



CRESTONE PEAK
RESOURCES

AIR QUALITY PLAN

FIELDWIDE - WATKINS

**Crestone Peak Resources Operating LLC
Watkins Air Quality Plan – City of Aurora**

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Acronyms and Abbreviations

ACRONYM	Definition
APCD	Air Pollution Control Division
ARL	Air Resources Laboratory
AVO	Audio, Visual, Olfactory
BTEX	Benzene, Toluene, Toluene, Ethylbenzene, Xylene
CDPHE	Colorado Department of Public Health & Environment
COGCC	Colorado Oil & Gas Conservation Commission
CPRO	Crestone Peak Resources Operating LLC
EPA	Environmental Protection Agency
GC-MS	Gas Chromatography-Mass Spectrometry
GC-FID	Gas Chromatography-Flame Ionization Detector
LDAR	Leak Detection and Repair
LEL	Lower Explosive Limit
NDIR	Nondispersive Infrared
NOAA	National Oceanic and Atmospheric Administration
OGI	Optical Gas Imaging
PID	Photoionization Detector
PM	Particulate Matter
ppbV	Parts per billion, by Volume
ppmV	Parts per million, by Volume
STEM	Storage Tank Emissions Management
VOC	Volatile Organic Compound

1. Purpose

The purpose of this plan is to provide the necessary information for meeting Air Quality requirements as required by the Oil and Gas Operator Agreement between Crestone Peak Resources Operating LLC, a Delaware limited liability company (“CPRO”) as assigned March 4, 2020, and the City of Aurora, Colorado, a municipal corporation. Air quality management is an integral component of the Best Management Practices in order to minimize degradation to air quality.

CPRO has a proud history of environmental awareness and sustainable development in the State of Colorado. CPRO seeks to be to the preferred oil and gas exploration and production company in every community in which we operate. One of the many ways to achieve this is to minimize our impact on the environment.

2. Scope

The overall focus of the Air Quality Plan is to document the requirements to minimize degradation to air quality through elimination, capture, or minimization of potential emissions and protection of exposures during certain activities.

This Air Quality Plan outlines the requirements related to air quality management for the Watkins Operations that are required to satisfy Federal, State, and Local regulations. More specifically, the Air Quality Plan includes detailed monitoring requirements which describes the use of real-time air monitoring data to demonstrate that CPRO activities are not adversely affecting the citizens and environment of the City of Aurora, Colorado. During Pre-Construction, Drilling, Completion and Production phases, CPRO will conduct sampling using a continuous emission monitoring system that detects Volatile Organic Compounds (VOC) including Benzene, Toluene, Ethyl Benzene, Xylene (BTEX) and Particulate Matter (PM). The presence of Methane will be represented by the ppmV

level's change overtime based on the NDIR sensor reading. For all stages, CPRO will conduct sampling using a continuous emission monitoring system that detects VOC including BTEX.

In addition to monitoring the air quality, CPRO will comply with the odor requirements of the Operator Agreement and CDPHE reg 2.

Targeted compounds can be separated across the two types of monitoring:

- Indicator-level monitoring involves using micro-sensors that react to a wide range of pollutants but do not provide audit quality quantitative data.
- Reference-quality samples involve collecting an air sample and having a certified lab analyze the sample using EPA approved methods. These samples can identify both the specific VOC pollutants in the air sample, as well as a specific concentration measurement for each of the measurable VOC's.

Micro sensors cannot provide actual measurements for specific compounds, but they are extremely useful for detection of air quality events (or sudden changes in air quality), discovery of emissions patterns, and for triggering the collection of a reference-quality sample.

Specific information on the monitoring system that will be employed for ambient air monitoring is located in Section 6.

3. Objectives

The following objectives are applied to the management of air quality:

- Compliance with the Oil and Gas Operator Agreement, Best Management Practices, and relevant regulations and requirements for the management of air emissions.
- Provide an early indication of potential issues that can be managed prior to a non-conformance.
- Provide guidance on the monitoring and reporting requirements including assignment of responsibilities.

4. Responsibilities

4.1. Asset Leadership

- Reinforce adherence to the Oil and Gas Operator Agreement, Best Management Practices, and relevant regulations.
- Provide resources for effective implementation of this Air Quality Plan.
- Monitor compliance with the Air Quality Plan through periodic reviews.

4.2. Operations and Maintenance Supervision

- Ensure compliance with and promote implementation of the Air Quality Plan.
- Provide resources for effective implementation of the Air Quality Plan.
- Ensure compliance with federal, state, and local laws and regulations and with company standards
- Ensure training is provided such that employees have the skills, knowledge, and understanding of the Oil and Gas Operator Agreement, Best Management Practices, and relevant regulations.

4.3. Health, Safety, and Environmental

- Provide advice, support, technical resources, and tools related to the Air Quality Plan.
- Overall responsibility for coordination of environmental matters associated with facility air emissions.
- Submission of required regulatory reports.
- Manage incident and non-conformance reporting.
- Review and report on pertinent matters arising from air quality monitoring specialist reports
- Ensure the Air Quality Plan is reviewed on a quarterly basis by internal team of environmental, operations, and maintenance staff. Results will be provided in quarterly reports to the City.
- Contact, as needed, the City Point of contact Jeffrey S. Moore, P.G., Manager, Oil & Gas Division, jsmoore@auroragov.org.

4.4. CPRO Watkins Operations Employees and Contract Designees

- Adhere to this Air Quality Plan.
- Monitor the performance of the facility equipment.
- Notification to Operations/Maintenance Superintendents and Environmental staff of any potential non-conformances.
- Provide relevant resources to enable completion of air emissions monitoring.

4.5. Contractors and Third-Party Emissions Monitoring Company

- Adhere to this Air Quality Plan.
- Perform air emissions monitoring in accordance with this Plan.
- Contact information of third-party emissions monitoring company:
Project Canary
Charlie Losche
303-653-6572
Charlie.losche@projectcanary.com

5. Process

5.1. Overview

CPRO is committed to ensuring that environmental impacts from emissions on air quality are to be minimized and managed from our operations. As an operator in Colorado, CPRO is required to comply with its obligations under the EPA, State of Colorado, and City of Aurora. These obligations include:

- Applying the relevant regulatory requirements to monitor the environmental performance of CPRO facilities.
- Reporting on environmental compliance as required by this Plan.
- CPRO must also comply with its own corporate requirements related to air quality.

5.2. Legal Requirements

The Federal Clean Air Act governs nationwide air quality, including key regulations that govern emissions from individual sources. The State of Colorado also governs air quality. These requirements include:

- Prevention of Significant Deterioration/ New Source Review (40 CFR part 51 subpart 1)
- Nonattainment provisions (40 CFR part 93, subpart A & B)
- New Source Performance Standards (40 CFR part 60)
- National Emission Standards for Hazardous Air Pollutants (40 CFR part 63)
- CDPHE reg 2, 3, 6, 7, 8 (5 CCR1001-4), (5 CCR 1001-5), (5 CCR1001-8), (5 CCR 1000-9) & (5CCR

1001-10)

- COGCC applicable standards (Rule 100-1200 series),

The State of Colorado, CDPHE, promulgated new requirements for leak detection utilizing optical gas imaging (OGI) in 2014. Two programs were created, one for leak detection and repair (LDAR) of fugitive emissions from components (valves, flanges, connectors) and another program that focuses on storage tanks and associated equipment (STEM). In 2017 CDPHE revised Regulation 7 to add an Enhanced Inspection and Repair program for pneumatic controllers to identify and reduce emissions. OGI inspection frequency is generally based on production. Larger producing facilities are inspected monthly and lower producing wells are inspected either quarterly, semi-annually, or annually.

All CPRO Watkins operations must ensure that processes and procedures are developed and implemented to ensure that all legislative requirements related to air quality are complied with. All future City/State/Federal standards and regulations will be complied with.

6. Best Management Practices

This section describes the Best Management Practices for CPRO Watkins operations related to:

1. Minimization of Emissions
2. Leak Detection and Repair
3. Ambient Air Sampling
4. Ozone Air Quality Action Days
5. Compliance
6. Reduced Emissions Completions
7. Combustion Devices

6.1. Minimization of Emissions

To protect air quality, the following will be required:

- Use of electric equipment and electric line power, for the Drilling Phase, starting June 1, 2020 if:
 - using electric line power is technically and economically feasible;
 - the Well Site is along Monaghan Road or west of Monaghan Road, and
 - sufficient electrical capacity and infrastructure exists to power a rig at the Well Site 6 months prior to drilling.
- Diesel engines are allowed onsite currently, and in the event of intermittent electric supply or other emergency.
- Use of electric line power for the Production Phase, to power permanent production equipment on Well Sites, such as motors and pump jacks, in order to mitigate noise and to reduce emissions. Other appropriate means to power equipment are currently utilized and may be used until electrical infrastructure becomes available. Reasonable efforts must be used to expedite use of electrical line power. CPRO does not have specifics regarding the future electricity delivery routes at this point. Electric line power to power compressors is not required.
- Use of Tier 2 hydraulic fracturing pumps. Use of Tier 4 fracturing pumps is required if they become technically and economically feasible and commercially available.
- Use of no-bleed continuous and intermittent pneumatic devices that do not bleed natural gas to the atmosphere. This requirement can be met by replacing natural gas with electricity or instrument air or routing the discharge emissions to a closed loop-system or process.
- Any combustion device, auto ignition system, recorder, vapor recovery device or other equipment used to meet the hydrocarbon destruction or control efficiency requirement shall be installed, calibrated, operated, and maintained in accordance with the manufacturer's recommendations, instructions, and operating manuals.

- Year-round compliance with the odor standards pursuant to COGCC and CDPHE regulations is achieved through combustion.
- Reduction of emissions from gas pipeline maintenance activities such as pigging or blowdowns. For planned maintenance activities involving the intentional venting of gas from a well tank, compressor or pipeline, provide forty-eight (48) hour advance written notice to the City of such proposed venting. Such notice shall identify the duration and nature of the venting event, a description as to why venting is necessary, a description of what vapors will likely be vented, what steps will be taken to limit the duration of venting, and what steps will be taken to minimize similar events in the future. If emergency venting is required, or if accidental venting occurs, provide such notice to the City of such event as soon as, but in no event longer than 24 hours from, the time of the event, with the information listed above and with an explanation as to the cause and how the event will be avoided in the future.
- Use of telemetric control and monitoring systems to detect when pilot lights on control devices are extinguished. Telemetric monitoring is also used for notification of pressure, temperature, and flow changes that may indicate issues or non-routine operation.
- Exhaust from all engines, motors, coolers, and all other equipment must be vented up.
- Operator agrees to continue participation in the CDPHE Environmental Leadership Program or other voluntary programs to encourage innovation in pollution control at well sites.
- Any permanent production tanks utilized during the Production Phase must be connected to a combustion device with 95% or better of total VOC destruction, provided that sufficient onsite gas is available to fuel a combustor if used or if alternative technology is available.

6.2. Leak Detection and Repair

Fugitive Emissions Management is essential to minimize fugitive emissions to prevent losses of hydrocarbon vapor at operating facilities. The control of fugitive emissions is a matter of minimizing the potential for large leaks and providing early detection and repair.

For the purpose of this plan, a leak is defined as an unintended emission, visible with an IR camera, and not associated with normal equipment operation.

Fugitive Emissions Management for Watkins Operations has three main components including operational practices and procedures and the leak detection program required by the Best Management Practices.

6.2.1 Informal Leak Detection During Normal Operations

Operational staff visit a site during the normal course of business wearing a personal gas detection monitor. Most sites are visited daily while some lower producing well sites are visited every 2-3 days if the operations center indicates all equipment is online. Personal monitors have the following alarms:

- LEL – 10%
- O₂ – 19.5% (low) and 23.5% (high)
- H₂S – 10 ppmV
- CO – 35 ppmV

6.2.2 CDPHE Air Permit compliance

As a component of CDPHE air permit compliance, Operations staff conduct internal monthly field inspections which include inspection of emission control equipment, i.e., flares, combustors, tanks, and truck loading equipment, to ensure proper operation and audio, visual, olfactory (AVO) or “look, listen, and smell” inspections to detect potential emissions.

