
# Air Pollution Control Division

# Technical Services Program

## APPENDIX GM10

Standard Operating Procedure for the Determination of
Toxic Organic Compounds in Ambient Air

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# TABLE OF CONTENTS

## LIST OF TABLES



## LIST OF FIGURES

# 1. SCOPE AND APPLICATION

An overview of the health and environmental effects of toxic organic compounds, including volatile organic compounds (VOCs), non-methane organic compounds (NMOCs), methane, and carbonyls, as well as a summary of their analytical methods are followed by a description of the format and purpose of the document.

## 1.1 Introduction

There are 188 Hazardous Air Pollutants (HAPs) defined in the Clean Air Act Amendments (CAA) of 1990. HAPs are also referred to as air toxics. Air toxics are those pollutants known or suspected to cause cancer or other serious health effects, such as reproductive effects or birth defects. The pollutants on this list can be broken down into various categories based on volatility and reactivity characteristics. For the purposes of this document, three main categories are discussed: VOCs, NMOCs and carbonyls.

Most air toxics originate from anthropogenic sources, including mobile sources (e.g., cars, trucks, and buses), stationary sources (e.g., factories, refineries, power plants) and indoor sources (e.g., some building materials and cleaning solvents). Some air toxics are also released from natural sources such as volcanic eruptions and forest fires.

### 1.1.1 VOCs

VOCs are a subset of the NMOCs, and include a variety of chemicals that can cause eye, nose and throat irritation, headache, nausea, dizziness, and skin problems. Higher concentrations may cause irritation of the lungs, as well as damage to the liver, kidney, or central nervous system. Some VOCs are suspected to cause cancer in humans and have been shown to cause cancer in animals. The health effects caused by VOCs depend on the level and length of exposure.

There are 98 VOCs on the list of HAPs in the CAA. The VOCs of interest to the CDPHE include a small subset of those compounds. They are gaseous compounds with vapor pressures that are greater than $10^{-1}$ torr at 25°C and 760 mm Hg. They generally have carbon content in the range of C1 to C12. They are also an important precursor in the formation of ozone and fine particulate matter, as they are highly reactive photochemically. The analytical method used for VOC analysis is TO-15. The concentrations for 78 different compounds are quantified via this analysis, and then summed up to provide a total concentration of speciated compounds (SNMOCs)

### 1.1.2 NMOCs

NMOC's participate in chemical reactions leading to the formation of ozone, which causes health effects. VOCs are a more reactive subset of the NMOCs. Ozone is created by sunlight acting on NOx and NMOC's in ambient air. Ozone leads to alterations in pulmonary function, aggravation of pre-existing respiratory disease, damage to lung structure, and adverse effects on blood enzymes, the central nervous system, and endocrine systems. Ozone also warrants control due to its welfare effects, specifically, reduced plant growth, decreased crop yield, necrosis of plant tissue, and deterioration of certain synthetic materials such as rubber.[1]

[1] "Standards of Performance for New Stationary Sources and Guidelines for Control of Existing Sources: Municipal Solid Waste Landfills." Federal Register 61:49 (Mar. 12, 1996) p. 9917. Available from: GPO Access®; Accessed: 9/15/09.

CDPHE's NMOC analyses are performed by a contract laboratory using the EPA's TO-12 method. The analysis provides a concentration for the total of all NMOCs in the sample, known as TNMOCs. Concentrations are given in ppbC. Using this concentration, and the SNMOC concentrations from above, a measure of the amount of compounds not being quantified by the TO-15 analysis is gained. Any additional compound concentrations not specifically tested for are lumped together in an "unknown" total. The sum of the SNMOCs and unknown concentrations will equal the TNMOC concentration.

### 1.1.3 Methane

Methane is the major component of natural gas. It is a colorless, odorless compound that can displace oxygen in enclosed spaces. It is produced naturally via the decomposition of plant and animal matter. It is used primarily as a fuel, for heat and light. It is a highly flammable compound that can form explosive mixtures with air if allowed to concentrate in a poorly ventilated or enclosed space. It is common in landfills, marshes, septic systems, and sewers.

Methane is a major greenhouse gas because it absorbs heat in the atmosphere, sending some of the absorbed heat back to the earth, and contributing to climate change. Methane emissions represent approximately ten percent of all greenhouse gas emissions in the United States. It is greater than 20 times more powerful than carbon dioxide in absorbing and keeping heat in the atmosphere. Its approximate lifetime in the atmosphere is nine to fifteen years.

The health effects related to methane exposure are primarily related to the displacement of oxygen in the air. Decreased oxygen content can cause suffocation and loss of consciousness. It can also cause headache, dizziness, weakness, nausea, vomiting, and loss of coordination. Skin contact with liquid methane can cause frostbite.[2]

The methane analysis is performed by a contract lab using a modified version of SAE J1151. The SOP for this analysis is available upon request from CDPHE.

### 1.1.4 Carbonyls

Carbonyls are a subset of 10 compounds on the HAPs list. They are compounds containing at least one carbon to oxygen double bond, which makes them very reactive compounds. The most important of these compounds include formaldehyde, acetaldehyde and acetone. CDPHE uses a contract lab to perform the carbonyl analyses using EPA Method TO-11A.

Carbonyl compounds are of great concern because of their adverse health effects. They are among the major species of organic compounds involved in photochemical air pollution. Aldehydes and ketones are a major source of free radicals that play an important role in the photo-oxidation of gas phase hydrocarbons. Motor vehicle exhaust gases are the primary emission source of carbonyl compounds in urban areas. Humans can be exposed to contaminants by inhalation, ingestion, and skin contact. Carbonyl compounds are also ozone precursors, which has detrimental health effects as well.

[2] U.S. National Library of Medicine, Tox Town Page on Methane. Found at: http://toxtown.nlm.nih.gov/text_version/chemicals.php?id=92

Moreover, at high concentrations, most carbonyls cause acute health effects such as skin, eye, nose, or throat irritation in humans.[3]

## 1.2 Method Overview

As discussed above, there are several different methods by which VOCs, NMOCs, methane, and carbonyls are quantified. Table 1 summarizes the sampling and analytical methods for each type of compound.

**Table 1. Summary of Sampling and Analytical Methods**

| Parameter | VOC | NMOC | SNMOC | Methane | Carbonyl |
|---|---|---|---|---|---|
| Sampling apparatus | Stainless steel canisters | Stainless steel canisters | Stainless steel canisters | Stainless steel canisters | Silica gel cartridge coated with DNPH |
| Analytical approach | Capillary gas chromatography with mass selective detection and flame ionization detection | Gas chromatography with cryogenic trap and flame ionization detection | Cryogenic trap at the inlet of a capillary gas chromatography column with flame ionization detection | Gas chromatography with flame ionization detection | High-performance liquid chromatography with ultraviolet detection |
| Output of analysis | Concentrations of 59 different volatile organic compounds, including halogenated hydrocarbons | Concentration of the total amount of non-methane organic compounds in the sample | Concentrations of 80 different organic hydrocarbons | Concentration of methane | Concentrations of 16 different carbonyl compounds |
| Units of measurement | ppbv | ppbC | ppbC or ppbv | ppmC or ppmv | ppbv |
| Detection limit | See Table 3 | 1 ppbC | See Table 4 | 0.033 ppmv | See Table 5 |

### 1.2.1 SNMOC, TNMOC, and Methane

The atmosphere is sampled by introduction of air into a specially-prepared stainless steel 6 liter canister. Both sub-atmospheric pressure and pressurized sampling modes use an initially evacuated canister. A pump ventilated sampling line is used during sample collection with most commercially available samplers. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into the pre-evacuated and passivated canister. After sample collection is complete, the canister is tagged, labeled and transported to the laboratory for analysis.

### 1.2.2 Carbonyls

[3] "Technical Background Document to Support Rulemaking Pursuant to the Clean Air Act--Section 112(g). Ranking of Pollutants with Respect to Hazard to Human Health." EPA-450/3-92-010, PB97-147201, Emissions Standards Division, Office of Air Quality Planning and Standards, Environmental Protection Agency, Research Triangle Park, NC.

A known volume of ambient air is drawn through chromatographic grade Waters Corporation Sep-Pak silica cartridges at a known sampling rate for an appropriate period of time (dependent on carbonyl concentration in the test atmosphere). The cartridges are coated with acidified 2,4-dinitrophenylhydrazine (DNPH). During sampling, carbonyl compounds react irreversibly with the DNPH to form derivatives that are called hydrazones.

When the sampling period is complete, the cartridges are removed from the sampling apparatus, individually capped and placed in shipping tubes with polypropylene caps. Sample identification tags and labels are attached to the capped tubes, which are then placed in cold storage (~4 ˚C or less) for delivery to the laboratory and subsequent analysis.

### 1.3 Format and Purpose

The sequence of topics covered in this air toxics method follows 2007 EPA guidance on preparing standard operating procedures (SOPs). This method was also written to help field operators understand **why** (not just **how**) key procedures are performed. Special attention is paid to interferences, equipment section, and, most importantly, calibration procedures.

Throughout, there are many cross references to other sections in this method, and to the **Quality Assurance Handbook for Air Pollution Measurement Systems, Volumes I and II**, which contain detailed information pertinent to all methods, not just VOCs/TNMOC, methane, and carbonyls. Cross-references to other sections of this method are cited simply by section number. For instance, "See also Section 6" refers to Section 6, Interferences. But "See also Part 10, Section 3" means Part 10, **Operation and Maintenance**, Section 3, Maintenance.

## 2. SUMMARY OF METHODS

### 2.1 SNMOC and TNMOC

#### 2.1.1 Atmospheric Sampling

2.1.1.1 The atmosphere is sampled by introduction of air into a specially-prepared stainless steel 6-liter SUMMA canister. Both sub-atmospheric pressure and pressurized sampling modes use an initially evacuated canister. A pump ventilated sampling line is used during sample collection with most commercially available samplers. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into the pre-evacuated and passivated canister.

2.1.1.2 All sample canisters received by ERG for sampling must have the CoC and must be initially checked for pressure differences to the laboratory using a calibrated gauge. Pressures need to be within ± 0.5 psia of the stated laboratory pressure, accounting for temperature differences (i.e., 10°C difference will result in a 0.5 psia pressure change). If the pressure difference is between 0.5 – 1.5 psia, it will be qualified as LJ (estimated). If it is greater than 1.5 psia, it will be invalidated as AA (sample pressure out of limits). Additionally, if a canister is not accompanied by a CoC, it shall be invalidated as EC.

2.1.1.2 After the air sample is collected, the canister valve is closed, the log book and chain of custody are filled out, and the canister is transported back to the office for shipment to the laboratory and subsequent analyses. Data stored on the ATEC thumb drive is reviewed for flow rate deviations that may indicate a problem with the sampler. Flow rate is critical to ensure a temporally representative sample and must be constant over the 3-hour sampling period. For subambient sampling, it is critical not to exceed the constant flow range, where flow rate decreases by more than 15%. Flow rates for this method of sampling will be set to achieve 90% of the final canister pressure.

### 2.1.2 Laboratory Analysis

All air toxics samples taken by CDPHE are sent to a contracted laboratory for analysis. The lab's SOPs regarding analyses are available on request from CDPHE. Below is a summary of the method for both SNMOCs and TNMOC.

**2.1.2.1** Upon receipt at the laboratory, the canister chain of custody data is recorded and the canister is diluted to a fixed pressure for analysis, and stored until analysis. The samples are analyzed via EPA Compendium Methods TO-15 (SNMOC) and/or TO-12 (TNMOC). The minimum detection limits are variable depending on each type of compound being analyzed. Current MDLs can be found in Table 3.

**2.1.2.2** The TO-12 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 -150°C with liquid argon. With the use of water and $CO_2$ management protocols, the sample is finally cryo-focused before desorption into a gas chromatograph (GC) using a single inlet to which two matched columns are connected. The cryogenic trap simultaneously collects and concentrates the NMOCs (either via condensation or adsorption) while allowing the methane, nitrogen, oxygen, etc. to pass through the trap without retention. A flame ionization detector (FID) is used to determine TNMOC concentrations.

**2.1.2.3** The TO-15 analysis is accomplished with the addition of a mass spectrometer (MS) to the GC system for the determination of SNMOC concentrations. Fused silica capillary columns are used to achieve high temporal resolution of the target compounds. Linear quadrupole or ion trap mass spectrometers are employed for compound detection. The heart of the system is composed of the sample inlet concentration device that is needed to increase sample loading into a detectable range.

**2.1.2.4** Upon separation in the GC, the sample stream is introduced into the FID (TO-12) or the MS (TO-15).

ERG uses the Agilent 6890 GC/FID and an Agilent 5975 MS with SIM using a 60 m x 0.32 mm Inner Diameter and a 1 µm film thickness Restek $R_{xi}$-$l_{ms}$ capillary column followed by a Y-union connector that splits the mobile phase between the MS and the FID. Instrument optimization at ERG is ongoing and the most up-to-date operating conditions is presented in the analytical SOP *for the Concurrent GC/FID/MS Analysis of Canister Air Toxic Samples using EPA Compendium Method T0-15* and *EPA Ozone Precursor Method (ERG-MOR-*

*005)* presented in the ERG NHAPS QAPP, Appendix D. Table 2 shows the operating conditions for the VOC GC/FID/MS analytical system.

**Table 2. VOC GC/FID/MS Operating Conditions**

| Parameter | GC/MS/FID System (Concurrent VOC/SNMOC analysis) |
|---|---|
| Sample Volume | 250 mL |
| Restek $R_{xi}$-$l_{ms}$ Capillary Column:<br>Length:<br>Inside Diameter:<br>Film Thickness:<br>Oven Temperature: | <br>60 m<br>0.32 mm<br>1 µm<br>-50°C for 5 minutes, 15°C/min to 0°C then 5°C/min to 150°C, then 25°C/min to 220°C for 1 minute then 25°C/min to 150°C for 4 minutes |
| Temperatures:<br>FID:<br>Injector Oven Temperature:<br>MS Quad Temperature:<br>MS Source Temperature: | <br>300°C<br>220°C<br>200°C<br>280°C (350°C 5975) |
| Gas Flow Rates:<br>Column Carrier Gas (Helium (He)):<br>FID Make-up (He):<br>FID (Hydrogen (H2)):<br>FID (Air): | <br>2 mL/min<br>30 mL/min<br>30 mL/min<br>300 mL/min |
| Entech Sample Interface Conditions:<br>Module 1 - Glass Bead/Tenax® Trap Initial Temperature:<br>Module 2 - Tenax® Trap Initial Temperature:<br>Module 3 – Cryofocuser Temperature: | <br>-150°C<br>-50°C<br>-196°C |

Figure 1 shows the GC/MS systems and Figure 2 shows the GC/MS/FID arrangement.

