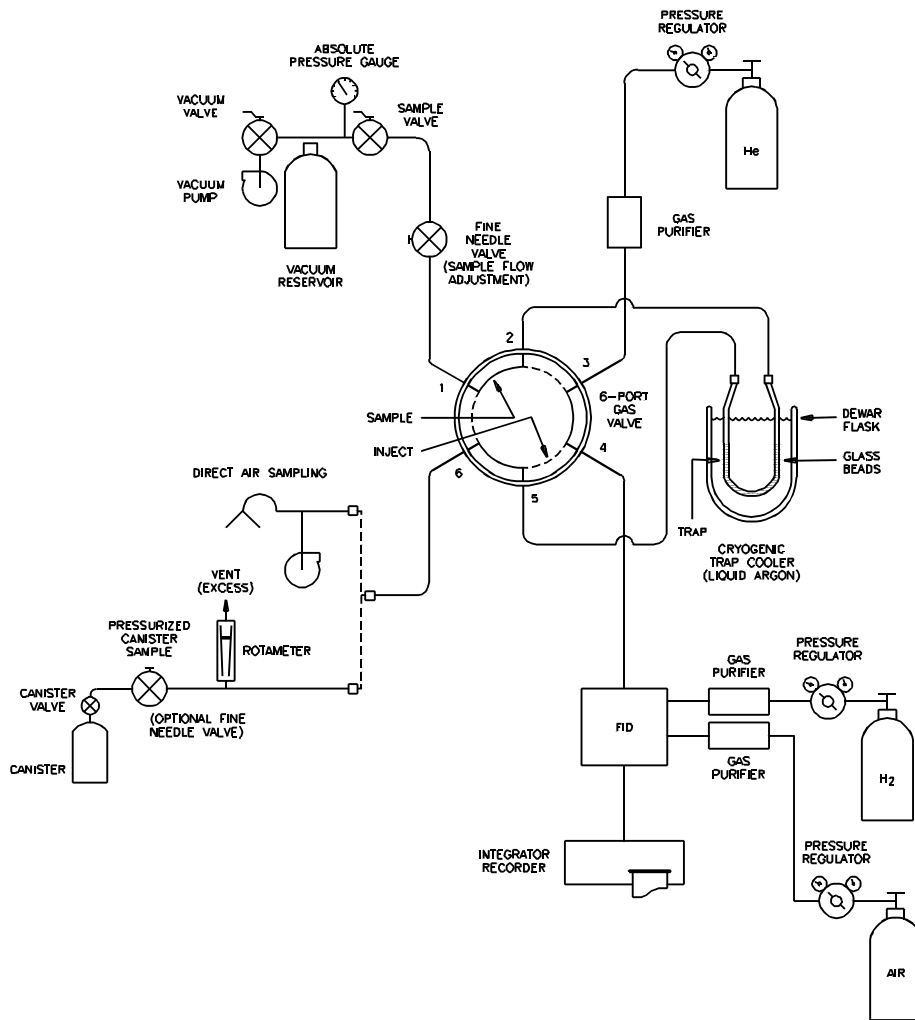


FIGURE 1. SCHEMATIC OF ANALYTICAL SYSTEM FOR NMOC-TWO SAMPLING MODES

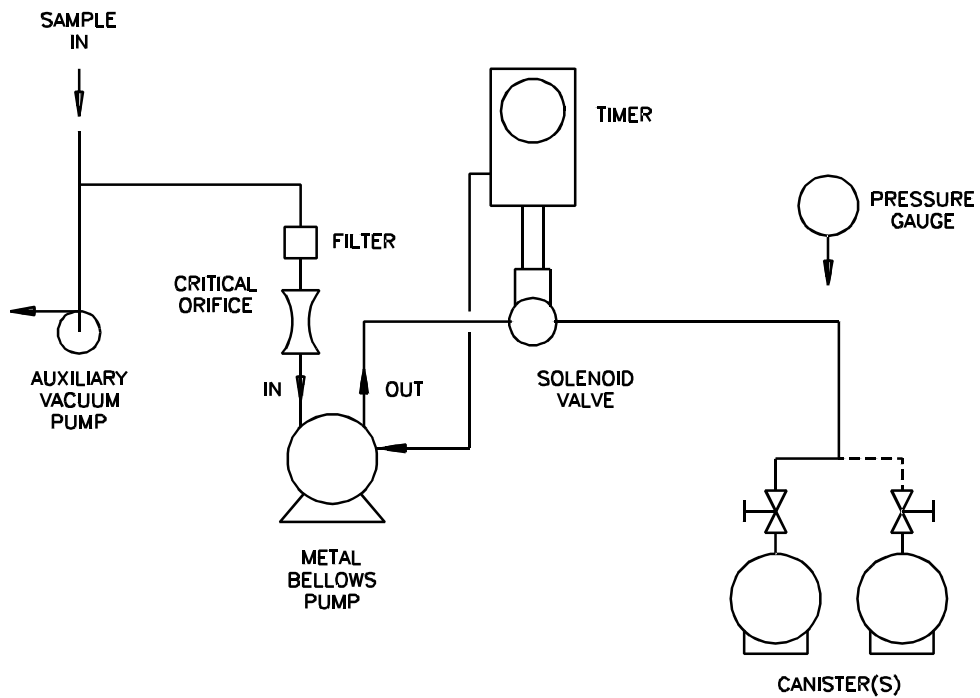
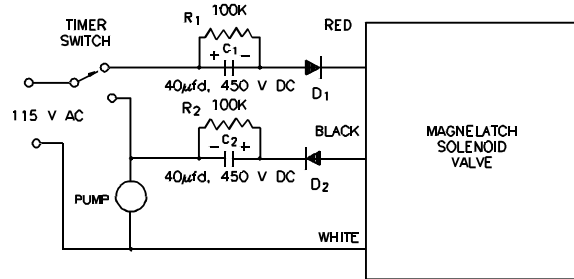
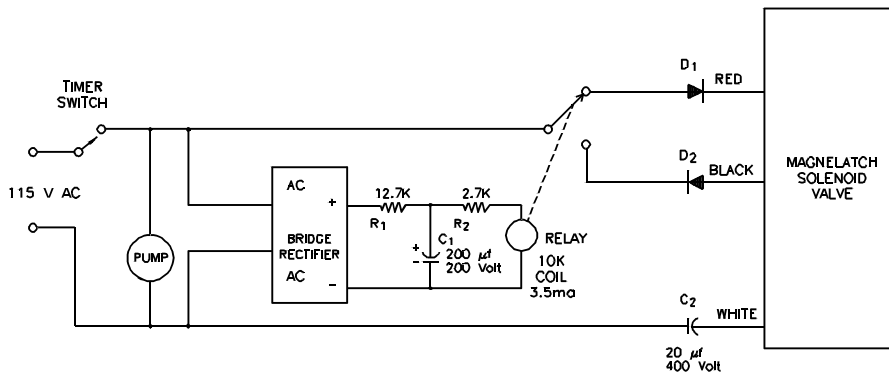


FIGURE 2. SAMPLE SYSTEM FOR AUTOMATIC COLLECTION OF 3-HOUR INTEGRATED AIR SAMPLES



COMPONENTS
 Capacitor C₁ and C₂ - 40 µf, 450 VDC (Sprague Atom[®] TWA 1712 or equivalent)
 Resistor R₁ and R₂ - 0.5 watt, 5% tolerance
 Diode D₁ and D₂ - 1000 PRV, 2.5 A (RCA, SK 3081 or equivalent)

FIGURE 3[a]. SIMPLE CIRCUIT FOR OPERATING MAGNELATCH VALVE



COMPONENTS
 Bridge Rectifier - 200 PRV, 1.5 A (RCA, SK 3105 or equivalent)
 Diode D₁ and D₂ - 1000 PRV, 2.5 A (RCA, SK 3081 or equivalent)
 Capacitor C₁ - 200 µf, 250 VDC (Sprague Atom[®] TWA 1528 or equivalent)
 Capacitor C₂ - 20 µf, 400 VDC Non-Polarized (Sprague Atom[®] TWA 1682 or equivalent)
 Relay - 10,000 ohm coil, 3.5 ma (AMF Potter and Brumfield, KCP 5, or equivalent)
 Resistor R₁ and R₂ - 0.5 watt, 5% tolerance