6.2.3 Formal leak detection program

Performed in accordance with State and Federal requirements for both CDPHE, EPA and the City of Aurora Best Management Practices as outlined. CPRO will follow the LDAR program as defined in APCD Regulation 7 using modern leak detection technologies such as OGI for equipment used on the Well Site. CPRO's LDAR program will utilize the infrared light spectrum to perform the OGI inspections. Unless the APCD Regulation 7 frequency is more stringent, locations within City of Aurora city limits will adhere to a plan as follows:

- For the five (5) year period beginning with the start of the Production Phase for each New Well, CPRO shall conduct IR camera monitoring of all equipment at the respective Well Site based on the following minimum frequency:
 - Year 1 – Monthly
 - Year 2 – Quarterly
 - Year 3-5 – Semi-annually
- After the initial five (5) year period, CPRO will conduct annual IR camera monitoring until all wells on the Well Site are plugged and abandoned. The first inspection will occur within 30 days of the facility commencing production. Records of all leaks found, date the leaks were repaired, and the date the location is re-screened to verify that the leak has been repaired will be maintained.
- The LDAR inspection consists of surveying all equipment and wellheads with an IR Camera. If leaks are identified an attempt is made to repair, identifying, and repairing natural gas leaks from all equipment at the facility including wellheads utilizing the IR Camera.
- LDAR records will be maintained for five years and must be made available to the City upon request. Except when an emergency circumstance would necessitate an immediate repair, leaks must be repaired as quickly as practicable. If more than five (5) business days repair time is needed after a leak is discovered, an explanation of why more time is required must be submitted to the City. At least once per year, the City shall be notified five (5) business days prior to an LDAR inspection of its facilities to provide the City the opportunity to observe the inspection.

6.3 Ambient Air Sampling

CPRO shall conduct, as approved by the City, specific ambient air quality testing following specific practices and procedures. Technology will include:

Table 1. Canary S™ Sensor Specifications

Monitoring System	Sensor Type	Range	Max Resolution	Description
Continuous monitoring system	PID 10.6 eV sensor A total VOC indicator sensor with ppbV sensitivity	0 to 50 ppmV	1 ppbV	The PID sensor responds to VOC compounds of concern, including BTEX and aromatic hydrocarbons.
Continuous Monitoring System	NDIR sensor A total hydrocarbon indicator with ppmV sensitivity	0 to 50,000 ppmV	100 ppmV	The NDIR sensor responds to methane, ethane and heavier hydrocarbons that can be emitted from oil & gas operations. This sensor does not have ppbV sensitivity but responds to methane which has a 1.9 ppmV background level worldwide.
Continuous Monitoring System	Optical PM sensor	0~1000 µg/m3	1 µg/m3	The optical particulate matter sensor uses light to measure the size and quantity of particulate matter particles in the air. These sensors measure PM 1.0, PM 2.5 and PM 10.
Continuous Monitoring System	Meteorological Sensors	0-75 m/s (0-168mph) And 0-360 deg (directionally)	0.01 m/s and +/- 2deg	Temperature, Pressure, Humidity, Wind Speed, and Wind Direction.
Whole-air canister sample with EPA TO-15 analysis (both triggered and manually deployed)	Lab Analysis using GC- MS and/or GC-FID	-40 to 85 °C (-40 to 185°F) 0-100% RH 300-1250 hPa (mbar)	(+ or - 2.7 °F), +/-3% humidity, and +/-3% hPa (mbar)+	The whole-air canister samples are analyzed at a lab for a suite of VOC's under the EPA's Method TO-15. There is a total of 72 analytes, including benzene, toluene, ethylbenzene, xylenes, ethane, and methane.

6.3.1 Data quality objectives

Every Canary S unit individually undergoes lab calibration with a variety of NIST traceable scientific gases with specifically known concentrations. This allows every unit to have an adjustment applied to it to compensate for any manufacturing differences. The in-field baseline setting is then conducted once the units are deployed to adjust for site-specific conditions. Distinct algorithms are utilized to account for temperature, humidity and atmospheric pressure impacts on sensor readings. Such ambient condition adjustment algorithms were developed after extensive testing in climate control environmental chambers capable of a wide range of temperatures and humidity levels. The Canary S unit was originally designed for air quality monitoring on the Lunar Gateway, a space station designed to orbit Earth's moon slated for crewed inhabitants in 2024. As a result, the Canary S unit was required to meet NASA specifications and reliability standards.

The Canary enclosure meets the following certifications: UL508A, UL 50, CSA-C22.2 No. 14, NEMA 1,2,3,3R,4,4X,5,6,6P,12,13, UL94V-0 Flame rating, and UL746C-F1 UV and submersion testing. The original enclosure before modification had an IP68 rating. The rating after modification is reduced due to the designed addition of vents for airflow, but the unit maintains protections against inclement

weather when mounted correctly. The enclosure is UV-Stabilized Polycarbonate and the units have undergone extensive testing in a variety of outdoor environments to ensure robust functionality. Canary units have an operational temperature range of -20F to 140F (-28.89C to 60C).

6.3.2 Baseline Monitoring

At least 10 days (preferably more) prior to startup of oil & gas operations. For new pads, sampling will be performed prior to construction and for existing pads sampling will be completed prior to moving in any additional equipment. CPRO will deploy one or more air quality monitoring stations within 500' of the pad site. The background monitoring station(s) will be placed away from and upwind of the emission concern areas. These air quality monitoring stations include the same sensor technologies (PID, NDIR, optical PM) that will be used for the duration of the oil & gas activities, which are listed in Table 1. Vendor will also manually deploy at least one whole-air canister collecting over a 1-week sampling period prior to oil & gas operations at a site. The 6-liter canister will be fitted with a flow rate restrictor to ensure a consistent flow rate (0.44 cubic centimeters per minute (ccm)) into an evacuated canister throughout the entire 7-day sampling period.

6.3.3 Continuous Monitoring Station

Air quality monitoring system manufactured and serviced by Project Canary, Inc., headquartered in Denver, with manufacturing facilities in Golden, Colorado. Project Canary calibrates all systems in an environmental chamber after assembly and before shipping. On an annual basis and as needed, systems undergo in-field calibration, sensor replacement (if needed), and sensor drift analysis. The in-field calibration procedure is described below in 6.3.3.1 The continuous air monitoring stations are solar-powered and take measurements every second. These second measurements are output as minute averages. The base Canary system currently utilizes an NDIR methane sensor to detect for the qualitative presence of high levels of methane. The Canary system utilizes a 10.6 eV PID sensor for VOC indicator measurements. This PID sensor responds to part-per-billion level changes in over 100 VOCs, including BTEX. The output from this sensor is measured in change in concentration of VOCs in ppmV and ppbV. The Canary system autonomously triggers the collection of a whole-air canister sample based on the predetermined concentration threshold, current set at 7 ppmV on the VOC sensor which will then be collected by staff and sent to a certified lab for analysis.

The whole-air canister speciated sampling results are performed to find concentrations of 72 different analytes, including BTEX. As the VOC sensor detects for over 100 different hydrocarbons, aggregate concentration results from speciated sampling may not match the concentrations provided by the VOC sensor.

The EPA has not defined standards for micro sensors. CPRO will work to align with guidelines published by the EPA in their "Air Sensor Toolbox" and the South Coast Air Quality Management District—both of which are active in working to consolidate learning and information around small sensor use. PM measurements are presented as concentration values, as the small PM sensors are typically within 10% to 20% accuracy when compared to a reference station.

6.3.3.1 In Field Calibration Process

Backend alerts are designed to evaluate sensor readings with assessment frequency ranging from every 15 minutes to one month to confirm the proper cellular connection, as well as accurate and precise data, is being maintained. Sensor drift is routinely monitored using larger quantities of data to assess persistent patterns such as median values consistently rising over months. Such alerts, if breached, are then evaluated to assess whether weather seasonality or nearby activity can possibly be the cause. If backend alerts are triggered and observations are inconsistent with known and predictable ambient circumstances, Project Canary technicians will work to understand the likely cause and address the issue. If the cause

cannot be determined after investigation, in-field sensor calibration, and sensor replacement, Project Canary can work with CPRO to determine the cause. Backend alerts are designed to alarm if:

1. The unit falls offline and all date field stops reporting for no attributable reason
2. A sensor on the Canary stops reporting accurate values (determined by historical data)
3. A sensor on the Canary stops reporting or reports 0ppm values persistently

Following months of samples taken in the field, conditions such as inclement weather, nearby wildfires, and on pad activity can result in sensor drift away from the initial lab calibration over time. In order to counteract the in-field impacts on sensor readings, in-field calibrations are performed on an annual basis, or more frequently if necessary, to analyze sensor drift and efficacy of every unit. This in-field calibration process uses the same National Institute of Standards and Technology (NIST) Traceable gas premixtures (0.5ppm, 1ppm, 3ppm) and procedures that are used to calibrate units before being deployed into the field. If in-field calibration cannot bring readings to sufficient accuracy, units will be replaced with a recently lab calibrated unit.

Step by Step Calibration Process

1. Field Technician will directly work with the internal components of the device to begin the “calibration test” process
2. Field Technician exposes the VOC sensor to National Institute of Standards and Technology (NIST) Traceable gas premixture, with extremely accurate known concentration levels
3. Project Canary staff monitor the readings coming from the VOC sensors in real-time
4. Input gas type & concentrations used calibrate based on live readings
5. Re-expose the VOC sensor to scientific grades gas(es)
6. Ensure the readings come back accurate and precise – 0.5ppm, 1ppm, and 3ppm gases utilized again following recalibration
7. If the Canary S unit’s readings do not match the premixture, the Field Technician will replace the existing unit with a new unit.
8. Field Tech will take the existing unit back to the lab for further calibration and testing

6.3.4 Whole-Air Canister

Whole-air canister samples may be collected in two ways:

- An instantaneous sample triggered by the continuous monitoring station when an air-quality event of 7 ppmV or greater is detected. The evacuated 6 liter summa canister is opened following an aggregated minute level reading above the 7 ppmV threshold, and the canister is kept open for a full 60 second sampling period. At the end of 60 seconds, the canister’s valve is closed. Instantaneous alarms are sent to Project Canary and CPRO with the sampling period, and field staff are deployed to gather the canister for analysis.
- A week-long sample deployed manually by staff. The trigger for a week-long sample will be to obtain the baseline sample prior to startup of construction at the site or on an as needed basis. The week-long canister sample will slowly draw air into the canister over the course of a week, and then will be closed and removed for analysis at the end of seven (7) days. The 6 liter canister’s passive sampling intake valve is fitted with a flow rate restrictor to ensure a consistent flow rate (0.44 cc/min) into an evacuated canister throughout the entire 7-day sampling period.

Whole air canisters, whether triggered by the continuous monitoring station or deployed manually by staff, are collected and analyzed under the guidelines of EPA Method TO-15. Lab analysis of whole-air

canisters can take up to 3-4 weeks, meaning it may be 4 weeks before the results of a canister sample are available in the platform. Crestone plans to use Pace Analytical Labs to perform the TO-15 analysis, but reserves the right to utilize different laboratories as needed.

Whole air canisters are cleaned and analyzed per EPA TO-15 methods. The TO-15 method outlines requirements for chain-of-custody, defines how canister equipment is to be cleaned and calibrated, and how the analysis is to be performed. Additionally, CPRO will maintain records of the results of all TO-15 analysis for the time period specified in Section 6.3.5

Upon receipt of the EPA TO-15 sample results, CPRO will compare the results to CDPHE health guidelines. If any results are elevated or above health guidelines, the CPRO will implement an immediate TapRoot investigation and implement immediate corrective actions and process changes as warranted. In order to determine if results are above health guidelines a certified toxicologist will be consulted with. The CDPHE public health guidelines are provided as Appendix A – Re: Updated acute and chronic health guideline values for use in preliminary risk assessments (referred to as “FA2019 HGVs”). In general, grab samples will be compared to the acute guidelines and the 7-day samples will be compared to the chronic guidelines. The toxicologist will use this data to describe potential risk to public health FA2019HGV recommends.

6.3.5 Continuous Monitoring Plan

Continuous monitoring will be performed for the life of the well. Continuous means that sampling will be performed with indicator-level sensors once per second and loaded to the cloud each minute. Monitor downtime may occur due to equipment malfunction or other reasons. Monitor downtime will be reported on the periodic reports provided to the City. It should also be noted that small amounts of monitor downtime or data exclusion periods may be necessary to relocate the monitors during transitions from one phase to another phase.