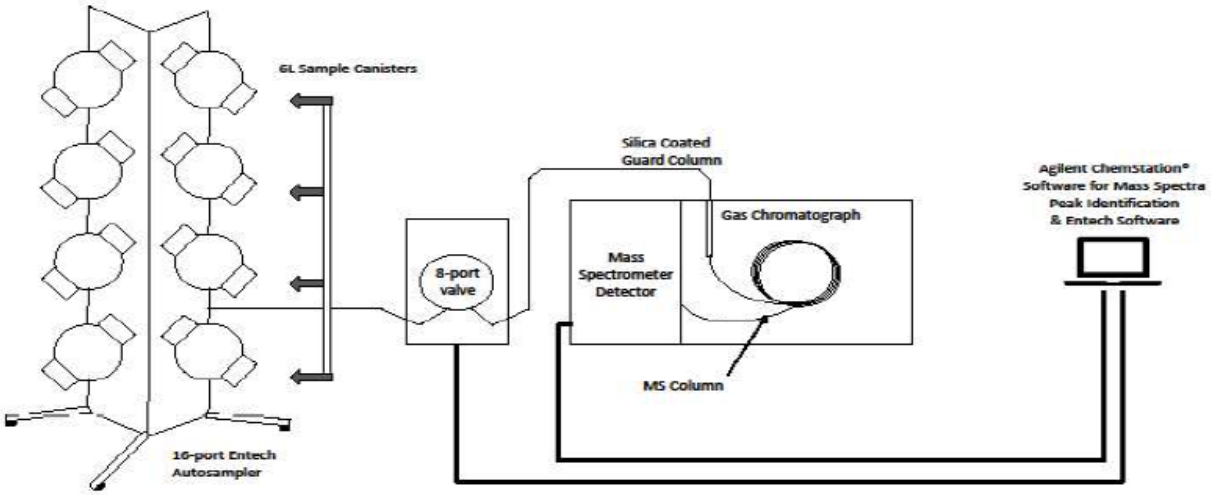



**Figure 1. ERG's VOC GC/MS Systems**

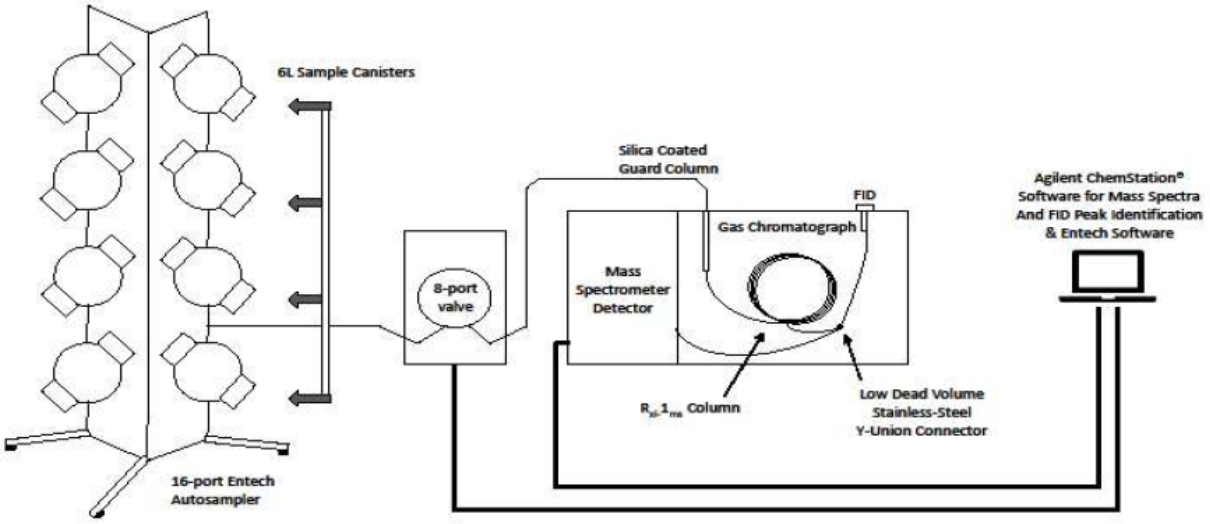



**Figure 2. ERG's VOC GC/MS/FID System**

**2.1.2.5** For FID analysis, the concentrations of the different compounds are calculated by the external standard method of calculation and identification is based on retention time.

**2.1.2.6** For MS analysis, the characteristic retention time and mass spectra identify each compound and its concentration.

**2.1.2.7** By convention, concentrations of SNMOC and TNMOC are reported in units of parts per billion carbon (ppbC). For a specified compound, ppbv is equivalent to the concentration in carbons (ppbC) divided by the number of carbon atoms in the compound. TNMOC concentrations cannot be converted from ppbC to ppbv, as the exact number of carbons in the total is not known. Therefore, the TNMOC, SNMOC and unknown concentrations are reported only as ppbC concentrations to facilitate inter-comparisons. The method detection limit, or MDL for TNMOC is 1 ppbC. Table 3 below lists the current ERG Tier I VOC MDLs and then lists the EPA target MDLs, updated via TAD r.4, to be compliant by August 2023. Table 4 lists the SNMOCs currently detected with method TO-15, their associated MDLs in both ppbC and ppbv, as well as the number of carbon atoms associated with each analyte.

**** As of December 2022, some of ERG's MDLs are higher than the current EPA target MDLs (Ref TAD r.4). ERG will address this discrepancy in their next QAPP and is expected to be compliant by August 2023.**

**Table 3. ERG 2021 VOC MDLs**

| Tier I VOC | MDL (ppbv) | EPA 2022 Target MDLs (TAD r.4) (ppbv) | Is ERG MDL < Target MDL?** |
|---|---|---|---|
| Acrolein | 0.102 | 0.039 | No |
| Carbon Tetrachloride | 0.011 | 0.027 | Yes |
| Chloroform | 0.007 | 0.10 | Yes |
| Ethylene Oxide | 0.026 | 0.030 | Yes |
| Tetrachloroethylene | 0.018 | 0.025 | Yes |
| Trichloroethylene | 0.0146 | 0.037 | Yes |
| Vinyl Chloride | 0.0086 | 0.043 | Yes |

**Table 4. ERG SNMOC 2021 MDLs**

| Target Compound | ppbC | # of Carbon Atoms | ppbv | Target Compound | ppbC | # of Carbon Atoms | ppbv |
|---|---|---|---|---|---|---|---|
| 1,2,3-Trimethylbenzene* | 0.093 | 9 | 0.0103 | 2,2,3-Trimethylpentane | 0.0504 | 8 | 0.0063 |
| 1,2,4-Trimethlybenzene* | 0.364 | 9 | 0.0404 | 2,2,4-Trimethylpentane* | 0.0274 | 8 | 0.0034 |
| 1,3,5-Trimethylbenzene* | 0.070 | 9 | 0.0078 | 2,2-Dimethylbutane* | 0.0237 | 6 | 0.0040 |
| 1-Dodecene | 0.548 | 12 | 0.0457 | 2,3,4-Trimethylpentane* | 0.0489 | 8 | 0.0061 |
| 1-Heptene | 0.030 | 7 | 0.0043 | Cyclohexane* | 0.0268 | 6 | 0.0045 |
| 1-Nonene | 0.074 | 9 | 0.0082 | Ethylbenzene* | 0.080 | 8 | 0.010 |
| 1,3-Butadiene* | 0.1143 | 4 | 0.0286 | Cyclopentane* | 0.0178 | 5 | 0.0036 |
| Isobutene | 0.056 | 4 | 0.014 | m-Diethylbenzene* | 0.121 | 10 | 0.0121 |
| Isopropylbenzene* | 0.049 | 9 | 0.0054 | Methylcyclohexane* | 0.0324 | 7 | 0.0046 |
| m,p-Xylene* | 0.086 | 8 | 0.0108 | m-Ethyltoluene* | 0.066 | 9 | 0.0073 |
| 1-Butene* | 0.035 | 4 | 0.0088 | Cyclopentene | 0.019 | 5 | 0.0038 |
| 1-Hexene* | 0.069 | 6 | 0.0115 | Ethane* | 0.336 | 2 | 0.1680 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1-Pentene* | 0.0559 | 5 | 0.0112 | Ethylene* | 0.17 | 2 | 0.0850 |
| 2,3-Dimethylbutane* | 0.0256 | 6 | 0.0043 | Isobutane* | 0.0615 | 4 | 0.0154 |
| 2,3-Dimethylpentane* | 0.0268 | 7 | 0.0038 | 2-Methylheptane* | 0.048 | 8 | 0.006 |
| 2,4-Dimethylpentane* | 0.0272 | 7 | 0.0039 | Isopentane* | 0.02 | 5 | 0.0040 |
| 2-Methylhexane* | 0.162 | 7 | 0.023 | α-Pinene* | 0.232 | 10 | 0.0232 |
| 2-Ethyl-1-Butene | 0.038 | 6 | 0.0063 | Isoprene* | 0.0188 | 5 | 0.0038 |
| 2-Methyl-1-Butene | 0.0222 | 5 | 0.0044 | Methylcyclopentane* | 0.085 | 6 | 0.0142 |
| 2-Methyl-1-Pentene | 0.0309 | 6 | 0.0052 | n-Butane* | 0.088 | 4 | 0.0220 |
| n-Decane* | 0.076 | 10 | 0.0076 | n-Dodecane* | 0.300 | 12 | 0.025 |
| 2-Methyl-2-Butene | 0.046 | 5 | 0.0092 | n-Hexane* | 0.1 | 6 | 0.0167 |
| n-Heptane* | 0.0520 | 7 | 0.0074 | n-Octane* | 0.064 | 8 | 0.008 |
| n-Nonane* | 0.055 | 9 | 0.0061 | n-Propylbenzene* | 0.049 | 9 | 0.0054 |
| n-Undecane* | 0.187 | 11 | 0.017 | o-Ehyltoluene* | 0.091 | 9 | 0.010 |
| o-Xylene* | 0.098 | 8 | 0.0122 | p-Diethylbenzene* | 0.109 | 10 | 0.0109 |
| p-Ethyltoluene* | 0.047 | 9 | 0.0052 | Styrene* | 0.428 | 8 | 0.0535 |
| Toluene* | 0.159 | 7 | 0.0227 | n-Pentane* | 0.025 | 5 | 0.0050 |
| 2-Methylpentane* | 0.445 | 6 | 0.0742 | Propane* | 0.087 | 3 | 0.0290 |
| 3-Methyl-1-Butene | 0.0393 | 5 | 0.0079 | Propylene* | 0.151 | 3 | 0.0503 |
| 3-Methylpentane* | 0.064 | 6 | 0.0107 | Propyne | 0.024 | 3 | 0.0080 |
| 4-Methyl-1-Pentene | 0.0329 | 6 | 0.0055 | *trans*-2-Butene* | 0.0179 | 4 | 0.0045 |
| Acetylene* | 0.0218 | 2 | 0.0109 | 3-Methylpentane* | 0.064 | 6 | 0.0107 |
| 3-Methylheptane* | 0.038 | 8 | 0.0048 | *trans*-2-Hexene | 0.039 | 6 | 0.0065 |
| Benzene* | 0.043 | 6 | 0.0072 | *trans*-2-Pentene* | 0.0251 | 5 | 0.0050 |
| *cis*-2-Butene* | 0.0269 | 4 | 0.0067 | 1-Tridecene | 0.308 | 13 | 0.0237 |
| *cis*-2-Hexene | 0.026 | 6 | 0.0043 | n-Tridecane | 0.353 | 13 | 0.0272 |
| *cis*-2-Pentene* | 0.0344 | 5 | 0.0069 | β-Pinene* | 0.723 | 10 | 0.0723 |

* PAMS compounds

## 2.2 Methane

### 2.2.1 Atmospheric Sampling

**2.2.1.1** The atmosphere is sampled by introduction of air into a specially-prepared stainless steel 6-liter SUMMA canister. Both sub-atmospheric pressure and pressurized sampling modes use an initially evacuated canister. A pump ventilated sampling line is used during sample collection with most commercially available samplers. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into the pre-evacuated and passivated canister.

**2.2.1.2** After the air sample is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to the laboratory for analysis. Figure 3 below shows that identification tag.

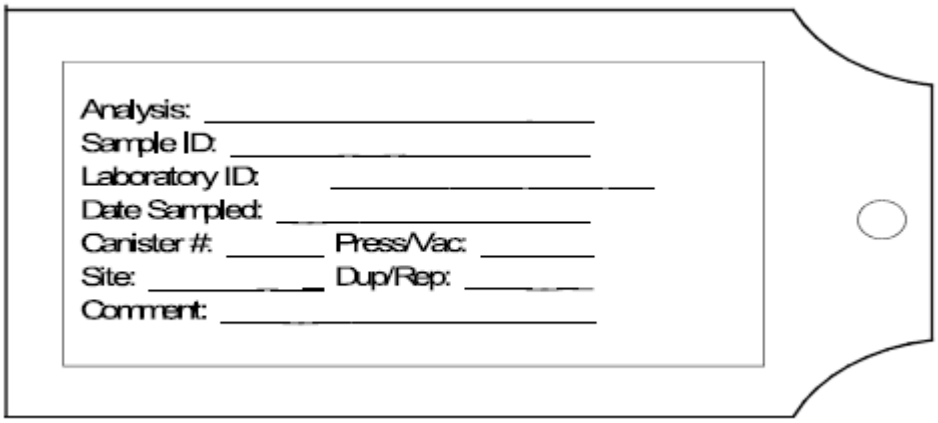
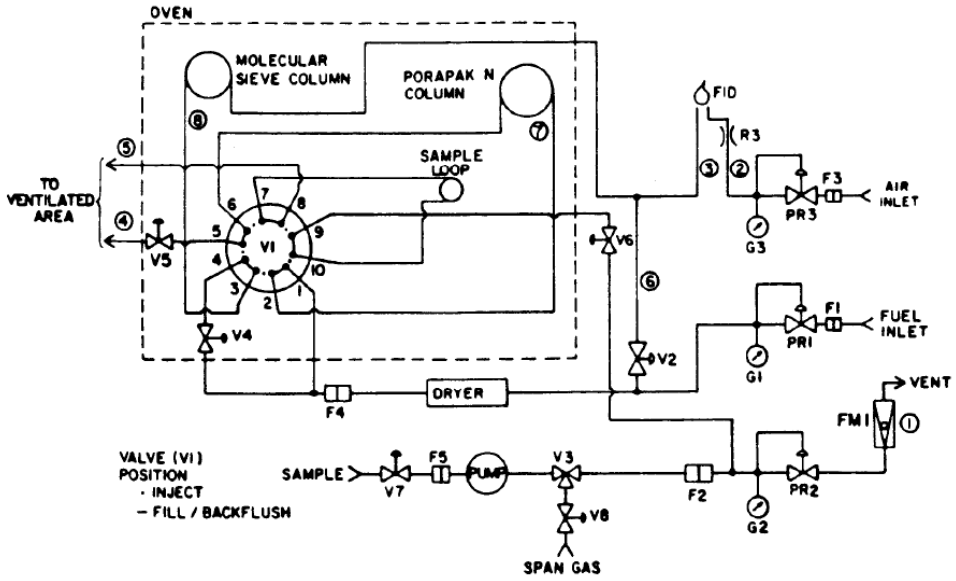



**Figure 3. Canister Tag**

### 2.2.2 Laboratory Analysis

All air toxics samples taken by CDPHE are sent to a contracted laboratory for analysis. The lab's SOPs regarding analyses are available on request from ERG. During analysis, the instrument measures the methane concentration in a sample swept from a fixed volume sample loop by a carrier gas stream when the valve (V1) is in the inject position. The carrier gas can be blended FID fuel. The stream enters the Porpak N gas chromatograph column which temporarily retains NMHC, $CO_2$, and water, and passes air, methane, and CO to the Molecular Sieve column. As soon as all of the methane elutes from the Porapak N column and has passed through valve V1 toward the Molecular Sieve column, the Porapak N column is backflushed to waste by switching the valve (V1) to the fill / backflush position. Switching V1 also starts filling the sample loop with the next sample. As soon as the methane peak passes through the FID, valve V1 can be switched back to the inject position to inject the next sample. A complete cycle, from injection of one sample to injection of a second, can be made in 30 s. Automation of injection and backflush switching assures reproducible peak times and shapes and is easily accomplished. Below is a summary of the method for methane. Figure 4 shows the instrument configuration used to analyze methane.