NON-POLARIZED

FIGURE 3[b]. IMPROVED CIRCUIT DESIGNED TO HANDLE POWER INTERRUPTIONS

FIGURE 3. ELECTRICAL PULSE CIRCUITS FOR DRIVING SKINNER MAGNELATCH SOLENOID VALVE WITH A MECHANICAL TIMER

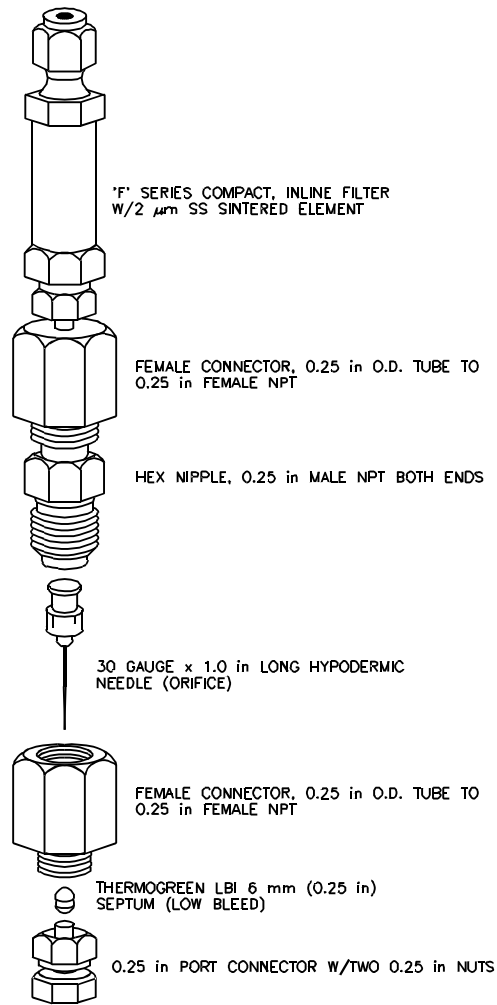


FIGURE 4. FILTER AND HYPODERMIC NEEDLE