- Periodic monitoring will be performed with whole-air canisters sampled on demand for the life of the facility as the alarm-level threshold of 7 ppmV is identified by the continuous monitoring system.
- Pre-Construction or pre-drilling baseline air quality testing – CPRO shall conduct baseline air sampling for a period of at least 7 days prior to any construction activities for any new Well Sites or prior to drilling additional wells on any Well Sites already constructed as of the Effective Date. CPRO shall conduct VOC baseline sampling using a continuous monitoring system that responds to methane and detects VOCs including BTEX. CPRO shall also conduct continuous monitoring for particulate matter. Deploying monitoring stations made up of continuous monitoring stations and whole-air canisters per siting principles in advance of any oil & gas operations in an area. Monitoring stations remain deployed for the duration of the oil & gas operations; including construction, drilling, completion, and production. As operational activity slows and a well site moves into production, CPRO may reduce the number of monitoring stations around the production site.
- Drilling Phase – CPRO shall conduct drilling rig sampling using a continuous monitoring station that responds to methane and detects VOCs including BTEX during the Drilling Phase at each Well Site. CPRO shall also conduct continuous monitoring for particulate matter.
- Completion Phase - CPRO shall conduct completion sampling using a continuous monitoring station that responds to methane and detects VOCs including BTEX during the Completion Phase and flowback at each Well Site. CPRO shall also conduct continuous monitoring for particulate matter.
- Production Phase – CPRO shall place on-site monitors capable of continuous monitoring, VOCs including BTEX in the parts per billion range, either automatically or manually. CPRO shall also conduct continuous monitoring for particulate matter and methane as described

in this plan.

- Seasonal, regional and meteorological influencers within the software platform are considered. Data is collected from monitoring stations, and bolstered with publicly available data from trusted sources, such as university research. With this expanded dataset, expected seasonal changes, temperature or humidity influence on sensors, and operational phase expectations, are incorporated into the analysis that identifies air quality events and separates oil & gas pad impact from other regional changes to air quality.
- Measurements are put into context, aiding in determining whether a change is expected due to regional or seasonal air quality patterns, or whether a change is a result of on-pad operational activities.
- The continuous monitoring system will have the ability to automatically trigger the collection of a summa canister capable of detecting VOCs including BTEX in the ppbV range and methane in parts per million range.
- Meteorological sensors on location will also record wind, temperature, humidity and pressure data to take into account seasonal and operational variations to help separate ambient background from local pad impacts.
- Continuous monitors will be capable of capturing and providing timely data to the City through a collection of quarterly. Reports shall include:
 - The month and year of the monitoring period,
 - A description of the monitored operations including the phase of operation (e.g., during pre-production operations) and activities occurring during the monitored period.
 - API number of the well(s)
 - Location of the operations, including latitude and longitude coordinates.
 - Any associated facility or equipment AIRS number(s).
 - The date and time of any monitoring equipment downtime.
 - Reports will be maintained for a period of 3 years, with the underlying data behind each report being available for 180 days from from date of report submission.
 - The City shall have full access and use of the collected data report following any phase. In addition, the City may require the Operator to use a third party to conduct additional air monitoring and analysis as needed in response to emergency events such as spill, process upsets, or accidental releases.
 - Alarm-level thresholds are evaluated in terms of VOC concentration thresholds. Currently, the alarms are upon a VOC concentration surpassing 3ppmV on a 5-minute rolling average, 1 ppmV on a 24-hour average, and 10ppmV on an instantaneous trigger. Alarms can be designed based on methane sensor readings, but due to the cross sensitivity of the sensor to light hydrocarbons and ability to be influenced by ambient conditions (i.e. humidity and temperature), alarms are more effectively engineered from the PID sensor data. VOC readings are accurate down to the parts per billion level, while the methane sensor's lower detection limit is substantially higher. By triggering alarms exclusively on VOCs, both Aurora and CPRO will have the ability to see emissions that may impact community health and environmental concerns much easier.
 - Alarms can be sent via email or SMStext, to any defined recipient. The alarm-level thresholds may be adjusted during the monitoring and in collaboration with City staff.
- Sample site locations rationale and data will include prevailing wind direction, comparative location of site operations, proximity to residential uses, proximity to off-site fueling stations, and possible nearby mobile source activity such as traffic. Upwind and downwind sampling near the well source will be considered and noted. Base principles that inform monitoring station site selection include:
 - Triangulate the concern areas with bias to prevailing wind directions. On a site-by-site basis. Units will be placed on pad in locations that can catch emissions that may

- drift toward areas where people live, work, and play.
- All units will come equipped with an anemometer in order to inform the direction of an emission from off pad that could influence measurements around the concern area including high traffic areas and fueling stations
- Avoid areas where wind swirls due to landscape or buildings.
- Select site spacing that may inform how pollutants move through an area.
- Account for prevailing wind direction, working to have a clear path to upwind emissions sources.
- Concern areas may include the targeted oil & gas operations as well as nearby pollutant sources, such as other industries or heavily trafficked roadways that could impact the measurements around the oil & gas pad.
- CPRO may evaluate other technologies throughout the life of the wells and may use other technologies if they are as effective in detecting target compounds.

6.3.6 Data Management and Response to Alarm.

Each air monitor is equipped with a modem that provides a cellular connection. The modem will transmit data to the Canary S™ website and dashboard where alarms will notify CPRO personnel if pollutant concentrations exceed the alarm-level thresholds.

All persistent alarms and any alarms for which notifications are received from the City of Aurora, will be considered a “critical alarm” and managed following CPRO’s CEM Data Evaluation and Response Procedure. This procedure is provided in Appendix C however, it is still under evaluation and may be subject to change based upon CDPHEs input. In the rare event that an alarm is received, and it is identified to be an emergency situation, the well would be remotely shut in. Otherwise upon receipt of an alarm or notification, CPRO field operations personnel would respond to the alarm by following the CEM Data Evaluation and Response Procedure.

If the investigation determines that the alarm was caused by a non-CPRO activity, a record of the findings will be entered in the operating log. Should the alarm be caused by a CPRO activity, CPRO personnel and/or its contractors will follow their existing procedures to eliminate and/or mitigate the source of the validated alarm. In the unlikely event that the event may impact the community, CPRO will follow its established Emergency Response procedures. Written response to the notification and/or alarm will be provided to the City regarding status and/or resolution will be provided within 24 hours.

6.3.7 Additional Monitoring Programs

- Air Modelling Study – As required by the Operator Agreement, CPRO shall contribute its proportionate share of collateral in a form of bond to the City for use in a dispersion model up to \$25,000.00. Operator shall post the bond ten days following execution of this Agreement by both parties.
- Optional City Program - If the City elects to take ownership of the ambient air monitoring program, CPRO may discontinue the program described in this Section, and the Operator shall contribute its proportionate share of collateral in the form of a bond to the City for use in sampling and monitoring. CPRO shall pay \$10,000 for every Well Site with a New Well drilled after the City elects to initiate the City Program and a yearly contribution which will be negotiated, but not to exceed \$100,000.
- As part of the City Program, the City may require CPRO to use a third party to conduct additional air monitoring and analysis as needed in response to emergency events such as spill, process upsets, or accidental releases.

6.4 Ozone Air Quality Action Days

CPRO shall respond to Air Quality Action Day advisories posted by the CDPHE for the Front Range Area by implementing the Crestone Peak Resources Ozone Action Plan (Action Plan). Alarms are received by Air Quality staff and disseminated to all CPRO employees. Employees are instructed to follow the Action Plan and reduce emissions wherever possible. Recommendations in the Action Plan include, but are not limited to:

- Minimize vehicle and engine idling
- Reduce truck traffic and worker traffic
- Delay vehicle refueling
- Postpone construction activities to the maximum extent practicable.

Within 30 days following the conclusion of each annual Ozone Air Quality Action Day season, Operator shall submit a report to the City that details which measures it implemented during any Action Day advisories.

6.5 Compliance

CPRO shall submit quarterly reports to the City of Aurora certifying:

- Compliance with these air quality requirements and documenting any deviations from the requirements of the OA, including the date and duration of each such deviation and a compliance plan and schedule to achieve compliance.
- Equipment at the Well Sites continues to operate within its design parameters, and if not, what steps will be taken to modify the equipment to enable the equipment to operate within its design parameters.
- Truth, accuracy, and completeness of the quarterly report by providing signature of the Responsible Official, as defined by CDPHE. The Operator shall also provide the City with a copy of any self-reporting submissions that the Operator provides to the CDPHE due to any incidence of non-compliance with any CDPHE air quality rules or regulations at the Well Sites.
- At a minimum these reports will be submitted within 60 days of the end of the quarter and contain the following information;
- For each automatically triggered or manually collected grab sample, the quarterly compliance report should include:
 - The monitoring location ID.
 - The type of sample (triggered instantaneous grab or week-long manual grab).
 - The start date and time of sampling. For week-long samples, also include the end date and time.
 - A table with the concentrations for each target pollutant. If a target pollutant is below the detection limit, the value should indicate that along with the detection limit for that compound (e.g., <1 ppbv).
- For the continuous Canary monitoring system, provide a summary of data that includes quarterly average concentration (ppmV), highest hourly concentration (ppmV), and summary of alarm events (date, time, trigger threshold, cause, duration and corrective actions taken).

6.6 Reduced Emissions Completions

CPRO shall comply with EPA Reduced Emission Completion rules for oil and gas wells.

6.7 Combustion Devices

To the extent flares, thermal oxidizers, or combustion devices are utilized, all such flares shall be designed and operated as follows:

- A combustion device must be available at each Well Site during the entire Production Phase for maintenance or emergencies only.

- The combustion device must be fired with natural gas and designed to operate with a 98% or higher hydrocarbon destruction efficiency.
- The combustion device must be designed and operated in a manner that will ensure no visible emissions during normal operation. Visible emissions mean observations of smoke for any period or periods of duration greater than or equal to one minute in any 15-minute period during normal operation, pursuant to EPA Method 22. Visible emissions do not include radiant energy or water vapor.
- The combustion device must always be operated with a flame present when emissions may be vented to it, or other mechanism that does not allow uncontrolled emissions.
- All combustion devices must be equipped with an auto-igniter unless manned while in use.

7. Compliance Assurance

CPRO Environmental staff will develop an internal list of requirements in our EHS&R Management System to implement the Operator Agreement and Best Management Practices. The requirements will be communicated to impacted personnel supporting the Watkins operations.

Requirements of the Operator Agreement and Best Management Practices will be incorporated into compliance plans. A list of tasks and/or roles and responsibilities will also be developed to ensure compliance with obligations. Personnel responsible for completing tasks will be made aware of their responsibilities and be trained appropriately. Defined tasks will be incorporated into Watkins processes. To ensure timely compliance of requirements and tasks, reviews will be conducted to assess compliance status associated with these compliance activities.

8. References

- Oil and Gas Operator Agreement
- Best Management Practices
- CEM Data Evaluation and Response Procedure – outlines CPRO response requirements to Canary S™ alarms
- Crestone Peak Resources Ozone Action Plan – outlines CPRO response to CDPHE announced Air Quality Action Days
- Appendix A - Re: Updated acute and chronic health guideline values for use in preliminary risk assessments (referred to as “FA2019 HGVs”)
- Appendix B –
 - Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air Second Edition Compendium Method TO-15
 - PACE Analytical TO-15 Procedure
- Appendix C - CEM Data Evaluation and Response Procedure
- Appendix D – Canary System Info

APPENDIX A



Dedicated to protecting and improving the health and environment of the people of Colorado

Date: September 20, 2019 (effective September 20, 2019)
To: Interested Parties
From: Oil and Gas Health Information Response Program, Toxicology and Risk Assessment Section, Colorado Department of Public Health and Environment (CDPHE)

Re: Updated acute and chronic health guideline values for use in preliminary risk assessments (referred to as “FA2019 HGVs”)

Health guideline values (HGVs) were reviewed in the fall of 2019 based on the previously published¹ tiered approach (Table 1). These new values will be used in preliminary risk assessments starting September 20, 2019 and referred to as “FA2019 HGVs” where necessary for clarity. Previous HGVs will not be used after September 20, 2019 without approval from CDPHE’s state toxicologist. All chemicals associated with oil and gas operations are not included in this memo. Rather, the chemicals included here are those most commonly identified to be emitted from oil and gas operations¹.

HGVs are determined by the US Environmental Protection Agency and/or similar federal and state agencies for both acute and chronic exposures to volatile organic compounds (VOCs). A health guideline value is defined by the US Environmental Protection Agency as the exposure level that is likely to be without appreciable risk of adverse non-cancer health effects in an exposed population, including sensitive individuals (Table 2). Acute or short-term exposures represent intermittent exposures that could occur repeatedly for a few hours to a few days. Chronic or long term exposures assume a person is breathing the air continuously (24 hours per day, 365 days per year) for a lifetime (i.e. 70 years).