Where:

Valve, V1 – Sample injection and switching valve, should be low dead volume, gas tight, and heatable to at least 150°C.
Valve, V2 – Used to provide supplementary fuel to the FID burner.
Valve, V3 – Used to select span gas, sample, or no flow.
Valve, V4 – Used as a restrictor to match the flow resistance of the Porapak N column.

Valve, V5 – Used as a restrictor to match the flow resistance of the Molecular Sieve column. This valve allows equalizing backflush and foreflush flow rates through the Porapak column.
Valve, V6 – Used as a restrictor for controlling the rate of sample flow to fill the sample loop.
Pressure Regulator, PR1, and Pressure Gauge, G1 – To control flow rate of the fuel which is also the carrier gas.
Pressure Regulator, PR2, and Pressure Gauge, G2 – Back-pressure regulator for controlling the rate of sample flow to the sample loop in conjunction with valve V6. Should be adjusted in the pressure range of 7 to 34 kPa (1 to 5 psig).
GC Column – Porapak N, 180/300 µm (equivalent to 50/80 mesh), 610 mm (2 ft) length x 2.16 mm (0.085 in) ID x 3.18 mm (1/8 in) OD SS, to separate air, $CH_4$, and CO from the other sample constituents. The column is conditioned 12 h or more at 150°C with carrier gas flow prior to initial use. Valve V1 should be in the fill / backflush position during the conditioning.
GC Column – Molecular Sieve Type 13X, 250 / 350 µm (equivalent to 45/60 mesh), 1220 mm (4 ft) length x 2.16 mm (0.085 in) ID, 3.18 mm (1/8 in) OD SS, to separate methane from oxygen, nitrogen, and CO. The column is conditioned 12 h or more at 150°C with carrier gas flow prior to initial use. Valve V1 should be in the fill / backflush position during the conditioning.
Sample Loop – A sufficient length of SS tubing to obtain approximately 1 $cm^3$ volume.
Oven – To maintain columns and valves at a stable temperature for analyzer operation, and to condition columns at 150°C.
Valve Actuator – To actuate sample injection and switching valve.

Valve Programmer – Timing unit to control valve actuator.
Dryer – To remove water and other contaminants which might be present in the carrier gas, a filter dryer containing Molecular Sieve is used. If it is a visual-indicating type, the dryer is replaced when the need is indicated. Otherwise, it is replaced or reconditioned monthly. If the dryer has a metal body, it can be reconditioned after removing it from the instrument by flowing approximately 50 $cm^3$/min of dry nitrogen through the dryer while it is heated to 150°C in an oven for 12 h.
Restrictor, R3 – For controlling the rate of air flow to FID.
Pressure Regulator, PR3 – Used with pressure gauge, G3, and restrictor, R3, to control air flow to FID.
Filters, F1, F3, F4 – Sintered metal filters to prevent grift from entering the instrument.
Filters F2, F5 – Sintered metal filters in the sample stream to prevent grift from entering the pump or instrument. Should be of sufficiently large area to have a pressure drop of less than 15 kPa (2 psi) at the bypass flow rate used of approximately 2000 $cm^3$/min (4 scfh).
Pump – Used to bring sample to gas chromatograph.
Valve, V7 – Used with flowmeter, FM1, to regulate bypass sample flow rate. The bypass sample flow rate should be fast enough to flush out the entire sample line in a time less than the GC analysis time so that while an analysis is being made, the sample loop is filled with the next sample and is ready for the next analysis cycle. A typical bypass flow rate would be 2000 $cm^3$/min (4 scfh).
Valve, V8 – Used with flowmeter, FM1, to equalize bypass flow rates of span gas and sample.
Recorder – The recorder or other readout device should have an input compatible with the FID analyzer output, an accuracy (including the effects of deadband and linearity) of ± 0.25% of full scale or better, a span step response time of 0.4 s or less, and a chart speed of approximately 25 mm/min (1 in/min).
FID – The flame ionization detector generates an electrical current proportional to the flow rate of methane throughout the burner. The associated electrometer amplifier acts as a current to voltage converter and should have an electronic time constant of less than 0.20 s.

**Figure 4. Instrument Configuration for Methane**

**2.2.2.1** Measure and record the pressure of each sample canister immediately prior to analysis, and bleed to ambient air if canister is pressurized. The pressure will be used to correct the concentration of the sample using equations.

**2.2.2.2** Connect the sample canister to the interface sample arm.

**2.2.2.3** Follow the general sample analysis procedure outline below:

**2.2.2.3.1** On the Peak Simple software, verify that the current methane calibration has been loaded. Update sample headers and post-run conditions before analysis.

**2.2.2.3.2** Prior to opening the canister valve, open and then close the **Evacuate and Load** toggle valves to evacuate the sample lines and ensure that the sample injection valve is in the “Load” position.

**2.2.2.3.3** Open the sample valve and open the **Load** toggle valve to pull sample from the canister and through the sample loop until the vacuum decreases by 2 “Hg.

**2.2.2.3.4** Quickly move the sample injection valve from the "Load" to the "Inject" position while simultaneously pressing the space bar on the computer to start the data collection.

**2.2.2.3.5** Only after the methane peak has appeared in the trace, move the injection valve back to the "Load" position to prevent a double injection.

**2.2.2.4** Follow the procedure below for daily analysis.

**2.2.2.4.1** Perform a CCV daily before the analysis of samples to ensure that the response factor generated in the initial calibration is still valid. A 2 ppmC sample is normally used, but concentrations between 2 and 5 ppmC are acceptable. The result for the run can be checked by right-clicking the chromatogram either during the run or after having loaded the completed file and choosing "Results." The percent recovery must be 70 – 130% for the initial curve response factor to be valid.

**2.2.2.4.2** Additional continuing calibration verification samples must be analyzed following every ten injections of field samples, and at the end of the sequence. Results must meet the same criterion of being within 30% of the target value.

**2.2.2.4.3** Analyze a zero air canister containing purified, humidified air to verify that the analytical system is clean. A result less than the MDL must be obtained before the initiation of any field sample analysis.

**2.2.2.4.4** In LIMS, prepare the batch and sequence of samples to be analyzed. A replicate analysis should be run with each sequence and every pair of duplicate sample will be run in replicate.

**2.2.2.4.5** In the data analysis software, quantify each sample against the appropriate curve, verify that the peaks are identified and integrated correctly. Manual integration of a chromatographic peak or peak deletion is performed only to correct an obvious software integration error. All manual integration and peak deletion must follow procedures set forth by ERG-MOR-097.

**2.2.2.4.6** Retention time: the retention time for methane must be within 5% of the average retention time of the initial calibration standards.

**2.2.2.4.7** Use the pressure of the sample to correct the concentration measured using equations.

**2.2.2.4.8** At the conclusion of an analysis sequence, after the final CCV has been analyzed, close the hydrogen FID fuel gas cylinder and load the "Sleep" control file on the Peak Simple software.

**2.2.2.4.6** The current MDL for methane is **0.033 ppmv**.

## 2.3 Carbonyls

### 2.3.1 Atmospheric Sampling

**2.3.1.1** A known volume of ambient air is drawn through chromatographic grade Waters Corporation Sep-Pak silica cartridges at a sampling rate of 750 mL/min for three hours. The cartridges are coated with acidified 2,4-dinitrophenylhydrazine (DNPH). During sampling, carbonyl compounds react reversibly with the DNPH to form derivatives that are called hydrazones.

**2.3.1.2** When the sampling period is complete, the cartridges are removed from the sampling apparatus, individually capped and placed in shipping bags with polypropylene caps. Sample identification tags and labels are attached to the capped tubes, which are then placed in cold storage (~4˚C or less) for delivery to the laboratory.

### 2.3.2 Laboratory Analysis

**2.3.2.1** Upon receipt at the laboratory, the sampling data is recorded and the cartridge is placed in cold storage (4°C or less) until such time as it can be eluted and analyzed. The samples are extracted into a 5 mL Class A volumetric flask in which 5 mL of carbonyl-free acetonitrile is filtered through the cartridge via vacuum filtration.

**2.3.2.2** The extract is then transferred to a 2 mL autosampler vial fitted with a Teflon-lined, self-sealing septum and a 4 mL vial with a Teflon-lined cap. Both vials are stored in a dedicated refrigerator at 4°C or below until analysis.

**2.3.2.3** Fifteen microliters of the extract are analyzed by HPLC with Ultraviolet (UV) detection. Identification is based on matching the retention times of the peaks in the samples to those in the standards. Quantification is based on a multi-point curve generated from the peak area responses of the same standards.

ERG uses a Waters HPLC configured with a reverse-phase 250 mm x 4.6 mm C-18 silica analytical column with a 5-micron particle size. A mobile phase gradient of HPLC water, acetonitrile, and methanol is used to perform the analytical separation at a flow of 1.0 mL/minute. The multiwavelength UV detector operates at 360 nanometers (nm). Figure 5 below shows ERG's HPLC system setup.

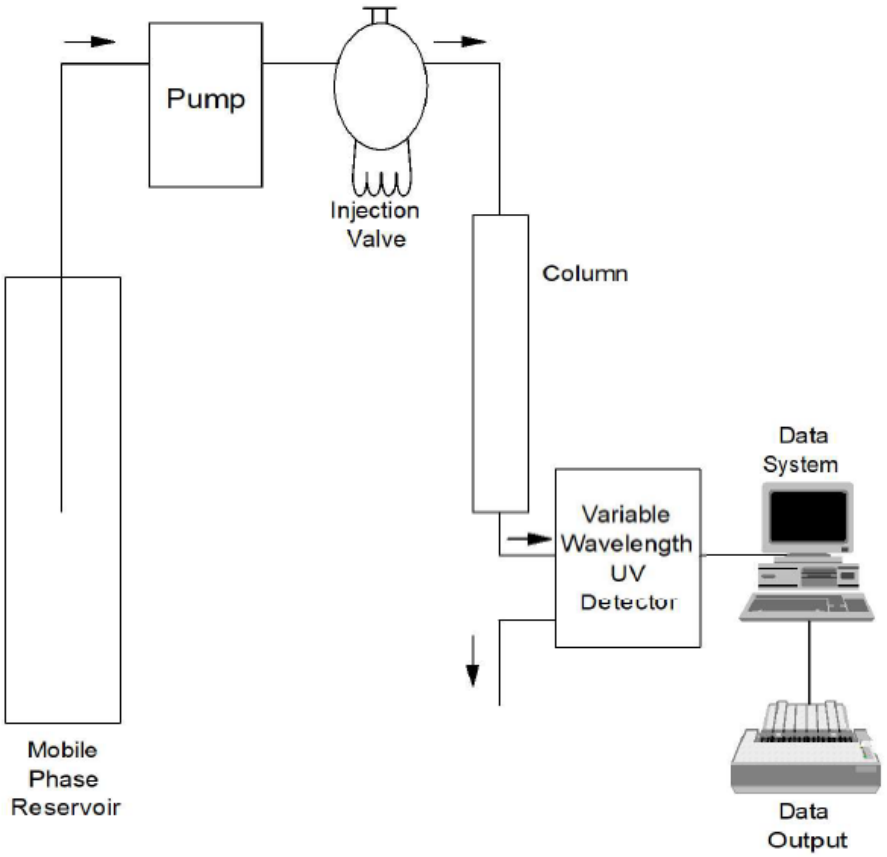



**Figure 5. ERG's HPLC System**

**2.3.2.4** Prepare a calibration curve with at least five levels with concentrations that span the range of interest by making dilutions of the working standard. Each calibration level is analyzed in triplicate.

**2.3.2.5** Prepare the HPLC, and follow the analysis sequence: system blank, continuing calibration verification, method blank, second source, laboratory control spike, matrix spike and matrix spike duplicate, sample, and sample duplicate. The sample and sample duplicate must go through the same stages of sample preparation and measurements.

**2.3.2.6** By convention, concentrations of carbonyls are reported in units of parts per billion volume (ppbv). Table 5 lists the compounds detected by Compendium Method TO-11A, and their associated method detection limits. The complete *SOP for Preparing, Extracting, and Analyzing DNPH Carbonyl Cartridges by Method T0-11A* (ERG-MOR-024) is presented in ERG's NHAPS QAPP, Appendix D. Sample and waste disposal procedures are outlined in ERG-MOR-033, the *SOP for Hazardous Waste.*

**Table 5. ERG Carbonyl Compound MDLs Detected by Compendium Method TO-11A (Underiviatized Concentration)**

| Compound | MDL (µg/m$^3$) |
|---|---|
| 2-Butanone (Methyl Ethyl Ketone) | 0.162 |
| Acetaldehyde* | 0.0401 |
| Acetone | 0.376 |
| Benzaldehyde | 0.0466 |
| Butyraldehyde | 0.0529 |
| Crotonaldehyde | 0.011 |
| Formaldehyde* | 0.0511 |
| Hexaldehyde | 0.0176 |
| Propionaldehyde | 0.086 |
| Valeraldehyde | 0.00749 |

NOTE: Assumes 1000 L sample volume.
*NATTS Tier I compounds

## 3. DEFINITIONS

The CDPHE/APCD/TSP QAPP contains an appendix of acronyms and definitions. Any commonly used shorthand designations for items such as the sponsoring organization, monitoring site, and the geographical area will be included in this document or in the QAPP.

## 4. HEALTH AND SAFETY WARNINGS

To prevent explosive hazard, do ***NOT*** pump combustible liquids or vapors with the Model 2200-2. In addition, the motor may be thermally protected and can automatically restart when there is an overload reset. Always disconnect the power source before servicing. Personal injury and/or property damage could result from improper use of the instrument.

## 5. CAUTIONS

When the cartridges are being handled, it is important to wear powder free gloves to prevent any sample contamination, as well as for the safety of the operator. The DNPH that coats the cartridges can react with various oils found in the skin to affect the results of the sampling. In addition, DNPH is a hazardous chemical that is toxic to the lungs, nervous system, and mucous membranes. It is also flammable.

For the canisters, it is important to ensure that the canisters remain closed and tightly sealed during transport and storage between the monitoring site and the laboratory so that there is no leakage of air into or out of the canister.

## 6. INTERFERENCES

### 6.1 NMOCs

In field and laboratory evaluations, water was found to cause a positive shift in the analytical detector (flame ionization detector) baseline. The effect can be minimized during analysis by carefully selecting the integration termination point and the adjusted baseline used for calculating the peak areas.

### 6.2 Methane

Analysis of methane by GC-FID usually has few, if any interferents. The low boiling point and non-polarity of the methane molecule provide very low retention on the GC stationary phase, resulting in full chromatographic separation from other compounds that respond to an FID. The methane peak elutes early, soon after a dip in the baseline from carbon dioxide, so any samples containing high levels of carbon dioxide (>0.04%) may affect the chromatographic results for methane. A humidified blank air sample must be analyzed prior to the analysis of field samples to ensure no contamination exists in the instrument.