ASSEMBLY FOR SAMPLE INLET FLOW
CONTROL

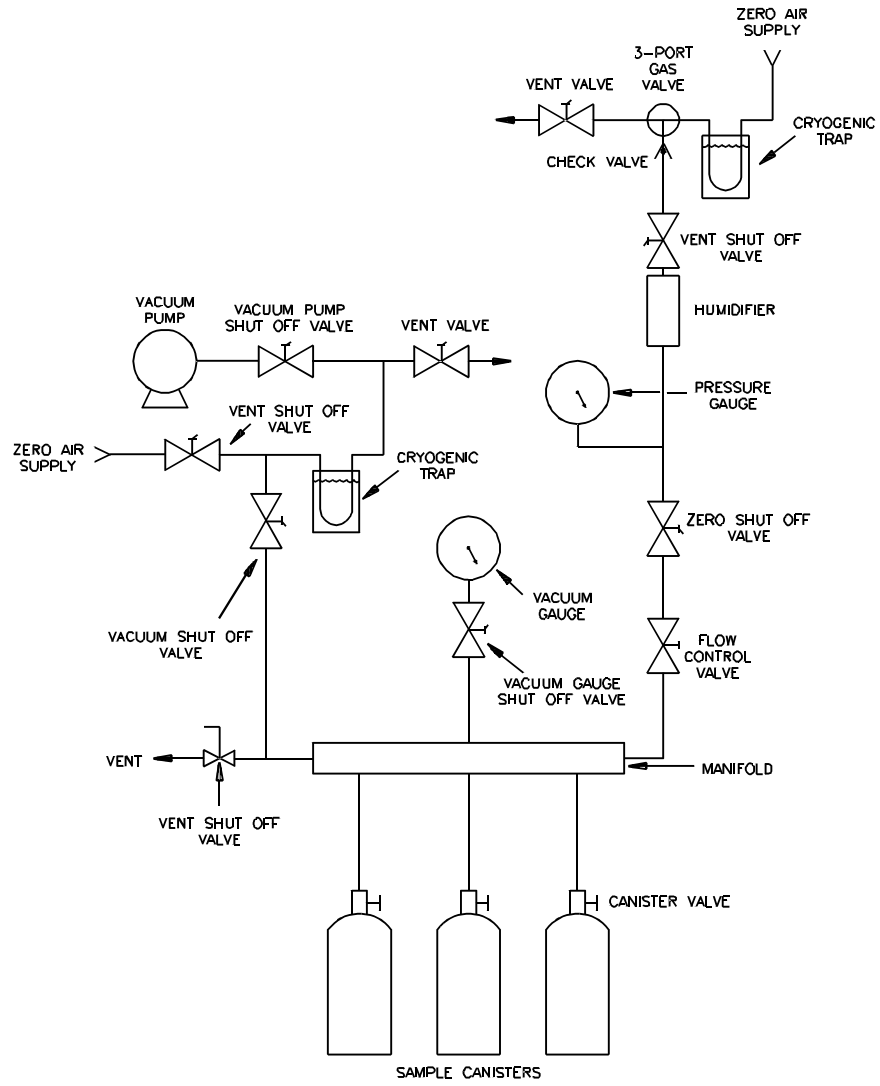


FIGURE 5. CANISTER CLEANING SYSTEM

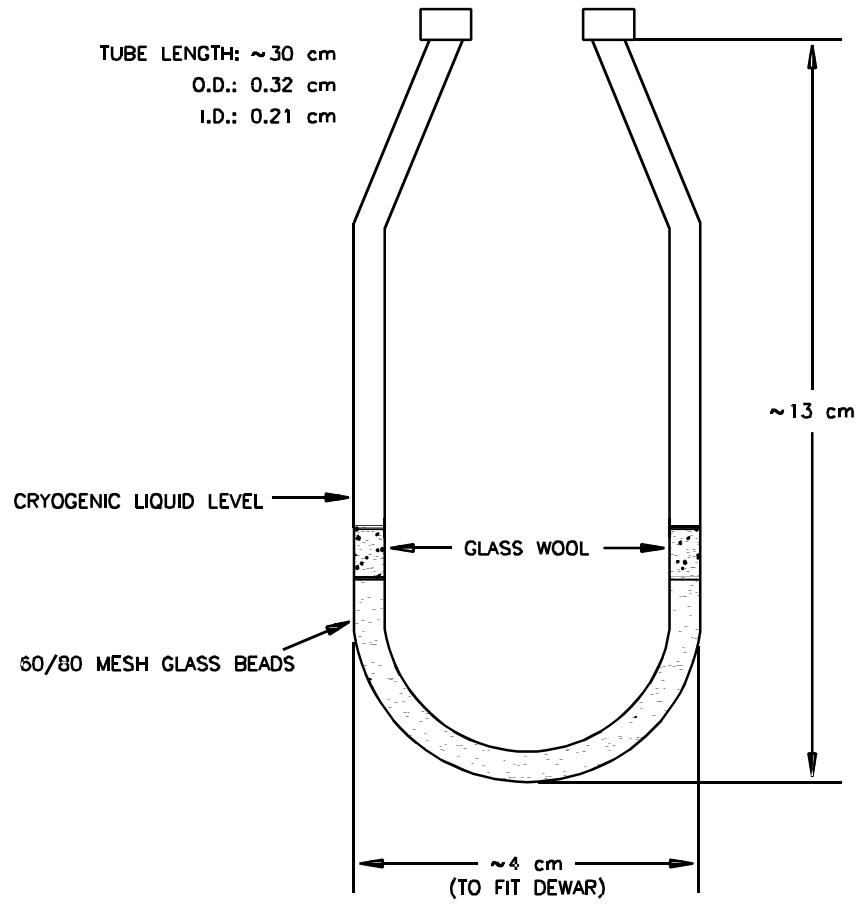


FIGURE 6. CRYOGENIC SAMPLE TRAP DIMENSIONS

PRESSURIZED CANISTER SAMPLING DATA SHEET

GENERAL INFORMATION:

PROJECT: _____ OPERATOR: _____
 SITE: _____ ORIFICE IDENTIFICATION: _____
 LOCATION: _____ FLOW RATE: _____
 MONITOR STATION NUMBER: _____ CALIBRATED BY: _____
 PUMP SERIAL NUMBER: _____ LEAK CHECK _____

Pass Fail

FIELD DATA:

Date	Canister Serial Number	Sample Number	Sample Time		Average Atmospheric Conditions			Canister pressure		Comments
			Start	Stop	Temperature	Pressure	Relative Humidity	Final	Laboratory	

Date Title Signature

FIGURE 7. EXAMPLE SAMPLING DATA SHEET

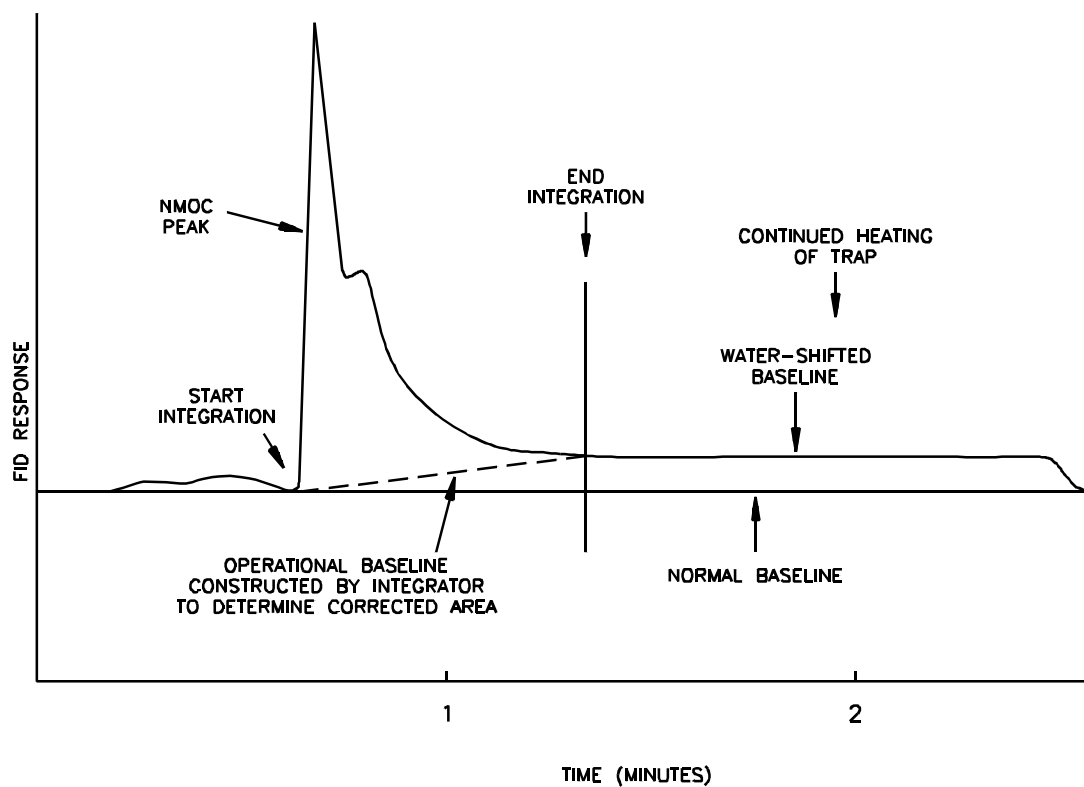


FIGURE 8. CONSTRUCTION OF OPERATIONAL BASELINE AND CORRESPONDING CORRECTION OF PEAK AREA