In order to estimate the risk of developing cancer from VOCs, the US Environmental Protection Agency develops inhalation unit risk factors. We compare each inhalation unit risk factor to an exposure concentration in order to estimate excess cancer risk from exposure to that concentration over a lifetime. The US Environmental Protection Agency typically considers risks below 1×10^{-6} to be so small as to be negligible and uses a cancer risk of one in a million (1×10^{-6}) as a regulatory goal. In general, risk levels below one in ten thousand (100 in one million; 1×10^{-4}) are considered low risk and within the US Environmental Protection Agency’s “acceptable” excess cancer risk range. VOCs with inhalation unit risk factors, as well as the air concentrations associated with various risks, are shown in Table 3.

Risk assessment is complicated and requires experience with the application and interpretation of these values and related calculations. Please strongly consider consulting either with us or with a professional risk assessor. Please contact us at cdphe_oghealth@state.co.us with additional questions or to request assistance.

¹ McMullin TS, Bamber AM, Bon D, Vigil DI, Van Dyke M. 2018. Exposures and Health Risks from Volatile Organic Compounds in Communities Located near Oil and Gas Exploration and Production Activities in Colorado (U.S.A.). *Int. J. Environ. Res. Public Health* 15(7), 1500: 1-19. doi.org/10.3390/ijerph15071500

Table 1. Tiered selection approach for health guideline values used in a preliminary risk assessment.

Acute	Chronic
1. ATSDR Acute Inhalation MRL	1. US EPA IRIS Chronic RfC or IUR
2. CalEPA Acute Inhalation REL	2. ATSDR Chronic Inhalation MRL
3. TCEQ Acute AMCV	3. PPRTV
4. DOE Protective Action Criteria	4. CalEPA Chronic Inhalation REL or IUR
5. Surrogate	5. TCEQ Chronic AMCV
	6. Surrogate

US EPA (US Environmental Protection Agency); ATSDR (US Agency for Toxic Chemicals and Disease Registry); PPRTV (US EPA Provisional Peer Reviewed Toxicity Values); CalEPA (California Office of Environmental Health Hazard Assessment); TCEQ (Texas Commission on Environmental Quality); DOE (Department of Energy); ppbV (parts per billion by volume); MRL (Minimum Risk Level); REL (Reference Exposure Level); AMCV (Air Monitoring Comparison Values); RfC (Reference Concentration); IUR (Inhalation Unit Risk Factor); "--" (no value has been established).

Table 2. List of substances and non-cancer acute and chronic health guideline values.

Substance (Synonym)	CAS #	Health Guideline Values (ppbV)			
		Acute	Source	Chronic	Source
1-Butene	106-98-9	27,000	TCEQ	2,300	TCEQ
1-Hexene	592-41-6	500	TCEQ	50	TCEQ
1-Pentene	109-67-1	12,000	TCEQ	560	TCEQ
1,2,3-Trimethylbenzene	526-73-8	3,000	TCEQ	12.2	US EPA
1,2,4-Trimethylbenzene	95-63-6	3,000	TCEQ	12.2	US EPA
1,3,5-Trimethylbenzene	108-67-8	3,000	TCEQ	12.2	US EPA
2-Methyl-2-butene	513-35-9	12,000	TCEQ	560	TCEQ
2-Methylheptane	592-27-8	4,100	TCEQ	380	TCEQ
2-Methylhexane	591-76-4	8,300	TCEQ	2,200	TCEQ
2-Methylpentane	107-83-5	5,400	TCEQ	190	TCEQ
2,2-Dimethylbutane	75-83-2	5,400	TCEQ	190	TCEQ
2,2,4-Trimethylpentane	540-84-1	4,100	TCEQ	380	TCEQ
2,3-Dimethylbutane	79-29-8	5,400	TCEQ	190	TCEQ
2,3-Dimethylpentane	565-59-3	8,300	TCEQ	2,200	TCEQ

(continued)

Substance (Synonym)	CAS #	Health Guideline Values (ppbV)			
		Acute	Source	Chronic	Source
2,3,4-Trimethylpentane	565-75-3	4,100	TCEQ	380	TCEQ
2,4-Dimethylpentane	108-08-7	8,300	TCEQ	2,200	TCEQ
3-Methylheptane	589-81-1	4,100	TCEQ	380	TCEQ
3-Methylhexane	589-34-4	8,300	TCEQ	2,200	TCEQ
3-Methylpentane	96-14-0	5,400	TCEQ	190	TCEQ
Acetylene	74-86-2	25,000	TCEQ	2,500	TCEQ
Benzene	71-43-2	9	ATSDR	9 and 3	US EPA and ATSDR ¹
cis-1,3-dimethylcyclohexane	638-04-0	4,000	SU ²	400	SU ²
cis-2-Butene	590-18-1	15,000	TCEQ	700	TCEQ
cis-2-Pentene	627-20-3	12,000	TCEQ	560	TCEQ
Cyclohexane	110-82-7	1,000	TCEQ	1,743	US EPA
Cyclopentane	287-92-3	5,900	TCEQ	590	TCEQ
Ethane	74-84-0	Simple Asphyxiant	-	-	-
Ethylbenzene	100-41-4	5,000	ATSDR	230	US EPA
Ethylcyclohexane	108-87-2	4,000	SU ²	400	SU ²
Ethylene	74-85-1	500,000	TCEQ	5,300	TCEQ
Isobutane	75-28-5	33,000	TCEQ	10,000	TCEQ
Isopentane (2-methylbutane)	78-78-4	68,000	TCEQ	8,100	TCEQ
Isoprene	78-79-5	1,400	TCEQ	140	TCEQ
Isopropylbenzene (cumene)	98-82-8	510	TCEQ	81.4	US EPA
m-Diethylbenzene	141-93-5	450	TCEQ	45	TCEQ
m-Ethyltoluene	620-14-4	250	TCEQ	25	TCEQ

(continued)

Substance (Synonym)	CAS #	Health Guideline Values (ppbV)			
		Acute	Source	Chronic	Source
m-Xylene/p-Xylene	108-38-3/106-42-3	2,000	ATSDR	23	US EPA
Methanol	67-56-1	21,400	CalEPA	15,300	US EPA
Methylcyclohexane	108-87-2	4,000	TCEQ	400	TCEQ
Methylcyclopentane	96-37-7	750	TCEQ	75	TCEQ
n-Butane	106-97-8	92,000	TCEQ	10,000	TCEQ
n-Decane	124-18-5	1,000	TCEQ	190	TCEQ
n-Dodecane	112-40-3	1,720	DOE	3.8	SU ³
n-Heptane	142-82-5	8,300	TCEQ	97.6	PPRTV
n-Hexane	110-54-3	5,400	TCEQ	198.6	US EPA
n-Nonane	111-84-2	3,000	TCEQ	3.8	PPRTV
n-Octane	111-65-9	4,100	TCEQ	380	TCEQ
n-Pentane	109-66-0	68,000	TCEQ	338.9	PPRTV
n-Propylbenzene	103-65-1	510	TCEQ	51	TCEQ
n-Undecane	1120-21-4	550	TCEQ	55	TCEQ
o-Ethyltoluene (2-ethyltoluene)	611-14-3	250	TCEQ	25	TCEQ
o-Xylene	95-47-6	2,000	ATSDR	23	US EPA
p-Diethylbenzene (1,4-diethylbenzene)	105-05-5	450	TCEQ	45	TCEQ
p-Ethyltoluene (4-ethyltoluene)	622-96-8	250	TCEQ	25	TCEQ
Propane	74-98-6	Simple Asphyxiant	-	-	-
Propylene (propene)	115-07-1	Simple Asphyxiant	-	1,743	CalEPA
Styrene	100-42-5	5,000	ATSDR	234.8	US EPA

(continued)

Substance (Synonym)	CAS #	Health Guideline Values (ppbV)			
		Acute	Source	Chronic	Source
Toluene	108-88-3	2,000	ATSDR	1,327	US EPA
trans-1,2-dimethylcyclohexane	6876-23-9	4,000	SU ²	400	SU ²
trans-1,3-dimethylcyclohexane	2207-03-6	4,000	SU ²	400	SU ²
trans-2-Butene	624-64-6	15,000	TCEQ	700	TCEQ
trans-2-Pentene	646-04-8	12,000	TCEQ	560	TCEQ

US EPA (US Environmental Protection Agency); ATSDR (US Agency for Toxic Chemicals and Disease Registry); PPRTV (US EPA Provisional Peer Reviewed Toxicity Values); CalEPA (California Office of Environmental Health Hazard Assessment); TCEQ (Texas Commission on Environmental Quality); SU = Surrogate; DOE (Department of Energy); ppbV (parts per billion by volume); “-” (no value has been established). ¹Both the US EPA inhalation reference concentration and the ATSDR inhalation minimum risk level will be considered when evaluating this substance to best protect human health from non-cancer effects. ²Value surrogated from methylcyclohexane as described in previously published tiered approach because no chronic value was available. ³Value surrogated from n-nonane chronic PPRTV because no chronic value was available.

Table 3. List of substances and measured concentrations for each cancer risk level.

Substance	CAS #	Inhalation Unit Risk Factor (per $\mu\text{g}/\text{m}^3$) (Source)	Cancer Risk Estimate		
			Air Concentration at 1 in a million (ppbV)	Air Concentration at 10 in a million (ppbV)	Air Concentration at 100 in a million (ppbV)
Benzene	71-43-2	7.8×10^{-6} (US EPA)	0.040	0.40	4.0
Ethylbenzene	100-41-4	2.50×10^{-6} (CalEPA)	0.092	0.92	9.2
Isoprene	78-79-5	2.20×10^{-8} (TCEQ)	16	163	1631

A one in a million cancer risk (1×10^{-6}) is considered a minimal cancer risk. A 100 in a million cancer risk (1×10^{-4}) is considered the upper limit of the EPA “acceptable” range. Risk estimates were determined by using each inhalation unit risk factor. US EPA (US Environmental Protection Agency); CalEPA (California Office of Environmental Health Hazard Assessment); TCEQ (Texas Commission on Environmental Quality); ppbV (parts per billion by volume).

**Compendium of Methods
for the Determination of
Toxic Organic Compounds
in Ambient Air**

Second Edition

Compendium Method TO-15

**Determination Of Volatile Organic
Compounds (VOCs) In Air Collected In
Specially-Prepared Canisters And
Analyzed By Gas Chromatography/
Mass Spectrometry (GC/MS)**

**Center for Environmental Research Information
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268**

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DISCLAIMER

This Compendium has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

METHOD TO-15

Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)

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METHOD TO-15

Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)

1. Scope

1.1 This method documents sampling and analytical procedures for the measurement of subsets of the 97 volatile organic compounds (VOCs) that are included in the 189 hazardous air pollutants (HAPs) listed in Title III of the Clean Air Act Amendments of 1990. VOCs are defined here as organic compounds having a vapor pressure greater than 10^{-1} Torr at 25°C and 760 mm Hg. Table 1 is the list of the target VOCs along with their CAS number, boiling point, vapor pressure and an indication of their membership in both the list of VOCs covered by Compendium Method TO-14A (1) and the list of VOCs in EPA's Contract Laboratory Program (CLP) document entitled: *Statement-of-Work (SOW) for the Analysis of Air Toxics from Superfund Sites (2)*.

Many of these compounds have been tested for stability in concentration when stored in specially-prepared canisters (see Section 8) under conditions typical of those encountered in routine ambient air analysis. The stability of these compounds under all possible conditions is not known. However, a model to predict compound losses due to physical adsorption of VOCs on canister walls and to dissolution of VOCs in water condensed in the canisters has been developed (3). Losses due to physical adsorption require only the establishment of equilibrium between the condensed and gas phases and are generally considered short term losses, (i.e., losses occurring over minutes to hours). Losses due to chemical reactions of the VOCs with cocollected ozone or other gas phase species also account for some short term losses. Chemical reactions between VOCs and substances inside the canister are generally assumed to cause the gradual decrease of concentration over time (i.e., long term losses over days to weeks). Loss mechanisms such as aqueous hydrolysis and biological degradation (4) also exist. No models are currently known to be available to estimate and characterize all these potential losses, although a number of experimental observations are referenced in Section 8. Some of the VOCs listed in Title III have short atmospheric lifetimes and may not be present except near sources.

1.2 This method applies to ambient concentrations of VOCs above 0.5 ppbv and typically requires VOC enrichment by concentrating up to one liter of a sample volume. The VOC concentration range for ambient air in many cases includes the concentration at which continuous exposure over a lifetime is estimated to constitute a 10^{-6} or higher lifetime risk of developing cancer in humans. Under circumstances in which many hazardous VOCs are present at 10^{-6} risk concentrations, the total risk may be significantly greater.