### 6.3 Carbonyls

Ozone can cause significant negative interference at concentrations typical of clean ambient air. To prevent this, an ozone scrubber is placed in the sample stream line before the DNPH cartridge to effectively remove any ozone from the sample.

## 7. PERSONNEL QUALIFICATIONS

General Personnel Qualifications are discussed in the CDPHE/APCD/TSP QAPP.

## 8. APPARATUS AND MATERIALS

### 8.1 NMOCs/Methane

The NMOC and methane samples are collected in six-liter stainless steel SUMMA® canisters. The samples are collected using a Model 2200-2 Toxic Air Sampler manufactured by Atmospheric Technology (ATEC) of Malibu, California, which has the capability of simultaneously collecting air samples into canisters (for TNMOC and methane) and sorbent cartridges (for carbonyls). The sampler records start and stop times, initial and final canister pressure, and flow rate data, which are downloaded after each run.

### 8.2 Carbonyls

Carbonyl (e.g., formaldehyde, acetaldehyde) samples are collected on a Waters Corporation Sep-Pak cartridge coated with 2,4-dinitrophenylhydrazine (DNPH). The samples are collected using a Model 2200-2 Toxic Air Sampler manufactured by Atmospheric Technology (ATEC) of Malibu, California, which has the capability of simultaneously collecting air samples into canisters (for VOCs and TNMOC) and sorbent cartridges (for carbonyls). The sampler records start and stop times, cartridge flow rate and sample volume, which are downloaded after each run.

# 9. CALIBRATION[4]

There is one type of instrument being used in the air toxics monitoring network for NMOC detection in Colorado, the ATEC Model 2200-2. The instrument is a microcomputer controlled sampler that can be programmed to draw ambient air into cartridges and canisters for subsequent analysis of carbonyls, TNMOC, and methane according to the processes outlined in EPA methods TO-11A, TO-14A, and Method 18, respectively. The sampler has been specifically designed to simultaneously collect both cartridge and canister samples using one instrument. The Model 2200-2 uses independent mass flow controllers in each channel to accurately monitor and control the flow rate to the canisters and cartridges. Figure 10 and Schematic 3 at the end of this document show the internal components and flow diagram for the Model 2200-2.

Each mass flow controller in the Model 2200-2 should be calibrated on a 4 month schedule. There are 4 separate mass flow controllers, and a hybrid manual / electronic calibration process is used. Manual calibration consists of adjusting the zero (no flow) potentiometers on the mass flow controllers. The potentiometers can be accessed on the side of the flow controller housing. Electronic calibration is performed by inserting the appropriate calibration constants into the advanced portion of the Set-Up Screen. Note that the mass flow controller calibrations are based on standard conditions of 25 °C and 1 atm pressure.

## 9.1 NMOCs/Methane

This procedure covers the calibration of an ATEC Model 2200-2 sampling instrument.

If frequent pressure tolerance errors occur, either the pressure tolerance value entered in the set-up screen is set too low, or the mass flow controller needs to be re-calibrated. The calibration procedure is as follows:

1. Remove the top cover of the sampler.
2. Disconnect the 1/8” stainless steel tubing at the inlet to the mass flow controller.
3. Connect the NIST traceable flow measurement device to the inlet of the mass flow controller. The flow is measured using the standard atmospheric condition settings on the flow measurement device, giving the flows at standard temperature and pressure. IMPORTANT: Use a standard that will not contaminate the sampler components.
4. Connect an evacuated canister to the canister fitting associated with the MFC being calibrated on the rear of the sampler.
5. Perform a leak check on the canister by following the procedure on the “Leak Check” tab for the appropriate MFC. Once complete, record the value on the calibration sheet (Figure 11).
6. Go to the “Advanced” tab and record the slope and intercept values for each MFC being calibrated in the appropriate area of the calibration sheet.

[4] Information contained in this section is taken directly from the ATEC Model 2200-2’s instrument manual.
Atmospheric Technology (ATEC). 2007. “Model 2200 Toxic Air Sampler Operations and Maintenance Manual.” Version 1.40. Malibu, CA. June.

7. Change the slope values for each canister MFC to 1.0, and leave the values for the intercept as is. These values are always left at -1.5% of the full scale of the MFC. So, if it is a 2 LPM MFC, the intercept will be -0.030.
8. Exit the "Advanced" tab and enter the "Manual" tab. Touch the check box next to the phrase "Show calibrated values."
9. For each MFC to be calibrated, use a small screwdriver and adjust the zero potentiometer to obtain a value as close to zero as possible in the appropriate MFC flow box. If the values are greater than ± 0.05, then a physical adjustment of the MFC is required.
10. Open the valve on the canister and activate the internal canister valve by checking Can1 or Can2 on the Manual Screen.
11. Click in the Flow Set box on the far right for the appropriate canister channel, and change the flow to 5.0, then click Accept, then click Set.
12. Allow the flow to stabilize and record the flow rate shown in Flow1 or Flow2 on the calibration sheet on the line labeled "ATEC =" Also record the flow rate indicated by the mass flow meter on the line "300VUE =".
13. Calculate the MFC slope constant by dividing the value from the 300VUE line by the value from the ATEC line and record it on the calibration sheet on the "Calculated Slope (M)" line.
14. Repeat steps 11 – 13 for each of the five set points (5.0, 15.0, 25.0, 35.0, and 45.0 scc/min).
15. Average all of the slopes obtained.
16. Uncheck the box next to the MFC being calibrated to stop the flow, and then exit the Manual tab.
17. Enter the "Advanced" tab again.
18. Input the slope value calculated in step 15 into the appropriate MFC slope box, then hit the exit button to leave the tab.
19. Return to the Manual tab and activate the MFC just calibrated. Set the flow to 25.0 scc/min, and after the flow is steady, compare the values from the ATEC screen and the 300VUE. If they are within 5% of each other the calibration is valid.
20. Uncheck the box next to the MFC, and close the valve on the canister.
21. Remove the canister from the channel 1 line and place it on the channel 2 line.
22. Remove the flow standard from the channel 1 MFC inlet, and connect it to the channel 2 MFC inlet.
23. Follow steps 4 through 20 of this procedure for the 2$^{nd}$ MFC.
24. When the 2$^{nd}$ can channel calibration is complete remove the can from the channel 2 line, and the 300VUE from the inlet to the channel 2 MFC.
25. Reconnect the inlet tubing to the canister MFCs.
26. The pressure transducers should be electronically calibrated on an annual schedule. Follow the procedure in Figure 13 to calibrate the pressure transducers.
27. Replace the cover of the 2200-2 and secure with screws.

## 9.2 Carbonyls

If frequent flow tolerance errors occur, the mass flow controller needs to be re-calibrated. The calibration procedure is as follows:

1. Complete a leak check of the cartridge channel via the Leak Check tab. The result is recorded on the form.
2. Remove the Luer connector or cartridge on the channel to be calibrated.
3. Connect a calibrated flow standard on the Luer fitting on the outlet tubing on the front panel of the sampler.
4. Go to the "Advanced" tab and record the slope and intercept values for each MFC being calibrated in the appropriate area of the calibration sheet (Figure 12).
5. Change the slope values for each cartridge MFC to 1.0, and leave the values for the intercept as is. These values are always left at -1.5% of the full scale of the MFC. So, if it is a 2 LPM MFC, the intercept will be -0.030.
6. Exit the "Advanced" tab and enter the "Manual" tab. Touch the check box next to the phrase "Show calibrated values."
7. For each MFC to be calibrated, use a small screwdriver and adjust the zero potentiometer to obtain a value as close to zero as possible in the appropriate MFC flow box. If the values are greater than 0.007, then a physical adjustment of the MFC is required.
8. Set the cartridge flow rate to 0.2 SLPM in the Flow Set box on the far right for the appropriate cartridge channel.
9. Activate the internal cartridge valve by checking Cart1 or Cart2 on the Manual tab.
10. Activate the internal pump by checking the box next to it.
11. Allow the flow to stabilize and record the flow rate shown in Flow1 or Flow2 on the calibration sheet on the line labeled" ATEC =" Also record the flow rate indicated by the mass flow meter on the line "300VUE =."
12. Calculate the MFC slope constant by dividing the value from the 300VUE line by the value from the ATEC line and record it on the calibration sheet on the "Calculated Slope (M)" line.
13. Repeat steps 8 – 11 for each of the five set points (0.2, 0.5, 1.0, 1.5 and 1.8 SLPM).
14. Average all slopes obtained.
15. Uncheck the box next to the MFC being calibrated to stop the flow, and then exit the Manual tab.
16. Enter the "Advanced" tab again.
17. Input the slope value calculated in step 14 into the appropriate MFC slope box, then hit the exit button to leave the tab.
18. Return to the Manual tab and activate the pump and MFC just calibrated. Set the flow to 0.75 SLPM , and after the flow is steady, compare the values from the ATEC screen and the 300VUE. If they are within 5% of each other, the calibration is valid.
19. Uncheck the box next to the MFC and the pump.
20. Remove the flow standard from the cartridge channel 1 MFC outlet, and connect it to the cartridge channel 2 MFC outlet. Reconnect the channel 1 tubing lines.
21. Follow steps 1 through 19 of this procedure for the 2$^{nd}$ MFC.
22. When the 2$^{nd}$ cartridge channel calibration is complete remove the 300VUE from the outlet to the channel 2 MFC, and reconnect the sampling lines.

# 10. OPERATION AND MAINTENANCE[5]

The ATEC Model 2200-2 uses a ¼ VGA LCD color touch screen display to show current operating status and to enter information into the computer. The computer is accessed using tabs and buttons which are displayed on the screen and can be activated by finger touch or stylus. The touch level of the screen can be calibrated by selecting the touch screen button under the Set-Up tab, and following the directions on the screen. For detailed sample setup and removal procedures, see the SOP titled *"Standard Operating Procedure for the Set-Up, Sampling, and Collection of Ambient Air Toxics and Carbonyl Compound Samples Using the ATEC 2200-2 Sampling System – NFROPS."*

The Model 2200-2 uses nine tab functions to allow the operator to enter or retrieve information from the sampler: **Main, Time/Date, Setup, Schedules, Data, Leak Check, SOP, Manual,** and **Advanced**. **Setup** is used to configure the sampler and store sampling parameters. Sampling schedules are entered through the **Schedules** tab. Data can be displayed, sent to an optional label printer or downloaded to a jump drive using the **Data** tab. Canisters and cartridges are manually leak checked with the **Leak Check** option. The **SOP** tab uses a standard operating procedure to install and leak check canisters and cartridges and program sampling schedules. The **Manual** tab allows operational check-out of the sampler hardware and the **Advanced** tab allows configuration of critical hardware parameters.

## 10.1 NMOCs/Methane Operations

The procedures for sample set up and retrieval for Methane and TNMOC are the same.

### 10.1.1 Sample Set-up

1. Connect the new sampling canister to the Canister Ch. 1 inlet located above the top of the Model 2200-2 via the 9/16" stainless steel fittings on the instrument. Make sure to properly tighten the appropriate fittings between the canister and the sampler.
   **Note: If duplicate samples are to be run, one canister should be connected to each of the Canister Ch. 1 and Ch. 2 inlets on the instrument.
2. Once the canister(s) has been installed, the ATEC can be set up for sampling by pressing the **SOP** tab on the Model 2200-2's touch screen.
3. On the initial screen, select the appropriate canister channels for sampling, then push the Next button.
4. Follow the on-screen instructions for the leak check procedure:
   a. Open and close the canister valve.
   b. Push the Next button and the instrument will begin performing leak checks for the canister(s) and cartridge(s). Each canister and cartridge must pass the leak check procedure or the program will not continue. A failing leak check will be ≥ 0.1 scc/min.
5. Once all leak checks have been performed and passed, the scheduling screen comes up. Enter the sampling start date and start time, as well as the duration of the sampling. CDPHE

[5] Information contained in this section is taken directly from the ATEC Model 2200-2's instrument manual.
Atmospheric Technology (ATEC). 2007. "Model 2200 Toxic Air Sampler Operations and Maintenance Manual." Version 1.40. Malibu, CA. June.

typically follows a 3 hour long, 1 in 6 day sampling schedule. This 1 in 6 day schedule can, and has been adjusted at various times to perform special studies at the sites. In general, samples will be run from 06:00 to 09:00 MST.

6. Once all sampling information is entered, press the Next button. This will take the operator back to the main screen of the instrument. The instrument is now set up for sampling. The status window(s) on the main screen should say "WAITING" next to the channel(s) that have a sample ready.
7. Power cycle the instrument by using the toggle switch on the back of the analyzer to turn the unit off and then back on again. This resets any possible software issues that may prevent the unit from operating properly.
8. Fill out the appropriate Chain-of-Custody paperwork, and note the sample setup in the site logbook.

#### 10.1.2 Sample Retrieval

**NOTE: When recording sampling data in the log book and downloading run data from the instrument, make sure to do so for both the canister and cartridge channels at the same time, and ***before*** setting up for the next round of sampling. Failure to do so will result in all the sampling data from the previous session to be erased.

1. Upon arrival at the site, enter the information from the main screen into the log book for the instrument. A snap shot of the **Main** screen can be found in Figure 14. Record the date, maximum, minimum and average flow rates and pressures for each canister and cartridge channel used in the previous sampling period.
2. To view the data from the sample run, press the **Data** tab. The tab brings up the data for canister channel one first. Place the thumb drive in one of the USB ports on the front of the instrument, and press the **Download** button in the lower right corner of the screen. This will download the run data to the drive. When complete, the drive can be removed. Record the information for canister / cartridge sample date, can starting and ending pressures, total cartridge volume, the average flow rates on each channel, and any errors that occurred during sampling in the log book. Scroll through each canister and cartridge channel sampled by hitting the NEXT or PREVIOUS buttons at the bottom of the touchscreen.
3. Once all the data is recorded in the log book, remove the sampling media from the analyzer. Close the valve on the canister, and remove it from the rear of the instrument using the 9/16" wrench. Re-plug the canister line, and replace the cap on the top of the canister valve.
4. Fill out the Chain-of-Custody data sheets with the information recorded in the log book. See an example data sheet in Figure 15.
5. Place the canister in the appropriate shipping container, along with the associated data sheet, and take it back to the office to be shipped FedEx 2Day.

### 10.2 Carbonyl Operations

#### 10.2.1 Sample Set-up

1. Put on Nitrile Gloves. Remove the cartridge from the foil pouch and connect it to the Cartridge Ch. 1 inlet on the front of the Model 2200-2 via the Luer fittings on the instrument.

Make sure the cartridge fits snugly in the fittings. Figure 6 below shows the inlet / outlet configuration of the cartridge.

**Note: If duplicate samples are to be run, both Cartridge Channel 1 and Channel 2 will have cartridges installed in them.


**Figure 6. Carbonyl Sampling Cartridge**

2. Once the canister(s) and carbonyl cartridge(s) have been installed, the ATEC can be set up for sampling by pressing the **SOP** tab on the Model 2200-2's touch screen.
3. On the initial screen select Canister Channel 1and Cartridge Channel 1 for sampling, then push the Next button. If duplicate cartridge samples are being run, make sure to select Cartridge Channel 2 as well.
4. Follow the on-screen instructions for the leak check procedure. Each canister and cartridge must pass the leak check procedure or the program will not continue. A failing leak check rate for cartridges is ≥ 0.1 LPM.
5. Once all leak checks have been performed and passed, the scheduling screen comes up. Enter the sampling start date and start time, as well as the duration of the sampling. CDPHE follows a 3 hour long, 1 in 6 day sampling schedule. This means that a sample is taken from 06:00 to 09:00 every sixth day.
6. Once all sampling information is entered, press the Next button. This will take the operator back to the main screen of the instrument. The instrument is now set up for sampling.