1.3 This method applies under most conditions encountered in sampling of ambient air into canisters. However, the composition of a gas mixture in a canister, under unique or unusual conditions, will change so that the sample is known not to be a true representation of the ambient air from which it was taken. For example, low humidity conditions in the sample may lead to losses of certain VOCs on the canister walls, losses that would not happen if the humidity were higher. If the canister is pressurized, then condensation of water from high humidity samples may cause fractional losses of water-soluble compounds. Since the canister surface area is limited, all gases are in competition for the available active sites. Hence an absolute storage stability cannot be assigned to a specific gas. Fortunately, under conditions of normal usage for sampling ambient air, most VOCs can be recovered from canisters near their original concentrations after storage times of up to thirty days (see Section 8).

1.4 Use of the Compendium Method TO-15 for many of the VOCs listed in Table 1 is likely to present two difficulties: (1) what calibration standard to use for establishing a basis for testing and quantitation, and (2) how

to obtain an audit standard. In certain cases a chemical similarity exists between a thoroughly tested compound and others on the Title III list. In this case, what works for one is likely to work for the other in terms of making standards. However, this is not always the case and some compound standards will be troublesome. The reader is referred to the Section 9.2 on standards for guidance. Calibration of compounds such as formaldehyde, diazomethane, and many of the others represents a challenge.

1.5 Compendium Method TO-15 should be considered for use when a subset of the 97 Title III VOCs constitute the target list. Typical situations involve ambient air testing associated with the permitting procedures for emission sources. In this case sampling and analysis of VOCs is performed to determine the impact of dispersing source emissions in the surrounding areas. Other important applications are prevalence and trend monitoring for hazardous VOCs in urban areas and risk assessments downwind of industrialized or source-impacted areas.

1.6 Solid adsorbents can be used in lieu of canisters for sampling of VOCs, provided the solid adsorbent packings, usually multisorbent packings in metal or glass tubes, can meet the performance criteria specified in Compendium Method TO-17 which specifically addresses the use of multisorbent packings. The two sample collection techniques are different but become the same upon movement of the sample from the collection medium (canister or multisorbent tubes) onto the sample concentrator. Sample collection directly from the atmosphere by automated gas chromatographs can be used in lieu of collection in canisters or on solid adsorbents.

2. Summary of Method

2.1 The atmosphere is sampled by introduction of air into a specially-prepared stainless steel canister. Both subatmospheric 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 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.

2.3 Upon receipt at the laboratory, the canister tag data is recorded and the canister is stored until analysis. Storage times of up to thirty days have been demonstrated for many of the VOCs (5).

2.4 To analyze the sample, a known volume of sample is directed from the canister through a solid multisorbent concentrator. A portion of the water vapor in the sample breaks through the concentrator during sampling, to a degree depending on the multisorbent composition, duration of sampling, and other factors. Water content of the sample can be further reduced by dry purging the concentrator with helium while retaining target compounds. After the concentration and drying steps are completed, the VOCs are thermally desorbed, entrained in a carrier gas stream, and then focused in a small volume by trapping on a reduced temperature trap or small volume multisorbent trap. The sample is then released by thermal desorption and carried onto a gas chromatographic column for separation.

As a simple alternative to the multisorbent/dry purge water management technique, the amount of water vapor in the sample can be reduced below any threshold for affecting the proper operation of the analytical system by

reducing the sample size. For example, a small sample can be concentrated on a cold trap and released directly to the gas chromatographic column. The reduction in sample volume may require an enhancement of detector sensitivity.

Other water management approaches are also acceptable as long as their use does not compromise the attainment of the performance criteria listed in Section 11. A listing of some commercial water management systems is provided in Appendix A. One of the alternative ways to dry the sample is to separate VOCs from condensate on a low temperature trap by heating and purging the trap.

2.5 The analytical strategy for Compendium Method TO-15 involves using a high resolution gas chromatograph (GC) coupled to a mass spectrometer. If the mass spectrometer is a linear quadrupole system, it is operated either by continuously scanning a wide range of mass to charge ratios (SCAN mode) or by monitoring select ion monitoring mode (SIM) of compounds on the target list. If the mass spectrometer is based on a standard ion trap design, only a scanning mode is used (note however, that the Selected Ion Storage (SIS) mode for the ion trap has features of the SIM mode). Mass spectra for individual peaks in the total ion chromatogram are examined with respect to the fragmentation pattern of ions corresponding to various VOCs including the intensity of primary and secondary ions. The fragmentation pattern is compared with stored spectra taken under similar conditions, in order to identify the compound. For any given compound, the intensity of the primary fragment is compared with the system response to the primary fragment for known amounts of the compound. This establishes the compound concentration that exists in the sample.

Mass spectrometry is considered a more definitive identification technique than single specific detectors such as flame ionization detector (FID), electron capture detector (ECD), photoionization detector (PID), or a multidetector arrangement of these (see discussion in Compendium Method TO-14A). The use of both gas chromatographic retention time and the generally unique mass fragmentation patterns reduce the chances for misidentification. If the technique is supported by a comprehensive mass spectral database and a knowledgeable operator, then the correct identification and quantification of VOCs is further enhanced.

3. Significance

3.1 Compendium Method TO-15 is significant in that it extends the Compendium Method TO-14A description for using canister-based sampling and gas chromatographic analysis in the following ways:

- Compendium Method TO-15 incorporates a multisorbent/dry purge technique or equivalent (see Appendix A) for water management thereby addressing a more extensive set of compounds (the VOCs mentioned in Title III of the CAAA of 1990) than addressed by Compendium Method TO-14A. Compendium Method TO-14A approach to water management alters the structure or reduces the sample stream concentration of some VOCs, especially water-soluble VOCs.
- Compendium Method TO-15 uses the GC/MS technique as the only means to identify and quantitate target compounds. The GC/MS approach provides a more scientifically-defensible detection scheme which is generally more desirable than the use of single or even multiple specific detectors.
- In addition, Compendium Method TO-15 establishes method performance criteria for acceptance of data, allowing the use of alternate but equivalent sampling and analytical equipment. There are several new and viable commercial approaches for water management as noted in Appendix A of this method on which to base a VOC monitoring technique as well as other approaches to sampling (i.e., autoGCs and solid

adsorbents) that are often used. This method lists performance criteria that these alternatives must meet to be acceptable alternatives for monitoring ambient VOCs.

- Finally, Compendium Method TO-15 includes enhanced provisions for inherent quality control. The method uses internal analytical standards and frequent verification of analytical system performance to assure control of the analytical system. This more formal and better documented approach to quality control guarantees a higher percentage of good data.

3.2 With these features, Compendium Method TO-15 is a more general yet better defined method for VOCs than Compendium Method TO-14A. As such, the method can be applied with a higher confidence to reduce the uncertainty in risk assessments in environments where the hazardous volatile gases listed in the Title III of the Clean Air Act Amendments of 1990 are being monitored. An emphasis on risk assessments for human health and effects on the ecology is a current goal for the U.S. EPA.

4. Applicable Documents

4.1 ASTM Standards

- **Method D1356** *Definitions of Terms Relating to Atmospheric Sampling and Analysis.*
- **Method E260** *Recommended Practice for General Gas Chromatography Procedures.*
- **Method E355** *Practice for Gas Chromatography Terms and Relationships.*
- **Method D5466** *Standard Test Method of Determination of Volatile Organic Compounds in Atmospheres (Canister Sampling Methodology).*

4.2 EPA Documents

- *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II*, U. S. Environmental Protection Agency, EPA-600/R-94-038b, May 1994.
- *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air*, U. S. Environmental Protection Agency, EPA-600/4-83-027, June 1983.
- *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-14, Second Supplement*, U. S. Environmental Protection Agency, EPA-600/4-89-018, March 1989.
- *Statement-of-Work (SOW) for the Analysis of Air Toxics from Superfund Sites*, U. S. Environmental Protection Agency, Office of Solid Waste, Washington, D.C., Draft Report, June 1990.
- *Clean Air Act Amendments of 1990*, U. S. Congress, Washington, D.C., November 1990.

5. Definitions

[Note: Definitions used in this document and any user-prepared standard operating procedures (SOPs) should be consistent with ASTM Methods D1356, E260, and E355. Aside from the definitions given below, all pertinent abbreviations and symbols are defined within this document at point of use.]

5.1 Gauge Pressure—pressure measured with reference to the surrounding atmospheric pressure, usually expressed in units of kPa or psi. Zero gauge pressure is equal to atmospheric (barometric) pressure.

5.2 Absolute Pressure—pressure measured with reference to absolute zero pressure, usually expressed in units of kPa, or psi.

5.3 Cryogen—a refrigerant used to obtain sub-ambient temperatures in the VOC concentrator and/or on front of the analytical column. Typical cryogenes are liquid nitrogen (bp -195.8°C), liquid argon (bp -185.7°C), and liquid CO_2 (bp -79.5°C).

5.4 Dynamic Calibration—calibration of an analytical system using calibration gas standard concentrations in a form identical or very similar to the samples to be analyzed and by introducing such standards into the inlet of the sampling or analytical system from a manifold through which the gas standards are flowing.

5.5 Dynamic Dilution—means of preparing calibration mixtures in which standard gas(es) from pressurized cylinders are continuously blended with humidified zero air in a manifold so that a flowing stream of calibration mixture is available at the inlet of the analytical system.

5.6 MS-SCAN—mass spectrometric mode of operation in which the gas chromatograph (GC) is coupled to a mass spectrometer (MS) programmed to SCAN all ions repeatedly over a specified mass range.

5.7 MS-SIM—mass spectrometric mode of operation in which the GC is coupled to a MS that is programmed to scan a selected number of ions repeatedly [i.e., selected ion monitoring (SIM) mode].

5.8 Qualitative Accuracy—the degree of measurement accuracy required to correctly identify compounds with an analytical system.

5.9 Quantitative Accuracy—the degree of measurement accuracy required to correctly measure the concentration of an identified compound with an analytical system with known uncertainty.

5.10 Replicate Precision—precision determined from two canisters filled from the same air mass over the same time period and determined as the absolute value of the difference between the analyses of canisters divided by their average value and expressed as a percentage (see Section 11 for performance criteria for replicate precision).

5.11 Duplicate Precision—precision determined from the analysis of two samples taken from the same canister. The duplicate precision is determined as the absolute value of the difference between the canister analyses divided by their average value and expressed as a percentage.

5.12 Audit Accuracy—the difference between the analysis of a sample provided in an audit canister and the nominal value as determined by the audit authority, divided by the audit value and expressed as a percentage (see Section 11 for performance criteria for audit accuracy).

6. Interferences and Contamination

6.1 Very volatile compounds, such as chloromethane and vinyl chloride can display peak broadening and co-elution with other species if the compounds are not delivered to the GC column in a small volume of carrier gas. Refocusing of the sample after collection on the primary trap, either on a separate focusing trap or at the head of the gas chromatographic column, mitigates this problem.

6.2 Interferences in canister samples may result from improper use or from contamination of: (1) the canisters due to poor manufacturing practices, (2) the canister cleaning apparatus, and (3) the sampling or analytical system. Attention to the following details will help to minimize the possibility of contamination of canisters.

6.2.1 Canisters should be manufactured using high quality welding and cleaning techniques, and new canisters should be filled with humidified zero air and then analyzed, after “aging” for 24 hours, to determine cleanliness. The cleaning apparatus, sampling system, and analytical system should be assembled of clean, high quality components and each system should be shown to be free of contamination.

6.2.2 Canisters should be stored in a contaminant-free location and should be capped tightly during shipment to prevent leakage and minimize any compromise of the sample.

6.2.3 Impurities in the calibration dilution gas (if applicable) and carrier gas, organic compounds out-gassing from the system components ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running humidified zero air blanks. The use of non-chromatographic grade stainless steel tubing, non-PTFE thread sealants, or flow controllers with Buna-N rubber components must be avoided.

6.2.4 Significant contamination of the analytical equipment can occur whenever samples containing high VOC concentrations are analyzed. This in turn can result in carryover contamination in subsequent analyses. Whenever a high concentration (>25 ppbv of a trace species) sample is encountered, it should be followed by an analysis of humid zero air to check for carry-over contamination.

6.2.5 In cases when solid sorbents are used to concentrate the sample prior to analysis, the sorbents should be tested to identify artifact formation (see Compendium Method TO-17 for more information on artifacts).

7. Apparatus and Reagents

[Note: Compendium Method To-14A list more specific requirements for sampling and analysis apparatus which may be of help in identifying options. The listings below are generic.]

7.1 Sampling Apparatus

[Note: Subatmospheric pressure and pressurized canister sampling systems are commercially available and have been used as part of U.S. Environmental Protection Agency's Toxic Air Monitoring Stations (TAMS), Urban Air Toxic Monitoring Program (UATMP), the non-methane organic compound (NMOC) sampling and analysis program, and the Photochemical Assessment Monitoring Stations (PAMS).]

7.1.1 Subatmospheric Pressure (see Figure 1, without metal bellows type pump).

7.1.1.1 Sampling Inlet Line. Stainless steel tubing to connect the sampler to the sample inlet.

7.1.1.2 Sample Canister. Leak-free stainless steel pressure vessels of desired volume (e.g., 6 L), with valve and specially prepared interior surfaces (see Appendix B for a listing of known manufacturers/resellers of canisters).

7.1.1.3 Stainless Steel Vacuum/Pressure Gauges. Two types are required, one capable of measuring vacuum (–100 to 0 kPa or 0 to - 30 in Hg) and pressure (0–206 kPa or 0–30 psig) in the sampling system and a second type (for checking the vacuum of canisters during cleaning) capable of measuring at 0.05 mm Hg (see Appendix B) within 20%. Gauges should be tested clean and leak tight.

7.1.1.4 Electronic Mass Flow Controller. Capable of maintaining a constant flow rate ($\pm 10\%$) over a sampling period of up to 24 hours and under conditions of changing temperature (20–40°C) and humidity.

7.1.1.5 Particulate Matter Filter. 2- μm sintered stainless steel in-line filter.

7.1.1.6 Electronic Timer. For unattended sample collection.

7.1.1.7 Solenoid Valve. Electrically-operated, bi-stable solenoid valve with Viton® seat and O-rings. A Skinner Magnelatch valve is used for purposes of illustration in the text (see Figure 2).

7.1.1.8 Chromatographic Grade Stainless Steel Tubing and Fittings. For interconnections. All such materials in contact with sample, analyte, and support gases prior to analysis should be chromatographic grade stainless steel or equivalent.

7.1.1.9 Thermostatically Controlled Heater. To maintain above ambient temperature inside insulated sampler enclosure.

7.1.1.10 Heater Thermostat. Automatically regulates heater temperature.

7.1.1.11 Fan. For cooling sampling system.

7.1.1.12 Fan Thermostat. Automatically regulates fan operation.

7.1.1.13 Maximum-Minimum Thermometer. Records highest and lowest temperatures during sampling period.

7.1.1.14 Stainless Steel Shut-off Valve. Leak free, for vacuum/pressure gauge.

7.1.1.15 Auxiliary Vacuum Pump. Continuously draws air through the inlet manifold at 10 L/min. or higher flow rate. Sample is extracted from the manifold at a lower rate, and excess air is exhausted.

[Note: The use of higher inlet flow rates dilutes any contamination present in the inlet and reduces the possibility of sample contamination as a result of contact with active adsorption sites on inlet walls.]

7.1.1.16 Elapsed Time Meter. Measures duration of sampling.

7.1.1.17 Optional Fixed Orifice, Capillary, or Adjustable Micrometering Valve. May be used in lieu of the electronic flow controller for grab samples or short duration time-integrated samples. Usually appropriate only in situations where screening samples are taken to assess future sampling activity.

7.1.2 Pressurized (see Figure 1 with metal bellows type pump and Figure 3).

7.1.2.1 Sample Pump. Stainless steel, metal bellows type, capable of 2 atmospheres output pressure. Pump must be free of leaks, clean, and uncontaminated by oil or organic compounds.

[Note: An alternative sampling system has been developed by Dr. R. Rasmussen, The Oregon Graduate Institute of Science and Technology, 20000 N.W. Walker Rd., Beaverton, Oregon 97006, 503-690-1077, and is illustrated in Figure 3. This flow system uses, in order, a pump, a mechanical flow regulator, and a mechanical compensation flow restrictive device. In this configuration the pump is purged with a large sample flow, thereby eliminating the need for an auxiliary vacuum pump to flush the sample inlet.]

7.1.2.2 Other Supporting Materials. All other components of the pressurized sampling system are similar to components discussed in Sections 7.1.1.1 through 7.1.1.17.

7.2 Analytical Apparatus

7.2.1 Sampling/Concentrator System (many commercial alternatives are available).

7.2.1.1 Electronic Mass Flow Controllers. Used to maintain constant flow (for purge gas, carrier gas and sample gas) and to provide an analog output to monitor flow anomalies.

7.2.1.2 Vacuum Pump. General purpose laboratory pump, capable of reducing the downstream pressure of the flow controller to provide the pressure differential necessary to maintain controlled flow rates of sample air.

7.2.1.3 Stainless Steel Tubing and Stainless Steel Fittings. Coated with fused silica to minimize active adsorption sites.

7.2.1.4 Stainless Steel Cylinder Pressure Regulators. Standard, two-stage cylinder regulators with pressure gauges.

7.2.1.5 Gas Purifiers. Used to remove organic impurities and moisture from gas streams.

7.2.1.6 Six-port Gas Chromatographic Valve. For routing sample and carrier gas flows.

7.2.1.7 Multisorbent Concentrator. Solid adsorbent packing with various retentive properties for adsorbing trace gases are commercially available from several sources. The packing contains more than one type of adsorbent packed in series.

7.2.1.7.1A pre-packed adsorbent trap (Supelco 2-0321) containing 200 mg Carboxpack B (60/80 mesh) and 50 mg Carboxieve S-III (60/80 mesh) has been found to retain VOCs and allow some water vapor to pass through (6). The addition of a dry purging step allows for further water removal from the adsorbent trap. The steps constituting the dry purge technique that are normally used with multisorbent traps are illustrated in Figure 4. The optimum trapping and dry purging procedure for the Supelco trap consists of a sample volume of 320 mL and a dry nitrogen purge of 1300 mL. Sample trapping and drying is carried out at 25°C. The trap is back-flushed with helium and heated to 220°C to transfer material onto the GC column. A trap bake-out at 260°C for 5 minutes is conducted after each run.

7.2.1.7.2 An example of the effectiveness of dry purging is shown in Figure 5. The multisorbent used in this case is Tenax/Ambersorb 340/Charcoal (7). Approximately 20% of the initial water content in the sample remains after sampling 500 mL of air. The detector response to water vapor (hydrogen atoms detected by atomic emission detection) is plotted versus purge gas volume. Additional water reduction by a factor of 8 is indicated at temperatures of 45°C or higher. Still further water reduction is possible using a two-stage concentration/dryer system.

7.2.1.8 Cryogenic Concentrator. Complete units are commercially available from several vendor sources. The characteristics of the latest concentrators include a rapid, "ballistic" heating of the concentrator to release any trapped VOCs into a small carrier gas volume. This facilitates the separation of compounds on the gas chromatographic column.

7.2.2 Gas Chromatographic/Mass Spectrometric (GC/MS) System.

7.2.2.1 Gas Chromatograph. The gas chromatographic (GC) system must be capable of temperature programming. The column oven can be cooled to subambient temperature (e.g., -50°C) at the start of the gas chromatographic run to effect a resolution of the very volatile organic compounds. In other designs, the rate of release of compounds from the focusing trap in a two stage system obviates the need for retrapping of compounds on the column. The system must include or be interfaced to a concentrator and have all required accessories including analytical columns and gases. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-polytetrafluoroethylene (PTFE) thread sealants or flow controllers with Buna-N rubber components must not be used.

7.2.2.2 Chromatographic Columns. 100% methyl silicone or 5% phenyl, 95% methyl silicone fused silica capillary columns of 0.25- to 0.53-mm I.D. of varying lengths are recommended for separation of many of the possible subsets of target compounds involving nonpolar compounds. However, considering the diversity of the target list, the choice is left to the operator subject to the performance standards given in Section 11.

7.2.2.3 Mass Spectrometer. Either a linear quadrupole or ion trap mass spectrometer can be used as long as it is capable of scanning from 35 to 300 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the instrument performance acceptance criteria when 50 ng or less of p-bromofluorobenzene (BFB) is analyzed.

7.2.2.3.1 Linear Quadrupole Technology. A simplified diagram of the heart of the quadrupole mass spectrometer is shown in Figure 6. The quadrupole consists of a parallel set of four rod electrodes mounted in a square configuration. The field within the analyzer is created by coupling opposite pairs of rods together and applying radiofrequency (RF) and direct current (DC) potentials between the pairs of rods. Ions created in the ion source from the reaction of column eluates with electrons from the electron source are moved through the

parallel array of rods under the influence of the generated field. Ions which are successfully transmitted through the quadrupole are said to possess stable trajectories and are subsequently recorded with the detection system. When the DC potential is zero, a wide band of m/z values is transmitted through the quadrupole. This "RF only" mode is referred to as the "total-ion" mode. In this mode, the quadrupole acts as a strong focusing lens analogous to a high pass filter. The amplitude of the RF determines the low mass cutoff. A mass spectrum is generated by scanning the DC and RF voltages using a fixed DC/RF ratio and a constant drive frequency or by scanning the frequency and holding the DC and RF constant. With the quadrupole system only 0.1 to 0.2 percent of the ions formed in the ion source actually reach the detector.

7.2.2.3.2 Ion Trap Technology. An ion-trap mass spectrometer consists of a chamber formed between two metal surfaces in the shape of a hyperboloid of one sheet (ring electrode) and a hyperboloid of two sheets (the two end-cap electrodes). Ions are created within the chamber by electron impact from an electron beam admitted through a small aperture in one of the end caps. Radio frequency (RF) (and sometimes direct current voltage offsets) are applied between the ring electrode and the two end-cap electrodes establishing a quadrupole electric field. This field is uncoupled in three directions so that ion motion can be considered independently in each direction; the force acting upon an ion increases with the displacement of the ion from the center of the field but the direction of the force depends on the instantaneous voltage applied to the ring electrode. A restoring force along one coordinate (such as the distance, r , from the ion-trap's axis of radial symmetry) will exist concurrently with a repelling force along another coordinate (such as the distance, z , along the ion traps axis), and if the field were static the ions would eventually strike an electrode. However, in an RF field the force along each coordinate alternates direction so that a stable trajectory may be possible in which the ions do not strike a surface. In practice, ions of appropriate mass-to-charge ratios may be trapped within the device for periods of milliseconds to hours. A diagram of a typical ion trap is illustrated in Figure 7. Analysis of stored ions is performed by increasing the RF voltage, which makes the ions successively unstable. The effect of the RF voltage on the ring electrode is to "squeeze" the ions in the xy plane so that they move along the z axis. Half the ions are lost to the top cap (held at ground potential); the remaining ions exit the lower end cap to be detected by the electron multiplier. As the energy applied to the ring electrode is increased, the ions are collected in order of increasing mass to produce a conventional mass spectrum. With the ion trap, approximately 50 percent of the generated ions are detected. As a result, a significant increase in sensitivity can be achieved when compared to a full scan linear quadrupole system.

7.2.2.4 GC/MS Interface. Any gas chromatograph to mass spectrometer interface that gives acceptable calibration points for each of the analytes of interest and can be used to achieve all acceptable performance criteria may be used. Gas chromatograph to mass spectrometer interfaces constructed of all-glass, glass-lined, or fused silica-lined materials are recommended. Glass and fused silica should be deactivated.

7.2.2.5 Data System. The computer system that is interfaced to the mass spectrometer must allow the continuous acquisition and storage, on machine readable media, of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as a Selected Ion Current Profile (SICP). Software must also be available that allows integrating the abundance in any SICP between specified time or scan number limits. Also, software must be available that allows for the comparison of sample spectra with reference library spectra. The National Institute of Standards and Technology (NIST) or Wiley Libraries or equivalent are recommended as reference libraries.

7.2.2.6 Off-line Data Storage Device. Device must be capable of rapid recording and retrieval of data and must be suitable for long-term, off-line data storage.

7.3 Calibration System and Manifold Apparatus (see Figure 8)

7.3.1 Calibration Manifold. Stainless steel, glass, or high purity quartz manifold, (e.g., 1.25-cm I.D. x 66-cm) with sampling ports and internal baffles for flow disturbance to ensure proper mixing. The manifold should be heated to ~50°C.

7.3.2 Humidifier. 500-mL impinger flask containing HPLC grade deionized water.

7.3.3 Electronic Mass Flow Controllers. One 0 to 5 L/min unit and one or more 0 to 100 mL/min units for air, depending on number of cylinders in use for calibration.