### 10.2.2 Sample Retrieval

**NOTE: When recording sampling data in the log book and downloading the run data, make sure to do so for both the canister and cartridge channels at the same time, and ***before*** setting up for the next round of sampling. Failure to do so will result in all the sampling data from the previous session to be erased.

1. Upon arrival at the site, enter the information from the main screen into the log book for the instrument. A snap shot of the **Main** screen can be found in Figure 14. Record the date, time,

flow rate and pressure for each canister and cartridge channel used in the previous sampling period.

2. Press the **Data** tab, and record the information for cartridge start date and time, flow rate set point, stop date and time, total volume, the average, minimum and maximum flow rates, and any errors listed in the log book.
3. Once all the data is recorded in the log book, the cartridge(s) can be removed from the front of the instrument. Put on nitrile gloves, and remove the cartridge(s) from the Luer fitting(s).
4. Place the cartridge(s) in the appropriate shipping container. This would be the container it was received in on-site.
5. Fill out the sampling label and data sheets with the information recorded in the log book. See Figure 16 for an example sample label and data sheet.
6. Place the cartridge container and data sheet in the pre-chilled transport container (ice chest with ice packs) for transport to the lab. It is imperative that the cartridge samples be kept at a temperature less than 4 degrees Celsius until they can be analyzed. Ship the cartridge(s) via Fedex Overnight.

### 10.2.3 Cartridge Field Blank Sample Collection

The following steps explain the procedure for conducting field blank determinations. This procedure is described in the Sample Retrieval Section because collecting a field blank is best conducted on the sample recovery day after all other sample recovery activities are completed.

1. Prepare the Chain-of-Custody for the blank sample. Document any pertaining information required in the "LAB. PRE-SAMP.","FIELD SETUP", and "FIELD RECOVERY" sections of the CCCOC, and in the instrument's log book. There are spaces for information (i.e., Pre- and Post-sampling rotameter reading, elapsed time, etc.) that is not applicable or feasible to supply. Place a slash or a check in those spaces.
2. Put on disposable gloves.
3. Remove the blank sample cartridge from the sealed packaging.
4. Remove the caps from the ends of the cartridge and place them back in the packaging.
5. Place the cartridge in the Luer lock fittings labeled as the BLANK channel on the front of the analyzer.
6. Allow the cartridge to remain static (i.e., with no flow) for approximately 30 seconds.
7. Remove the blank sample cartridge from the Luer lock fittings. Close the fittings up by inserting one side into the other to prevent contamination.
8. Replace the end caps on the cartridge.
9. Place the sample cartridge in the foil-lined shipping envelope and seal the envelope.
10. Place the sealed package and cartridge COC into the pre-chilled transport container (i.e, ice chest with ice packs) for transport to the lab. It is imperative that the cartridge samples be kept at a temperature less than 4 degrees Celsius until they can be analyzed.

## 10.3 Maintenance

### 10.3.1 Vacuum Pump

**WARNING:** The motor may be thermally protected and can automatically restart when the overload resets. Always disconnect the power source before servicing. Personal injury and/or property damage could result.

1. Turn the sampler off. Remove the cover of the sampler and unplug the inlet tube and disconnect the electrical connector.
2. Using a Phillips screwdriver, remove the 4 screws attaching the pump mounting bracket to the side of the sampler and remove the pump.
3. Inspect the pump, but do not, at any time, lubricate any of the parts with oil, grease, or petroleum products nor clean with acids, caustics or chlorinated solvents. Be very careful to keep the diaphragm from contacting any petroleum product or hydrocarbons. This will affect the service life of the pump.
4. Remove the 5 screws on the top of the pump.
5. Replace the filters and wash them in a solvent and/or blow off with air and replace. Note: The gasket may be cleaned with water.
6. Replace the filters, ensuring they are oriented properly, and then replace the gasket. Note: The gasket and top plate will fit in one position only, as noted in Figure 7 below.


**Figure 7. Pump Gasket Configuration**

7. Remove the socket cap screws from the head of the pump.
8. Remove the 2 Phillips head screws holding the diaphragm in place.
9. Remove the retainer plate and the diaphragm and then replace the plate and the two Phillips head screws with new ones.

10. Torque to 17-inch-pounds of pressure.

CAUTION: Do not raise any burrs or nicks on the heads of these screws. These burrs could cause damage to the inlet valve.

11. For replacing the inlet and outlet valve, remove the slotted machine screw that holds each valve in place. (Note: The stainless steel inlet and outlet valves are not interchangeable.)
12. Clean them with water. When replacing the outlet valve, place the new valve in location and note that there is a retaining bar near the machine screw hole. This retaining bar holds the valve in position. When replacing the inlet valve, note that the valve holder is marked with an X in one corner. This should be in the lower right hand corner toward the inlet of the air chamber. An example of this is illustrated below in Figure 8 below.

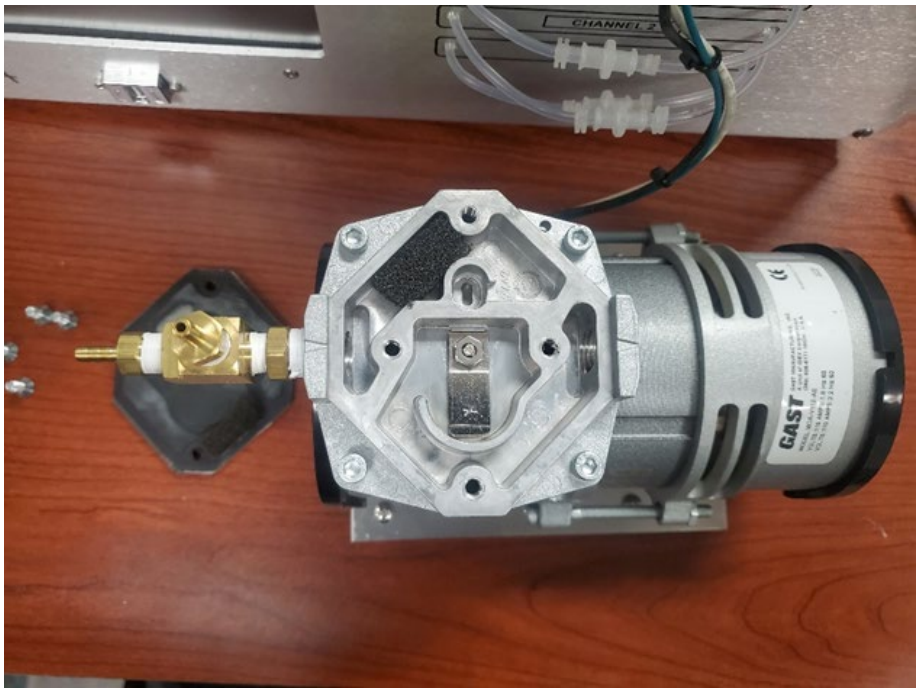



**Figure 8. Pump Inlet and Outlet Valve Replacement**

13. Replace the head and tighten the socket head screws.
14. Torque to 30-inch-pounds of pressure.

Do not attempt to replace the connecting rod or motor bearings. If after cleaning the unit and/or installing a new Service kit, the unit still does not operate properly, contact your representative, the factory, or return the pump to an authorized Service Center.

**NOTE – Make sure to document any maintenance procedures performed in the instrument's log book.

### 10.3.2 Canister Filter

CDPHE will replace the 2 micron sintered stainless steel filter in the canister flow path. The filter must be replaced annually or more frequently when the canister flow rate cannot be maintained.

1. Put on powder free nitrile gloves.
2. Remove the filter assembly at the canister inlet sample line 1/8" Swagelok fitting (See Schematic 1 at the end of this document for reference).
3. Using a wrench, disassemble the fittings to expose the pressed-in filter disk.
4. Using a small punch or rod, push the filter disk out the end of the fitting and replace with a new disk. The new disk may need to be tapped into the fitting with a clean hammer.
5. Document the filter change in the instrument's log book.

### 10.3.3 Cartridge Filter

The operator should periodically replace the Teflon filter located in the cartridge sample path. The replacement frequency will depend on site conditions. The filters must be replaced annually, or when the flow rate through the cartridges cannot be maintained. The operator should periodically check the filter and determine when it needs to be replaced. To replace the filter:

1. Put on powder free polyethylene gloves.
2. Turn off the main power to the sampler.
3. Remove the four screws that fasten the top to the sampler, and slide the top towards the rear of the instrument and remove.
4. Remove the retaining ring on the filter using the hand wrenches supplied with the sampler.
5. Replace the filter with a 1.0 micron Teflon filter and place the filter housing back in the sampler.
6. Document filter change in analyzer log book.

### 10.3.4 Ozone Scrubber

Note: The ozone scrubber should be replaced after approximately 100,000 ppb ozone hours of either sampling or purging at 1 LPM. This is generally every 6 to 12 months, depending on the sampling frequency. The operating life in hours can be estimated by:

Life (hrs) = 100,000 / Average Ozone concentration at site.

1. Turn off the main power to the sampler.
2. Unscrew the 2 retaining knobs encasing the copper ozone scrubber and using the two 9/16" wrenches, remove the connection between the ozone scrubber and ¼" sample line.
3. Unhook the filter holder connected to the ozone scrubber, and remove the insulation surrounding the heater block, the denuder and Return sticker that's fixed to the outside case and set aside.
4. Obtain a new ozone scrubber, and swage a ¼" nut and ferrule to the end where it will connect to the sample line.
5. Carefully install the ozone scrubber and affix the certification sticker to the outside case.
6. Replace the insulation and then replace the cover and carefully align the screws with the holes and finger tighten.

7. Place the new sticker on the cover and tape the Return sticker right above that for the next time maintenance is performed.
8. Manually leak check the system with the new ozone scrubber to ensure it is leak free.
9. Document maintenance in analyzer's log book.

### 10.3.5 Internal Line Changes

The internal sampling lines should be changed annually, before shipment back to ERG for certification. Follow the procedure outline below to change the internal sample lines. Schematic 1 in Section 18 shows the internal plumbing of the ATEC 2200-2 with all associated measurements in centimeters as a guide.

1. Make sure the analyzer is unplugged and turned off.
2. Slide the top of the analyzer off by unscrewing the four screws located on the top, or bottom four corners of the analyzer.
3. Change only one channel's lines at a time. Starting at the canister sample inlet, loosen the fittings and remove the lines. The replacement lines are for specific sections, and are labeled with their appropriate placements.
4. Take the ruler and measure out each line, marking the desired length with a sharpie.
5. Take the tubing cutter and align its razors with the mark you have just made.
6. Tighten the tubing cutter until it is snug against the line.
7. Circle the line with the tubing cutter and slowly continue to tighten it until either the line snaps off of the coil, or the tubing cutter is fully tightened.
8. Gently break off the line from the coil if it hasn't already and take it, the tubing reamer and safety grip gloves to the vice grip.
9. Obtain a clean shop towel and use it to cover the line at the points where it comes into contact with the vice grip to prevent deformations of the delicate lines. Place the line upright between the vice grip plates and slowly clamp the line into place.

Note: Do not over tighten the line with the vice grip as it will deform the line and prevent fittings from sitting properly and could break the glass inside the line.

10. Put on the safety grip gloves and take the tubing reamer and in a downward and clockwise motion, work to remove any burrs at the opening of both sides of the line. An example of an acceptable opening in the line is shown in Figure 9.

**Figure 9. Acceptable Silco-Line Opening**

11. Remove the safety grip gloves and add a nut, bottom and top ferrule to both ends of the line and use the smaller Swagelock (1/8") to tighten the fittings in place.
12. Install the new line in place of the old.
13. Following the sample flow path through the analyzer, change all the associated lines until the sample outlet is reached. When replacing the lines, also replace all the nuts, ferrules, and other associated fittings with new ones (Note: All fittings that may come into contact with an air sample must be at a minimum, stainless steel). If the ferrules are not fully swaged, (i.e., the bottom ferrule is not snug against the top) the system will not be leak-free.
14. Refer to Schematic 1 at the end of this document for line placements / measurements. Each line number corresponds to the specified length, in centimeters, below.

    1. 3.1 cm
    2. 7.8 cm
    3. 59.0 cm
    4. 5.2 cm
    5. 17.8 cm
    6. 8.74 cm
    7. 3.18 cm
    8. 50.0 cm
    9. 8.0 cm
    10. 2.0 cm
    11. 2.0 cm
    12. 20.2 cm
    13. 17.2 cm
    14. 17.5 cm

15. 2.0 cm
16. 22.5 cm
17. 16.99 cm
18. 13.1 cm
19. 25.8 cm
20. 48.2 cm
21. 10.5 cm
22. 10.1 cm
23. 31.8 cm
24. 32.0 cm

Please note: These measurements are meant as a guide and will fluctuate depending on the specific instrument.

15. After both of the internal canister sampling lines and fittings have been changed, replace both channels of the cartridge lines following the same procedure. Note: The Teflon lines shown in Schematic 2 should be replaced biannually.
16. When the line changes are complete, slide the top back on and replace the four screws.
17. Plug in the instrument and turn it on.
18. Leak check the sample paths by using the manual leak check procedure found in the instrument's manual.
19. Document maintenance in the analyzer's log book.

### 10.3.6 Sampler Certification

Each sampler in the network should be sent back to ERG for certification annually, once all the annual maintenance procedures have been performed, and the mass flow controllers have been calibrated. Follow the procedure outlined below to get the sampler certified.

1. Change all filters, the ozone scrubber, and all internal sampling lines.
2. Perform flow calibrations on all MFCs.
3. Contact ERG to set up shipment of the analyzer for certification and fill out the ERG certification paperwork, detailing the analyses needed.
4. Ship analyzer to ERG.
5. When the analyzer is certified and returned, make a note in the log book.
6. Take the certified analyzer out into the field and swap it out with one that has not been certified, or that is in need of recertification, making sure to install new external sample lines at the same time.
7. Return the uncertified analyzer to the shop, and follow this procedure again. Do this until all analyzers have been certified / recertified.

## 11. HANDLING AND PRESERVATION

Sample set-up of the air toxics samplers in the network takes place any day after the previous sample has been recovered. For instance, on a Sunday - Thursday sample day set-up when 1 in 6 day sampling is required, the pickup occurs the day after the run. However, on Friday and Saturday run dates, the pick-up

is on the following Monday. It is important to recognize that the only holding time that affects sample set-up is the 30 day window from the time samples are pre-weighed / processed to the time they are installed in the monitor.

This section details the requirements needed to prevent sample contamination, the volume of air to be sampled, how to protect the sample from contamination, temperature preservation requirements, and the permissible holding times to ensure against degradation of sample integrity.

## 11.1 NMOCs/Methane[6]

### 11.1.1 Sample Contamination Prevention

The quality system has rigid requirements for preventing sample contamination. The canister valve is tightly closed and capped to prevent any sample leakage.

### 11.1.2 Sample Volume

The volume of air to be sampled is specified in CDPHE's method specifications. Samples are expected to be collected for 3 hours. Therefore, the site operators must set the flow rates to collect sufficient sample to obtain the minimum sample volume. The sample flow rate is approximately 25 cubic centimeters per minute for a 3-hour sample. In some cases a shorter sample period may occur due to power outages. A valid sample run should not to be less than 3 hours. If the sample period is less than 2.5 hours or greater than 3.5 hours, the sample will be flagged.