7.3.4 Teflon Filter(s). 47-mm Teflon® filter for particulate collection.

7.4 Reagents

7.4.1 Neat Materials or Manufacturer-Certified Solutions/Mixtures. Best source (see Section 9).

7.4.2 Helium and Air. Ultra-high purity grade in gas cylinders. He is used as carrier gas in the GC.

7.4.3 Liquid Nitrogen or Liquid Carbon Dioxide. Used to cool secondary trap.

7.4.4 Deionized Water. High performance liquid chromatography (HPLC) grade, ultra-high purity (for humidifier).

8. Collection of Samples in Canisters

8.1 Introduction

8.1.1 Canister samplers, sampling procedures, and canister cleaning procedures have not changed very much from the description given in the original Compendium Method TO-14. Much of the material in this section is therefore simply a restatement of the material given in Compendium Method TO-14, repeated here in order to have all the relevant information in one place.

8.1.2 Recent notable additions to the canister technology has been in the application of canister-based systems for example, to microenvironmental monitoring (8), the capture of breath samples (9), and sector sampling to identify emission sources of VOCs (10).

8.1.3 EPA has also sponsored the development of a mathematical model to predict the storage stability of arbitrary mixtures of trace gases in humidified air (3), and the investigation of the SilcoSteel™ process of coating the canister interior with a film of fused silica to reduce surface activity (11). A recent summary of storage stability data for VOCs in canisters is given in the open literature (5).

8.2 Sampling System Description

8.2.1 Subatmospheric Pressure Sampling [see Figure 1 (without metal bellows type pump)].

8.2.1.1 In preparation for subatmospheric sample collection in a canister, the canister is evacuated to 0.05 mm Hg (see Appendix C for discussion of evacuation pressure). When the canister is opened to the atmosphere containing the VOCs to be sampled, the differential pressure causes the sample to flow into the canister. This technique may be used to collect grab samples (duration of 10 to 30 seconds) or time-weighted-average (TWA) samples (duration of 1-24 hours) taken through a flow-restrictive inlet (e.g., mass flow controller, critical orifice).

8.2.1.2 With a critical orifice flow restrictor, there will be a decrease in the flow rate as the pressure approaches atmospheric. However, with a mass flow controller, the subatmospheric sampling system can maintain a constant flow rate from full vacuum to within about 7 kPa (1.0 psi) or less below ambient pressure.

8.2.2 Pressurized Sampling [see Figure 1 (with metal bellows type pump)].

8.2.2.1 Pressurized sampling is used when longer-term integrated samples or higher volume samples are required. The sample is collected in a canister using a pump and flow control arrangement to achieve a typical 101-202 kPa (15-30 psig) final canister pressure. For example, a 6-liter evacuated canister can be filled at 10 mL/min for 24 hours to achieve a final pressure of 144 kPa (21 psig).

8.2.2.2 In pressurized canister sampling, a metal bellows type pump draws in air from the sampling manifold to fill and pressurize the sample canister.

8.2.3 All Samplers.

8.2.3.1 A flow control device is chosen to maintain a constant flow into the canister over the desired sample period. This flow rate is determined so the canister is filled (to about 88.1 kPa for subatmospheric pressure sampling or to about one atmosphere above ambient pressure for pressurized sampling) over the desired sample period. The flow rate can be calculated by:

$$F = \frac{P \times V}{T \times 60}$$

where:

F = flow rate, mL/min.

P = final canister pressure, atmospheres absolute. P is approximately equal to

$$\frac{\text{kPa gauge}}{101.2} + 1$$

V = volume of the canister, mL.

T = sample period, hours.

For example, if a 6-L canister is to be filled to 202 kPa (2 atmospheres) absolute pressure in 24 hours, the flow rate can be calculated by:

$$F = \frac{2 \times 6000}{24 \times 60} = 8.3 \text{ mL/min}$$

8.2.3.2 For automatic operation, the timer is designed to start and stop the pump at appropriate times for the desired sample period. The timer must also control the solenoid valve, to open the valve when starting the pump and to close the valve when stopping the pump.

8.2.3.3 The use of the Skinner Magnelatch valve (see Figure 2) avoids any substantial temperature rise that would occur with a conventional, normally closed solenoid valve that would have to be energized during the entire sample period. The temperature rise in the valve could cause outgassing of organic compounds from the Viton® valve seat material. The Skinner Magnelatch valve requires only a brief electrical pulse to open or close at the appropriate start and stop times and therefore experiences no temperature increase. The pulses may be obtained either with an electronic timer that can be programmed for short (5 to 60 seconds) ON periods, or with a conventional mechanical timer and a special pulse circuit. A simple electrical pulse circuit for operating the Skinner Magnelatch solenoid valve with a conventional mechanical timer is illustrated in Figure 2(a). However, with this simple circuit, the valve may operate unreliably during brief power interruptions or if the timer is manually switched on and off too fast. A better circuit incorporating a time-delay relay to provide more reliable valve operation is shown in Figure 2(b).

8.2.3.4 The connecting lines between the sample inlet and the canister should be as short as possible to minimize their volume. The flow rate into the canister should remain relatively constant over the entire sampling period.

8.2.3.5 As an option, a second electronic timer may be used to start the auxiliary pump several hours prior to the sampling period to flush and condition the inlet line.

8.2.3.6 Prior to field use, each sampling system must pass a humid zero air certification (see Section 8.4.3). All plumbing should be checked carefully for leaks. The canisters must also pass a humid zero air certification before use (see Section 8.4.1).

8.3 Sampling Procedure

8.3.1 The sample canister should be cleaned and tested according to the procedure in Section 8.4.1.

8.3.2 A sample collection system is assembled as shown in Figures 1 and 3 and must be cleaned according to the procedure outlined in Sections 8.4.2 and 8.4.4.

[Note: The sampling system should be contained in an appropriate enclosure.]

8.3.3 Prior to locating the sampling system, the user may want to perform "screening analyses" using a portable GC system, as outlined in Appendix B of Compendium Method TO-14A, to determine potential volatile organics present and potential "hot spots." The information gathered from the portable GC screening analysis would be used in developing a monitoring protocol, which includes the sampling system location, based upon the "screening analysis" results.

8.3.4 After "screening analysis," the sampling system is located. Temperatures of ambient air and sampler box interior are recorded on the canister sampling field test data sheet (FTDS), as documented in Figure 9.

[Note: The following discussion is related to Figure 1]

8.3.5 To verify correct sample flow, a "practice" (evacuated) canister is used in the sampling system.

[Note: For a subatmospheric sampler, a flow meter and practice canister are needed. For the pump-driven system, the practice canister is not needed, as the flow can be measured at the outlet of the system.]

A certified mass flow meter is attached to the inlet line of the manifold, just in front of the filter. The canister is opened. The sampler is turned on and the reading of the certified mass flow meter is compared to the sampler mass flow controller. The values should agree within $\pm 10\%$. If not, the sampler mass flow meter needs to be recalibrated or there is a leak in the system. This should be investigated and corrected.

[Note: Mass flow meter readings may drift. Check the zero reading carefully and add or subtract the zero reading when reading or adjusting the sampler flow rate to compensate for any zero drift.]

After 2 minutes, the desired canister flow rate is adjusted to the proper value (as indicated by the certified mass flow meter) by the sampler flow control unit controller (e.g., 3.5 mL/min for 24 hr, 7.0 mL/min for 12 hr). Record final flow under "CANISTER FLOW RATE" on the FTDS.

8.3.6 The sampler is turned off and the elapsed time meter is reset to 000.0.

[Note: Whenever the sampler is turned off, wait at least 30 seconds to turn the sampler back on.]

8.3.7 The "practice" canister and certified mass flow meter are disconnected and a clean certified (see Section 8.4.1) canister is attached to the system.

8.3.8 The canister valve and vacuum/pressure gauge valve are opened.

8.3.9 Pressure/vacuum in the canister is recorded on the canister FTDS (see Figure 9) as indicated by the sampler vacuum/pressure gauge.

8.3.10 The vacuum/pressure gauge valve is closed and the maximum-minimum thermometer is reset to current temperature. Time of day and elapsed time meter readings are recorded on the canister FTDS.

8.3.11 The electronic timer is set to start and stop the sampling period at the appropriate times. Sampling starts and stops by the programmed electronic timer.

8.3.12 After the desired sampling period, the maximum, minimum, current interior temperature and current ambient temperature are recorded on the FTDS. The current reading from the flow controller is recorded.

8.3.13 At the end of the sampling period, the vacuum/pressure gauge valve on the sampler is briefly opened and closed and the pressure/vacuum is recorded on the FTDS. Pressure should be close to desired pressure.

[Note: For a subatmospheric sampling system, if the canister is at atmospheric pressure when the field final pressure check is performed, the sampling period may be suspect. This information should be noted on the sampling field data sheet.]

Time of day and elapsed time meter readings are also recorded.

8.3.14 The canister valve is closed. The sampling line is disconnected from the canister and the canister is removed from the system. For a subatmospheric system, a certified mass flow meter is once again connected to the inlet manifold in front of the in-line filter and a "practice" canister is attached to the Magelatch valve of the sampling system. The final flow rate is recorded on the canister FTDS (see Figure 9).

[Note: For a pressurized system, the final flow may be measured directly.]

The sampler is turned off.

8.3.15 An identification tag is attached to the canister. Canister serial number, sample number, location, and date, as a minimum, are recorded on the tag. The canister is routinely transported back to the analytical laboratory with other canisters in a canister shipping case.

8.4 Cleaning and Certification Program

8.4.1 Canister Cleaning and Certification.

8.4.1.1 All canisters must be clean and free of any contaminants before sample collection.

8.4.1.2 All canisters are leak tested by pressurizing them to approximately 206 kPa (30 psig) with zero air.

[Note: The canister cleaning system in Figure 10 can be used for this task.]

The initial pressure is measured, the canister valve is closed, and the final pressure is checked after 24 hours. If acceptable, the pressure should not vary more than ± 13.8 kPa (± 2 psig) over the 24 hour period.

8.4.1.3 A canister cleaning system may be assembled as illustrated in Figure 10. Cryogen is added to both the vacuum pump and zero air supply traps. The canister(s) are connected to the manifold. The vent shut-off valve and the canister valve(s) are opened to release any remaining pressure in the canister(s). The vacuum pump is started and the vent shut-off valve is then closed and the vacuum shut-off valve is opened. The canister(s) are evacuated to <0.05 mm Hg (see Appendix B) for at least 1 hour.

[Note: On a daily basis or more often if necessary, the cryogenic traps should be purged with zero air to remove any trapped water from previous canister cleaning cycles.]

Air released/evacuated from canisters should be diverted to a fume hood.

8.4.1.4 The vacuum and vacuum/pressure gauge shut-off valves are closed and the zero air shut-off valve is opened to pressurize the canister(s) with humid zero air to approximately 206 kPa (30 psig). If a zero gas generator system is used, the flow rate may need to be limited to maintain the zero air quality.

8.4.1.5 The zero air shut-off valve is closed and the canister(s) is allowed to vent down to atmospheric pressure through the vent shut-off valve. The vent shut-off valve is closed. Repeat Sections 8.4.1.3 through 8.4.1.5 two additional times for a total of three (3) evacuation/pressurization cycles for each set of canisters.

8.4.1.6 At the end of the evacuation/pressurization cycle, the canister is pressurized to 206 kPa (30 psig) with humid zero air. The canister is then analyzed by a GC/MS analytical system. Any canister that has not tested clean (compared to direct analysis of humidified zero air of less than 0.2 ppbv of targeted VOCs) should not be used. As a "blank" check of the canister(s) and cleanup procedure, the final humid zero air fill of 100% of the canisters is analyzed until the cleanup system and canisters are proven reliable (less than 0.2 ppbv of any target VOCs). The check can then be reduced to a lower percentage of canisters.

8.4.1.7 The canister is reattached to the cleaning manifold and is then reevacuated to <0.05 mm Hg (see Appendix B) and remains in this condition until used. The canister valve is closed. The canister is removed from the cleaning system and the canister connection is capped with a stainless steel fitting. The canister is now ready for collection of an air sample. An identification tag is attached to the inlet of each canister for field notes and chain-of-custody purposes. An alternative to evacuating the canister at this point is to store the canisters and reevacuate them just prior to the next use.

8.4.1.8 As an option to the humid zero air cleaning procedures, the canisters are heated in an isothermal oven not to exceed 100°C during evacuation of the canister to ensure that higher molecular weight compounds are not retained on the walls of the canister.

[Note: For sampling more complex VOC mixtures the canisters should be heated to higher temperatures during the cleaning procedure although a special high temperature valve would be needed].