### 11.1.3 Temperature Preservation Requirements

The temperature requirements of the samples vary between methods. During transport from the laboratory to the sample location there are no specific requirements for temperature control for canisters. The temperature requirements are detailed in the following table.

**Table 6. Temperature Requirements for NMOCs/Methane**

| Item | Temperature Requirement | Reference |
|---|---|---|
| Canister pre- and post-sampling | No Requirements | N/A |

### 11.1.4 Holding Time Requirements

The sample holding time requirements are detailed in TO-14A, and the following table.

[6] Information in this section was taken from the following EPA method, unless otherwise noted:
U. S. Environmental Protection Agency (EPA). 1999. "Compendium Method TO-14A Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography." EPA-625/R-96/010b. Cincinnati, OH. January 1999.

**Table 7. Permissible Holding Times for NMOCs/Methane**

| Item | Holding Time | From: | To: | Reference |
|---|---|---|---|---|
| Canister | <30 days | Completion of sample period | Time of analysis | TO-15 |

## 11.2 Carbonyls[7]

### 11.2.1 Sample Contamination Prevention

The quality system has rigid requirements for preventing sample contamination. Powder free gloves are worn while handling DNPH cartridges. Cartridges are to be held in protective storage containers as provided by the sampler manufacturer during transport to and from the laboratory. Once samples have been analyzed, they are again stored in their protective containers.

### 11.2.2 Sample Volume

The volume of air to be sampled is specified in manufacturer's method specifications. The different methods specify that certain minimum volumes must be collected. Samples are expected to be collected for 3 hours. Therefore, the site operators must set the flow rates to collect sufficient sample to obtain the minimum sample volume. In some cases a shorter sample period may occur due to power outages. A valid sample run should not be less than 2.5 hours. If the sample period is less than 2.5 hours or greater than 3.5 hours, the sample will be flagged.

### 11.2.3 Temperature Preservation Requirements

The temperature requirements of the samples vary between methods. During transport from the laboratory to the sample location, there are specific requirements for temperature control. The DNPH cartridges for carbonyl analysis must be located in their protective container and in the transport container. Excessive heat must be avoided (e.g., do not leave in direct sunlight or a closed-up car during summer). Cartridges need to be stored at 4$^{o}$C until they are loaded into the sampler. The temperature requirements are detailed in the following table.

**Table 8. Temperature Requirements for Carbonyls**

| Item | Temperature Requirement | Reference |
|---|---|---|
| DNPH cartridge filter pre- and post-sampling | 4$^{o}$ C or less | TO-11A, Section 9.4.3 |

### 11.2.4 Holding Time Requirements

[7] Information in this section was taken from the following EPA method, unless otherwise noted:
U. S. Environmental Protection Agency (EPA). 1999. "Compendium Method TO-11A,Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology]." EPA-625/R-96/010b. Cincinnati, OH. January.

The sample holding time requirements are detailed in TO-11A, and the following table.

**Table 9. Holding Time Requirements for Carbonyls**

| Item | Holding Time | From: | To: | Reference |
|---|---|---|---|---|
| DNPH Cartridge Filter | <2 weeks | Sample end date/time | Date of Extraction | TO-11A, Section 11.1.2 |

## 12. SAMPLE PRESERVATION AND ANALYSIS

The NMOC/methane, and carbonyl samples are transported to and from the laboratory in cardboard boxes that are sent either by overnight mailing services (carbonyls), or by ground delivery services (NMOC/methane). Each sample day requires one SUMMA canister for NMOC and methane sampling, a DNPH cartridge for carbonyl sampling, a small foil envelope, and data sheets for the canister and cartridge media. After sampling, the closed summa canister is placed back in the sample box and shipped to the lab for analysis.

The DNPH cartridge is re-capped at both ends and put into the foil envelope. The site name, sample date, and channel number are written on the outside of the envelope, excess air is removed from the foil envelope by pressing it out, and the top zip-lock seal is pressed closed to seal it. If the DNPH cartridge is to be immediately shipped, place the foil envelope with the cartridge into the transport foil envelope, and place that in the shipping cooler with the ice packs. If it will not be immediately shipped, place the foil pouch with the cartridge in the freezer.

The local site operator will remove the pink carbon-copy Chain-of-Custody form from the other two copies, keeping the pink one for site records (to be picked up by the Site Operations Manager quarterly), and shipping the white and yellow forms with the sample to ERG for analysis. The site operator must also email the downloaded run data files to the CDPHE.

The canisters and cartridges should be analyzed within 30 days of the sample collection date. If the sample operator promptly picks up and mails back the canisters and cartridges, this 30-day limit can generally be met.

## 13. TROUBLESHOOTING[8]

Should the Model 2200-2 encounter flow problems, or operate at less than the expected parameters, the steps in the following table can be followed to try and correct the problem. In the event that the problem cannot be corrected by any means listed below, the site operator should contact the instrument's manufacturer to further troubleshoot.

**Table 10. Troubleshooting Options for Model 2200-2 Mass Flow Controller**

| SYMPTOM | CAUSE | ACTION |
|---|---|---|
| Output reads 40% of flow with no flow. Zero pot has not effect. | Power supply locked up or shorted out. | Turn off power supply for a few seconds, then turn back on. If this is ineffective, disconnect the unit from the power supply, as it is probably burned out. Check supply voltages and replace faulty regulator. If |

[8] Information contained in this section is taken directly from the ATEC Model 2200-2's instrument manual.
Atmospheric Technology (ATEC). 2007. "Model 2200 Toxic Air Sampler Operations and Maintenance Manual." Version 1.40. Malibu, CA. June.

| | | |
|---|---|---|
| | | display returns to zero after disconnecting the power supply from the unit there is a short in the unit to ground. Check capacitors C10 and C11 first. |
| Override switch is in CLOSE position, but flow remains or 0.00 VDC is commanded and flow remains. | Orifice out of adjustment or faulty op-amp. | Check valve voltage at connector pins TP-3 and TP-6. If voltage is less than 3.00 VDC, then turn orifice clockwise until flow stops. If voltage is greater than 3.00 VDC, replace U1; if less, replace transistor Q1. |
| Output of unit is proportional to flow but extremely small and not correctable by span pot. | Sensor is not being heated. | Unplug connector J2. Check the following resistance: The resistance between pins 2 and 3 of the sensor should be approximately 2500 ohms. The resistance between pins 1 and 4 should be approximately 2.3 ohms. The resistance between pins 2 and 3 and the base of the sensor should be essentially infinite. If not, replace the sensor unit. If sensor reads okay, check the voltage output on pins 2 and 3 of the jack in the board. If it does not read approximately 22 VDC then replace op-amp U2. |
| Sensor has proper resistance readings, but little or no output with flow. | Plugged sensor. | Shut off gas supply and power supply. Remove cover and PC board from unit. Remove sensor assembly and examine. If sensor has evidence of plugging, clean or replace as applicable. |
| Flow controller oscillates. | Flow controller not adjusted for the dynamics of the flow system. | Check upstream and downstream pressures. The gas supply regulator should not have excessive lockup when flow shuts off. Also ensure that there is not a large drop in pressure between the regulator and the instrument due to line resistance. Oscillations can also be caused if a large flow restriction is pneumatically close to the downstream end of the flow controller. The differential pressure across the unit must be between 10-50 psig. |
| Little or no flow, even with Valve Override switch OPEN. | Plugged orifice. | Verify the presence of a 10-50 psig pressure across the instrument. If present, shut off gas supply and power supply. Remove orifice and examine. If plugged, clean or replace as applicable. Reassemble valve. |
| Flow meter reads other than 0.00 VDC with no flow, or there is a small flow when flow meter reads 0.00 VDC. | ZERO potentiometer is out of adjustment. | Shut off all flow. Adjust ZERO potentiometer until output reads 0.00 VDC. |
| Flow meter out of calibration and nonlinear. | Leaks in gas inlet or outlet fittings. | Check all fitting for leaks by placing soap solution on all fittings between gas supply and final destination of gas. Check flow meter for leaks. Replace “O” rings if required or recalibrate as necessary. |

# 14. DATA ACQUISITION, CALCULATIONS AND DATA REDUCTION

## 14.1 Acquisition of Non-Direct Measurement Data

All the NMOC, methane, and carbonyl data are from laboratory analyses. Field data that are recorded on log sheets include run date/time, lot numbers, setup and recovery dates/times, pre and post flow readings, beginning and ending pressures, and comments. This data can also be found in the electronic data run files. Additional modes of acquisition of non-direct measurement data protocols are explained in the CDPHE QAPP.

## 14.2 Acquisition of Direct Measurement Data

This project is collecting supporting meteorological data at a monitoring station that is part of the CDPHE’s routine network. These data include wind speed, wind direction, temperature and relative humidity. All of these parameters are directly recorded on a data logger and transmitted to the CDPHE office. Since

operation of the routine meteorological network is already addressed in the CDPHE QAPP, it is not covered here.

## 15. COMPUTER HARDWARE AND SOFTWARE

No special computer hardware or software is required. A thumb drive can be used to download the previous sampling session's data.

## 16. DATA MANAGEMENT AND RECORDS MANAGEMENT

### 16.1 Background and Overview

Each air monitoring project must have means of ensuring that data are properly recorded, transmitted, and stored. The data are recorded in the field and at the laboratory. The data will be summarized and stored on the EPA's Air Quality System (AQS). This section summarizes data management practices.

### 16.2 Data Recording

Figure 15 and Figure 16 show example formats for recording field sample data for the ATEC sampler.

### 16.3 Data Validation

For NMOC, methane, and carbonyl samples, most data validation is done at the laboratory. In-house validation includes statistical analyses of the annual data sets for each compound to determine any outliers. This procedure is detailed in the CDPHE NATTS QAPP for 2023.

### 16.4 Data Transformation

To determine concentrations of air pollutants in air with these sampling methods, a number of calculations are necessary. For example, NMOC and methane data are expressed as parts of contaminant per million parts of air, so no data transformation is necessary. Carbonyl data are determined by dividing the concentration of each contaminant by the total airflow through the cartridge or filter.

### 16.5 Data Transmittal

Data will be transmitted from the lab onto the EPA Air Quality System (AQS). Information on entering data into the AQS system is given in EPA guidance relating to that system.

### 16.6 Data Reduction

CDPHE will generate a report summarizing all the data with statistical calculations such as the population mean, maximum, minimum, and standard deviation. CDPHE will also attempt to do some correlation of different pollutants at the air monitoring site.

### 16.7 Data Summary

Data from the air monitoring pilot trends project locations will all be entered on the EPA AQS data system. AQS will serve as a data summary that will be available to agencies and researchers on a nationwide basis.

### 16.8 Data Flagging – Sample Qualifiers

The laboratory group coordinators at EPA have continued to work with the AQS system personnel to ensure that AQS will include means of entering all data flags the projects will need.

### 16.9 Data Tracking

Data will be packaged and summarized on a quarterly basis. Each report is due 120 days after the end of each calendar quarter. The report consists of putting all quarterly data onto AQS. Reporting data on a quarterly basis ensures that all samples stay on-target for processing in a timely manner, and decreases the possibility that records will be lost or misplaced.

### 16.10 Data Storage and Retrieval

As noted previously, data will be stored on AQS in order to permit nationwide access by EPA, States, and air pollution researchers.

## 17. QUALITY ASSURANCE AND QUALITY CONTROL

Quality assurance (QA) and quality control (QC) are two terms commonly discussed, but often confused. Quality **assurance** refers to the overall process of ensuring that the data collected meet previously stated measurement quality objectives (MQOs). Quality **control** covers specific procedures established for maintaining data collection within those limits.

The main quality assurance measures for the NMOCs, methane, and carbonyl sampling will be carried out by the laboratory analysis team, and are thus the responsibility of the laboratory. The laboratory will maintain a full set of standard operating procedures and quality assurance documents for the analysis of NMOCs, methane, and carbonyls. Quality assurance includes periodic checks of blank canisters to ensure adequate performance of the canister cleaning system, as well as the analysis of replicate samples. Most of these replicate analyses will be conducted by drawing a second sample aliquot from a canister analyzed on the previous day. On at least a 10% frequency, two canisters will sample at the site on a collocated basis, to generate statistics about the method precision. In addition, each analyzer in the network will be sent to ERG annually for canister and cartridge systems certifications. Detailed quality control procedures utilized by ERG can be found in the ERG QAPP, or the CDPHE NATTS QAPP for 2023.

The DNPH cartridges will also have analyses of blank cartridges, as described in the laboratory's procedures. CDPHE will do duplicate sampling on at least a 10% frequency, as required by the national network, and field blanks as requested by the laboratory. Some samples will undergo duplicate analysis. The laboratory will maintain a full set of standard operating procedures and quality assurance documents for the analysis of carbonyls.

CDPHE will conduct quality assurance associated with the field procedures for these NMOC, methane and carbonyl monitoring methods. Field quality assurance includes documentation of stable flow rates, and determination of total run times.

## 18. TABLES, DIAGRAMS, SCHEMATICS, AND VALIDATION DATA

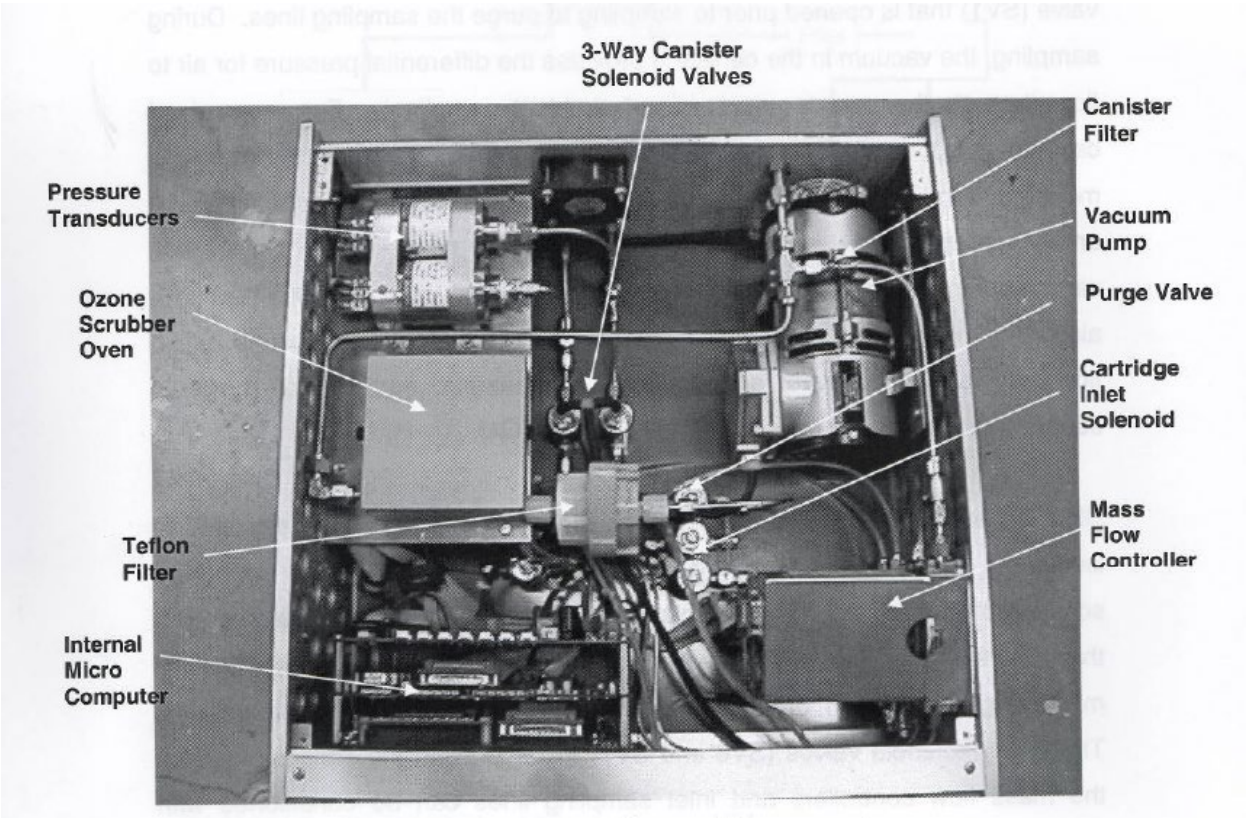
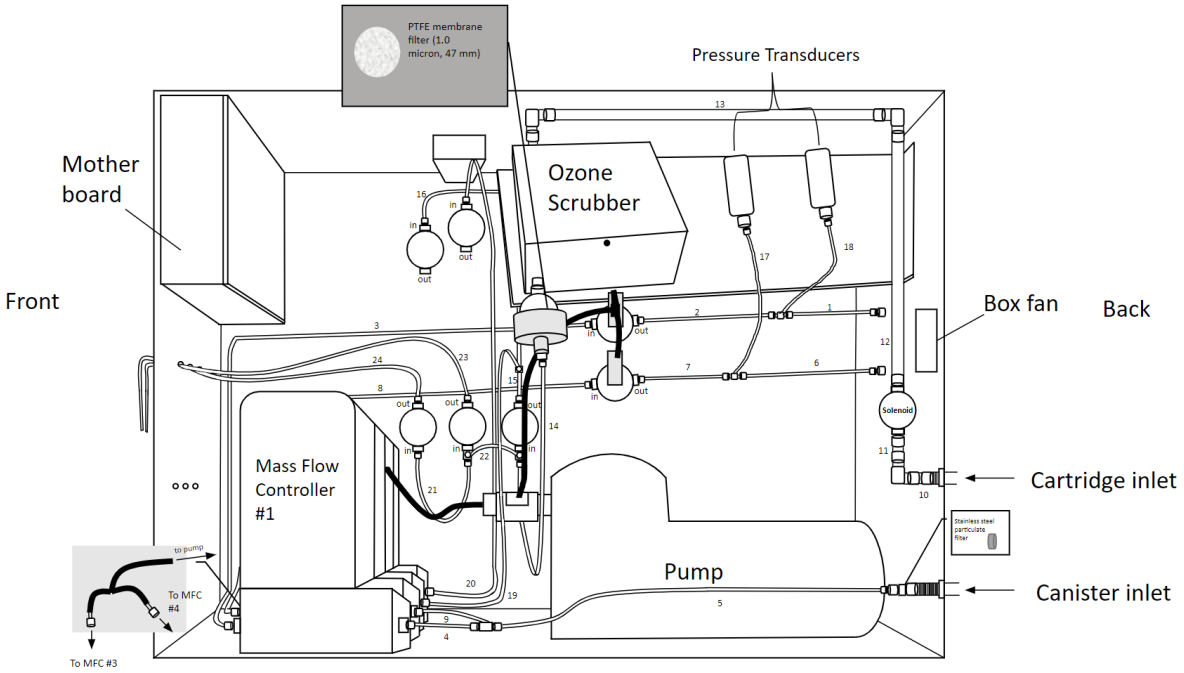



**Figure 10. ATEC Model 2200-2 Internal Components**



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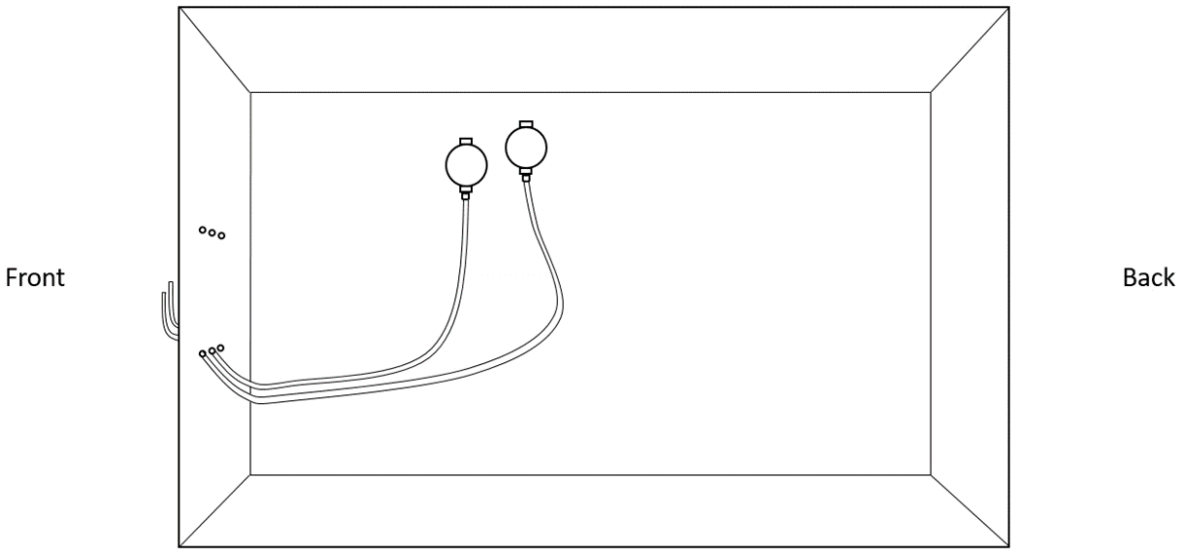
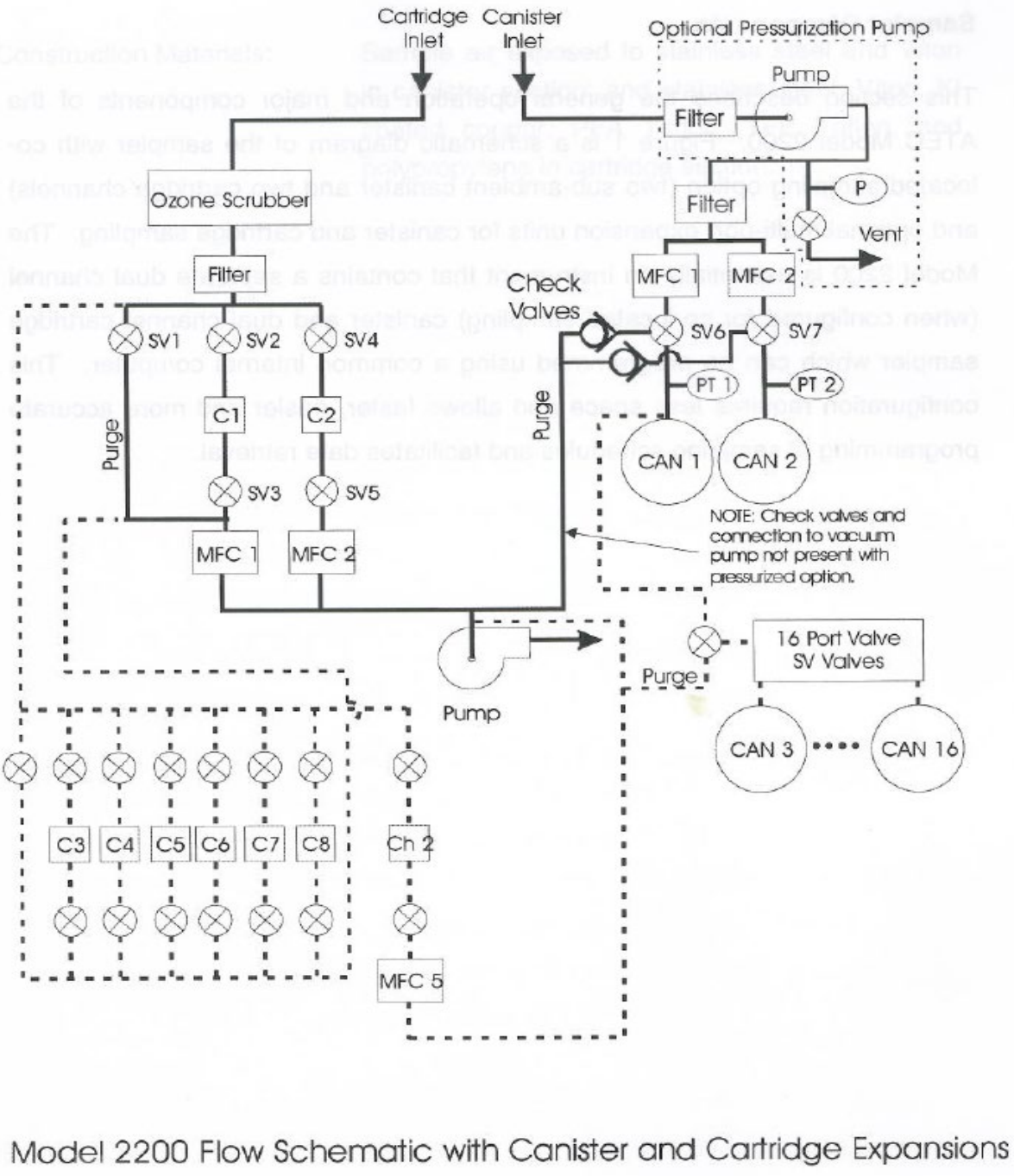
3. 59.0 cm
4. 5.2 cm
5. 17.8 cm
6. 8.74 cm
7. 3.18 cm
8. 50.0 cm
9. 8.0 cm
10. 2.0 cm
11. 2.0 cm
12. 20.2 cm
13. 17.2 cm
14. 17.5 cm
15. 2.0 cm
16. 22.5 cm
17. 16.99 cm
18. 13.1 cm
19. 25.8 cm
20. 48.2 cm
21. 10.5 cm
22. 10.1 cm
23. 31.8 cm
24. 32.0 cm

**Schematic 1. ATEC 2200-2 Internal Sampling Lines**




**Schematic 2. ATEC 2200-2 Teflon Lines**




**Schematic 3. ATEC Model 2200-2 Flow Schematic with Canister and Cartridge Expansions**

| ATEC 2200-2 CALIBRATION SHEET FOR NFROPS SAMPLERS | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| SITE NAME: | | | | ATEC S/N: | | | | | |
| DATE: | | | | MFM S/N FOR CANISTER CALIBRATIONS: | | | | | |
| CALIBRATOR NAME: | | | | | | | | | |
| **CANISTERS** | | | | | | | | | |
| **CHANNEL 1** | | | | | | | | | |
| CAN LEAK RATE: | | PASS? | | M= | | | B= | | |
| MFM ZERO READING: | | | | | | | | | |
| ZERO BEFORE ADJUSTMENT: | | | ZERO AFTER ADJUSTMENT | | | | | | |
| **SET POINTS=** | **5.0 CCM** | **15.0 CCM** | **25.0 CCM** | **35.0 CCM** | **45.0 SCCM** | | | | |
| **300VUE =** | | | | | | | | | |
| **ATEC =** | | | | | | | | | |
| **CALCULATED SLOPE (M) =** | | | | | | AVG. SLOPE = | | | |
| M = 300 VUE/ATEC | | | | | | | | | |
| CHECKPOINT AFTER CALIBRATION: | | | | | | | | | |
| 300VUE = | | SCCM | | % DIFFERENCE = | | | | | |
| ATEC = | | SCCM | | | PASS? | | | | |
| **CHANNEL 2** | | | | | | | | | |
| CAN LEAK RATE: | | PASS? | | M= | | | B= | | |
| MFM ZERO READING: | | | | | | | | | |
| ZERO BEFORE ADJUSTMENT: | | | ZERO AFTER ADJUSTMENT | | | | | | |
| **SET POINTS=** | **5.0 CCM** | **15.0 CCM** | **25.0 CCM** | **35.0 CCM** | **45.0 SCCM** | | | | |
| **300VUE =** | | | | | | | | | |
| **ATEC =** | | | | | | | | | |
| **CALCULATED SLOPE (M) =** | | | | | | AVG. SLOPE = | | | |
| M = 300 VUE/ATEC | | | | | | | | | |
| CHECKPOINT AFTER CALIBRATION: | | | | | | | | | |
| 300VUE = | | SCCM | | % DIFFERENCE = | | | | | |
| ATEC = | | SCCM | | | PASS? | | | | |

**Figure 11. Canister Mass Flow Controller Calibration Data Sheet**

# ATEC 2200-2 CALIBRATION SHEET

| | | | |
|---|---|---|---|
| SITE NAME: | | ATEC S/N: | |
| DATE: | | MFM S/N FOR CARTRIDGE CALIBRATIONS: | |
| CALIBRATOR NAME: | | | |

## CARTRIDGES

### CHANNEL 1

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| CARTRIDGE LEAK RATE: | | PASS? | | M= | | | B= | | |
| MFM ZERO READING: | | | | | | | | | |
| ZERO BEFORE ADJUSTMENT: | | | ZERO AFTER ADJUSTMENT | | | | | | |

| SET POINTS= | 0.2 LPM | 0.5 LPM | 1.0 LPM | 1.5 LPM | 1.8 LPM | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 300VUE = | | | | | | | | | |
| ATEC = | | | | | | | | | |
| CALCULATED SLOPE (M) = | | | | | | AVG. SLOPE = | | | |

M = 300 VUE/ATEC

CHECKPOINT AFTER CALIBRATION AT **0.75 SLPM**:

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 300VUE = | | SLPM | | % DIFFERENCE = | | | | | |
| ATEC = | | SLPM | | | PASS? | | | | |

### CHANNEL 2

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| CARTRIDGE LEAK RATE: | | PASS? | | M= | | | B= | | |
| MFM ZERO READING: | | | | | | | | | |
| ZERO BEFORE ADJUSTMENT: | | | ZERO AFTER ADJUSTMENT | | | | | | |

| SET POINTS= | 0.2 LPM | 0.5 LPM | 1.0 LPM | 1.5 LPM | 1.8 LPM | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 300VUE = | | | | | | | | | |
| ATEC = | | | | | | | | | |
| CALCULATED SLOPE (M) = | | | | | | AVG. SLOPE = | | | |

M = 300 VUE/ATEC

CHECKPOINT AFTER CALIBRATION AT **0.75 SLPM**:

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 300VUE = | | SLPM | | % DIFFERENCE = | | | | | |
| ATEC = | | SLPM | | | PASS? | | | | |

**Figure 12. Cartridge Mass Flow Controller Calibration Data Sheet**

## Pressure Transducer Calibration Procedure

To perform the following steps, the following will be needed:

- Evacuated canister at 0.0 psia or known pressure
- Accurate barometric or absolute pressure gauge

1. In the Manual screen, without the canister attached and without the "Calibrated Values" checkbox checked. Record the raw ambient pressure value ***Prm*** and enter in Step 5 below.
2. Attach the evacuated canister, open the canister valve, and record the raw evacuated pressure value ***Pre*** and enter in Step 5 below.
3. Record the local ambient pressure using a barometer or absolute pressure gauge. Enter this value ***PA*** in Step 5 below.
4. Enter the known evacuated canister pressure ***Pec*** in Step 5
5. The slope is calculated by:

$$Slope = \frac{PA - Pec}{Prm - Pre}$$

***PA*** = _____

***Pec*** = _____

***Prm*** = _____

***Pre*** = _____

***Slope*** = _____

6. The intercept value is calculated by:

$$Intercept = PA - (Slope \times PRM)$$

***Intercept*** = _____

7. Verify the slope and intercept values using the following equation:

$$P_0 = Slope \times Prm - Intercept$$

$P_0$ = _____

8. The value calculated in Step 7 should be very close to ***Pec***. If not, check the calculations.
9. In the Advanced screen, enter the values for the slope and intercept.
10. In the Main Screen and without a canister attached, verify that the pressure is very close to ambient.

**Figure 13. Pressure Transducer Calibration Procedure**

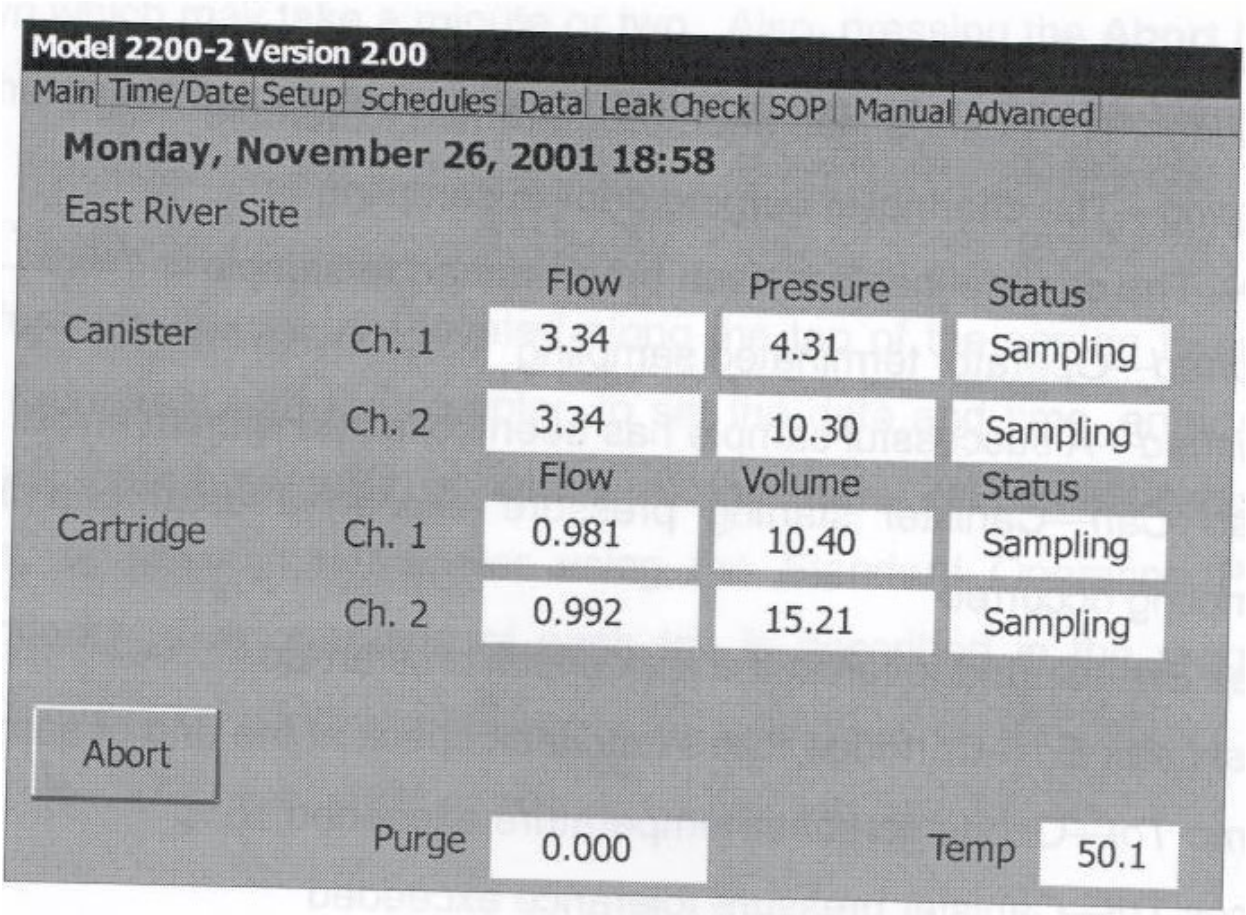
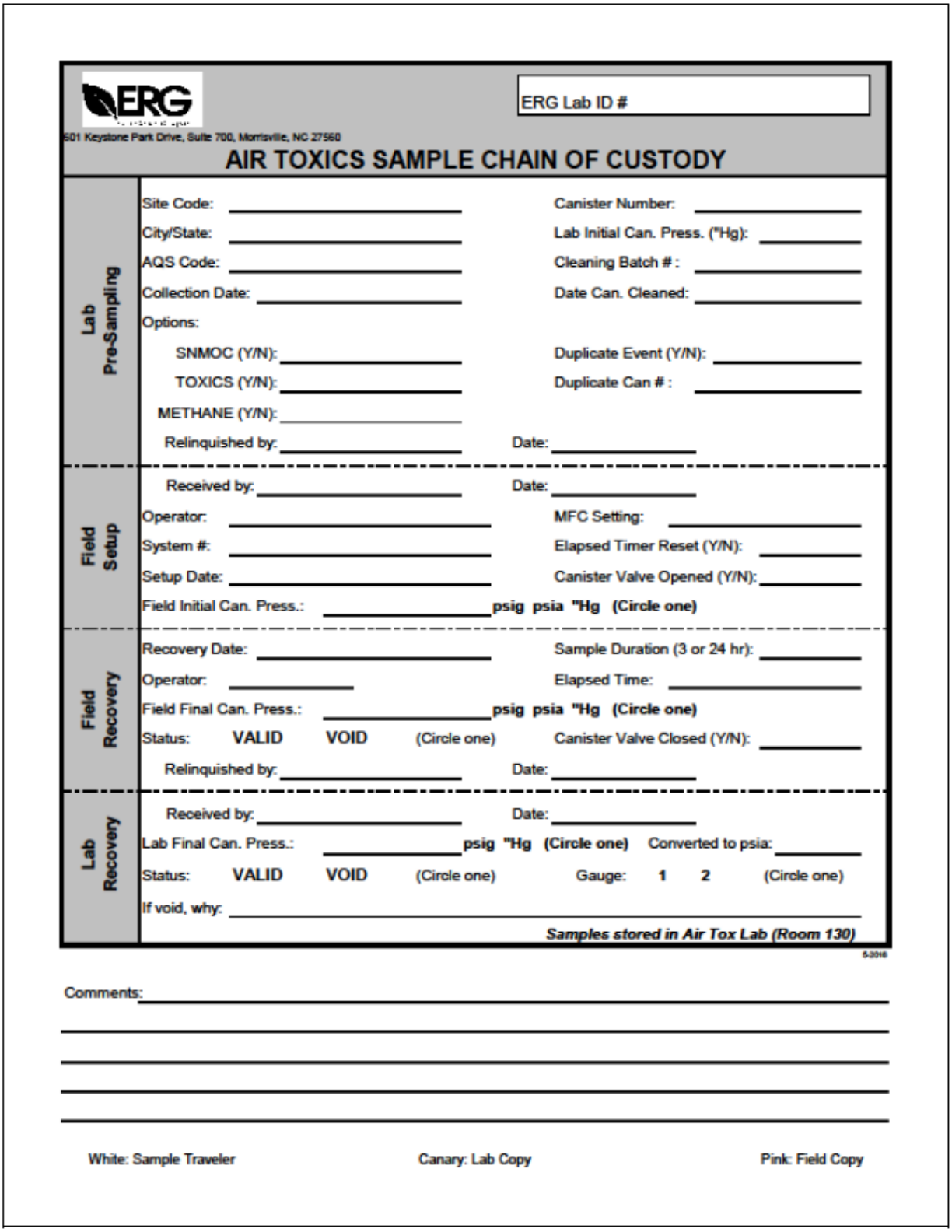



**Figure 14. ATEC Model 2200-2 Main Screen Example**



ERG

ERG Lab ID #

601 Keystone Park Drive, Suite 700, Morrisville, NC 27560

## AIR TOXICS SAMPLE CHAIN OF CUSTODY

**Lab Pre-Sampling**

Site Code: _____ Canister Number: _____

City/State: _____ Lab Initial Can. Press. ("Hg): _____

AQS Code: _____ Cleaning Batch # : _____

Collection Date: _____ Date Can. Cleaned: _____

Options:

SNMOC (Y/N): _____ Duplicate Event (Y/N): _____

TOXICS (Y/N): _____ Duplicate Can # : _____

METHANE (Y/N): _____

Relinquished by: _____ Date: _____

**Field Setup**

Received by: _____ Date: _____

Operator: _____ MFC Setting: _____

System #: _____ Elapsed Timer Reset (Y/N): _____

Setup Date: _____ Canister Valve Opened (Y/N): _____

Field Initial Can. Press.: _____ **psig psia "Hg (Circle one)**

**Field Recovery**

Recovery Date: _____ Sample Duration (3 or 24 hr): _____

Operator: _____ Elapsed Time: _____

Field Final Can. Press.: _____ **psig psia "Hg (Circle one)**

Status: **VALID VOID** (Circle one) Canister Valve Closed (Y/N): _____

Relinquished by: _____ Date: _____

**Lab Recovery**

Received by: _____ Date: _____

Lab Final Can. Press.: _____ **psig "Hg (Circle one)** Converted to psia: _____

Status: **VALID VOID** (Circle one) Gauge: **1 2** (Circle one)

If void, why: _____

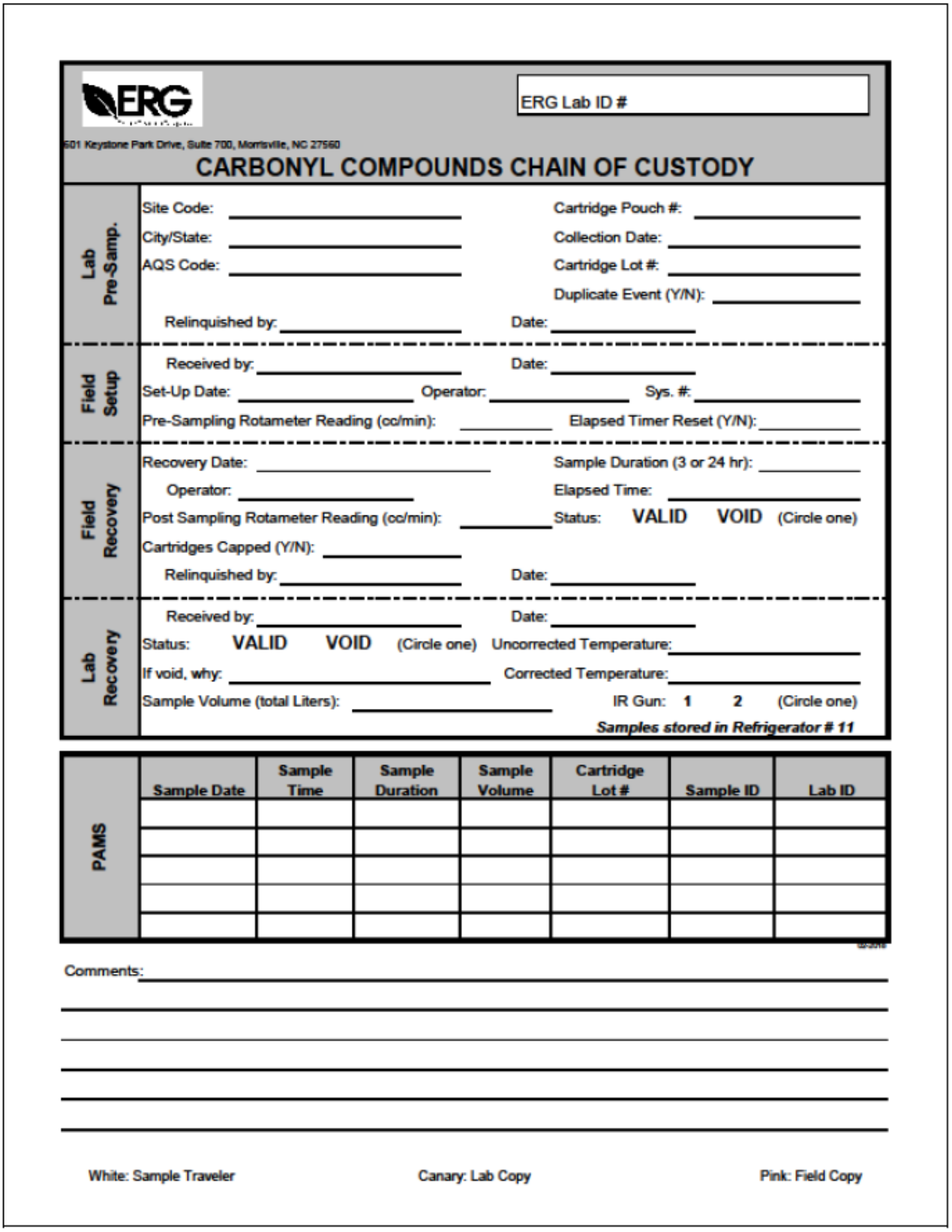
***Samples stored in Air Tox Lab (Room 130)***

5-2016

Comments: _____

White: Sample Traveler Canary: Lab Copy Pink: Field Copy

**Figure 15. Example NMOC and Methane Sample Data Sheet**



ERG

ERG Lab ID #

601 Keystone Park Drive, Suite 700, Morrisville, NC 27560

## CARBONYL COMPOUNDS CHAIN OF CUSTODY

**Lab Pre-Samp.**

Site Code: _____ Cartridge Pouch #: _____

City/State: _____ Collection Date: _____

AQS Code: _____ Cartridge Lot #: _____

Duplicate Event (Y/N): _____

Relinquished by: _____ Date: _____

**Field Setup**

Received by: _____ Date: _____

Set-Up Date: _____ Operator: _____ Sys. #: _____

Pre-Sampling Rotameter Reading (cc/min): _____ Elapsed Timer Reset (Y/N): _____

**Field Recovery**

Recovery Date: _____ Sample Duration (3 or 24 hr): _____

Operator: _____ Elapsed Time: _____

Post Sampling Rotameter Reading (cc/min): _____ Status: VALID VOID (Circle one)

Cartridges Capped (Y/N): _____

Relinquished by: _____ Date: _____

**Lab Recovery**

Received by: _____ Date: _____

Status: VALID VOID (Circle one) Uncorrected Temperature: _____

If void, why: _____ Corrected Temperature: _____

Sample Volume (total Liters): _____ IR Gun: 1 2 (Circle one)

***Samples stored in Refrigerator # 11***

**PAMS**

| Sample Date | Sample Time | Sample Duration | Sample Volume | Cartridge Lot # | Sample ID | Lab ID |
|---|---|---|---|---|---|---|
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |

Comments: _____

White: Sample Traveler Canary: Lab Copy Pink: Field Copy

**Figure 16. Example Carbonyl Sample Labels and Data Sheet**