Once heated, the canisters are evacuated to <0.05 mm Hg (see Appendix B) and maintained there for 1 hour. At the end of the heated/evacuated cycle, the canisters are pressurized with humid zero air and analyzed by a GC/MS system after a minimum of 12 hrs of "aging." Any canister that has not tested clean (less than 0.2 ppbv each of targeted compounds) should not be used. Once tested clean, the canisters are reevacuated to <0.05 mm Hg (see Appendix B) and remain in the evacuated state until used. As noted in Section 8.4.1.7, reevacuation can occur just prior to the next use.

8.4.2 Cleaning Sampling System Components.

8.4.2.1 Sample components are disassembled and cleaned before the sampler is assembled. Nonmetallic parts are rinsed with HPLC grade deionized water and dried in a vacuum oven at 50°C. Typically, stainless steel parts and fittings are cleaned by placing them in a beaker of methanol in an ultrasonic bath for 15 minutes. This procedure is repeated with hexane as the solvent.

8.4.2.2 The parts are then rinsed with HPLC grade deionized water and dried in a vacuum oven at 100°C for 12 to 24 hours.

8.4.2.3 Once the sampler is assembled, the entire system is purged with humid zero air for 24 hours.

8.4.3 Zero Air Certification.

[Note: In the following sections, "certification" is defined as evaluating the sampling system with humid zero air and humid calibration gases that pass through all active components of the sampling system. The system is "certified" if no significant additions or deletions (less than 0.2 ppbv each of target compounds) have occurred when challenged with the test gas stream.]

8.4.3.1 The cleanliness of the sampling system is determined by testing the sampler with humid zero air without an evacuated gas sampling canister, as follows.

8.4.3.2 The calibration system and manifold are assembled, as illustrated in Figure 8. The sampler (without an evacuated gas canister) is connected to the manifold and the zero air cylinder is activated to generate a humid gas stream (2 L/min) to the calibration manifold [see Figure 8(b)].

8.4.3.3 The humid zero gas stream passes through the calibration manifold, through the sampling system (without an evacuated canister) to the water management system/VOC preconcentrator of an analytical system.

[Note: The exit of the sampling system (without the canister) replaces the canister in Figure 11.]

After the sample volume (e.g., 500 mL) is preconcentrated on the trap, the trap is heated and the VOCs are thermally desorbed and refocused on a cold trap. This trap is heated and the VOCs are thermally desorbed onto the head of the capillary column. The VOCs are refocused prior to gas chromatographic separation. Then, the oven temperature (programmed) increases and the VOCs begin to elute and are detected by a GC/MS (see Section 10) system. The analytical system should not detect greater than 0.2 ppbv of any targeted VOCs in order for the sampling system to pass the humid zero air certification test. Chromatograms (using an FID) of a certified sampler and contaminated sampler are illustrated in Figures 12(a) and 12(b), respectively. If the sampler passes the humid zero air test, it is then tested with humid calibration gas standards containing selected VOCs at concentration levels expected in field sampling (e.g., 0.5 to 2 ppbv) as outlined in Section 8.4.4.

8.4.4 Sampler System Certification with Humid Calibration Gas Standards from a Dynamic Calibration System

8.4.4.1 Assemble the dynamic calibration system and manifold as illustrated in Figure 8.

8.4.4.2 Verify that the calibration system is clean (less than 0.2 ppbv of any target compounds) by sampling a humidified gas stream, *without* gas calibration standards, with a previously certified clean canister (see Section 8.1).

8.4.4.3 The assembled dynamic calibration system is certified clean if less than 0.2 ppbv of any targeted compounds is found.

8.4.4.4 For generating the humidified calibration standards, the calibration gas cylinder(s) containing nominal concentrations of 10 ppmv in nitrogen of selected VOCs is attached to the calibration system as illustrated in Figure 8. The gas cylinders are opened and the gas mixtures are passed through 0 to 10 mL/min certified mass flow controllers to generate ppb levels of calibration standards.

8.4.4.5 After the appropriate equilibrium period, attach the sampling system (containing a certified evacuated canister) to the manifold, as illustrated in Figure 8(b).

8.4.4.6 Sample the dynamic calibration gas stream with the sampling system.

8.4.4.7 Concurrent with the sampling system operation, realtime monitoring of the calibration gas stream is accomplished by the on-line GC/MS analytical system [Figure 8(a)] to provide reference concentrations of generated VOCs.

8.4.4.8 At the end of the sampling period (normally the same time period used for experiments), the sampling system canister is analyzed and compared to the reference GC/MS analytical system to determine if the concentration of the targeted VOCs was increased or decreased by the sampling system.

8.4.4.9 A recovery of between 90% and 110% is expected for all targeted VOCs.

8.4.5 Sampler System Certification without Compressed Gas Cylinder Standards.

8.4.5.1 Not all the gases on the Title III list are available/compatible with compressed gas standards. In these cases sampler certification must be approached by different means.

8.4.5.2 Definitive guidance is not currently available in these cases; however, Section 9.2 lists several ways to generate gas standards. In general, Compendium Method TO-14A compounds (see Table 1) are available commercially as compressed gas standards.

9. GC/MS Analysis of Volatiles from Canisters

9.1 Introduction

9.1.1 The analysis of canister samples is accomplished with a GC/MS system. Fused silica capillary columns are used to achieve high temporal resolution of 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 concentrating device that is needed to increase sample loading into a detectable range. Two examples of concentrating systems are discussed. Other approaches are acceptable as long as they are compatible with achieving the system performance criteria given in Section 11.

9.1.2 With the first technique, a whole air sample from the canister is passed through a multisorbent packing (including single adsorbent packings) contained within a metal or glass tube maintained at or above the surrounding air temperature. Depending on the water retention properties of the packing, some or most of the water vapor passes completely through the trap during sampling. Additional drying of the sample is accomplished after the sample concentration is completed by forward purging the trap with clean, dry helium or another inert gas (air is not used). The sample is then thermally desorbed from the packing and backflushed from the trap onto a gas chromatographic column. In some systems a "refocusing" trap is placed between the primary trap and the gas chromatographic column. The specific system design downstream of the primary trap depends on technical factors such as the rate of thermal desorption and sampled volume, but the objective in most cases is to enhance chromatographic resolution of the individual sample components before detection on a mass spectrometer.

9.1.3 Sample drying strategies depend on the target list of compounds. For some target compound lists, the multisorbent packing of the concentrator can be selected from hydrophobic adsorbents which allow a high percentage of water vapor in the sample to pass through the concentrator during sampling and without significant loss of the target compounds. However, if very volatile organic compounds are on the target list, the adsorbents required for their retention may also strongly retain water vapor and a more lengthy dry purge is necessary prior to analysis.

9.1.4 With the second technique, a whole air sample is passed through a concentrator where the VOCs are condensed on a reduced temperature surface (cold trap). Subsequently, the condensed gases are thermally desorbed and backflushed from the trap with an inert gas onto a gas chromatographic column. This concentration technique is similar to that discussed in Compendium Method TO-14, although a membrane dryer is not used. The sample size is reduced in volume to limit the amount of water vapor that is also collected (100 mL or less may be necessary). The attendant reduction in sensitivity is offset by enhancing the sensitivity of detection, for example by using an ion trap detector.

9.2 Preparation of Standards

9.2.1 Introduction.

9.2.1.1 When available, standard mixtures of target gases in high pressure cylinders must be certified traceable to a NIST Standard Reference Material (SRM) or to a NIST/EPA approved Certified Reference Material (CRM). Manufacturer's certificates of analysis must be retained to track the expiration date.

9.2.1.2 The neat standards that are used for making trace gas standards must be of high purity; generally a purity of 98 percent or better is commercially available.

9.2.1.3 Cylinder(s) containing approximately 10 ppmv of each of the target compounds are typically used as primary stock standards. The components may be purchased in one cylinder or in separate cylinders depending on compatibility of the compounds and the pressure of the mixture in the cylinder. Refer to manufacturer's specifications for guidance on purchasing and mixing VOCs in gas cylinders.

9.2.2 Preparing Working Standards.

9.2.2.1 Instrument Performance Check Standard. Prepare a standard solution of BFB in humidified zero air at a concentration which will allow collection of 50 ng of BFB or less under the optimized concentration parameters.

9.2.2.2 Calibration Standards. Prepare five working calibration standards in humidified zero air at a concentration which will allow collection at the 2, 5, 10, 20, and 50 ppbv level for each component under the optimized concentration parameters.

9.2.2.3 Internal Standard Spiking Mixture. Prepare an internal spiking mixture containing bromochloromethane, chlorobenzene-d₅, and 1,4-difluorobenzene at 10 ppmv each in humidified zero air to be added to the sample or calibration standard. 500 µL of this mixture spiked into 500 mL of sample will result in a concentration of 10 ppbv. The internal standard is introduced into the trap during the collection time for all calibration, blank, and sample analyses using the apparatus shown in Figure 13 or by equivalent means. The volume of internal standard spiking mixture added for each analysis must be the same from run to run.

9.2.3 Standard Preparation by Dynamic Dilution Technique.

9.2.3.1 Standards may be prepared by dynamic dilution of the gaseous contents of a cylinder(s) containing the gas calibration stock standards with humidified zero air using mass flow controllers and a calibration manifold. The working standard may be delivered from the manifold to a clean, evacuated canister using a pump and mass flow controller.

9.2.3.2 Alternatively, the analytical system may be calibrated by sampling directly from the manifold if the flow rates are optimized to provide the desired amount of calibration standards. However, the use of the canister as a reservoir prior to introduction into the concentration system resembles the procedure normally used to collect samples and is preferred. Flow rates of the dilution air and cylinder standards (all expressed in the same units) are measured using a bubble meter or calibrated electronic flow measuring device, and the concentrations of target compounds in the manifold are then calculated using the dilution ratio and the original concentration of each compound.

$$\text{Manifold Conc.} = \frac{(\text{Original Conc.}) (\text{Std. Gas Flowrate})}{(\text{Air Flowrate}) + (\text{Std. Gas Flowrate})}$$

9.2.3.3 Consider the example of 1 mL/min flow of 10 ppmv standard diluted with 1,000 mL/min of humid air provides a nominal 10 ppbv mixture, as calculated below:

$$\text{Manifold Conc.} = \frac{(10 \text{ ppm})(1 \text{ mL/min})(1000 \text{ ppb/1 ppm})}{(1000 \text{ mL/min}) + (1 \text{ mL/min})} = 10 \text{ ppb}$$

9.2.4 Standard Preparation by Static Dilution Bottle Technique

[Note: Standards may be prepared in canisters by spiking the canister with a mixture of components prepared in a static dilution bottle (12). This technique is used specifically for liquid standards.]

9.2.4.1 The volume of a clean 2-liter round-bottom flask, modified with a threaded glass neck to accept a Mininert septum cap, is determined by weighing the amount of water required to completely fill up the flask. Assuming a density for the water of 1 g/mL, the weight of the water in grams is taken as the volume of the flask in milliliters.

9.2.4.2 The flask is flushed with helium by attaching a tubing into the glass neck to deliver the helium. After a few minutes, the tubing is removed and the glass neck is immediately closed with a Mininert septum cap.

9.2.4.3 The flask is placed in a 60°C oven and allowed to equilibrate at that temperature for about 15 minutes. Predetermined aliquots of liquid standards are injected into the flask making sure to keep the flask temperature constant at 60°C.

9.2.4.4 The contents are allowed to equilibrate in the oven for at least 30 minutes. To avoid condensation, syringes must be preheated in the oven at the same temperature prior to withdrawal of aliquots to avoid condensation.

9.2.4.5 Sample aliquots may then be taken for introduction into the analytical system or for further dilution. An aliquot or aliquots totaling greater than 1 percent of the flask volume should be avoided.

9.2.4.6 Standards prepared by this method are stable for one week. The septum must be replaced with each freshly prepared standard.

9.2.4.7 The concentration of each component in the flask is calculated using the following equation:

$$\text{Concentration, mg/L} = \frac{(V_a)(d)}{V_f}$$

where: V_a = Volume of liquid neat standard injected into the flask, μL .

d = Density of the liquid neat standard, $\text{mg}/\mu\text{L}$.

V_f = Volume of the flask, L.

9.2.4.8 To obtain concentrations in ppbv, the equation given in Section 9.2.5.7 can be used.

[Note: In the preparation of standards by this technique, the analyst should make sure that the volume of neat standard injected into the flask does not result in an overpressure due to the higher partial pressure produced by the standard compared to the vapor pressure in the flask. Precautions should also be taken to avoid a significant decrease in pressure inside the flask after withdrawal of aliquot(s).]

9.2.5 Standard Preparation Procedure in High Pressure Cylinders

[Note: Standards may be prepared in high pressure cylinders (13). A modified summary of the procedure is provided below.]

9.2.5.1 The standard compounds are obtained as gases or neat liquids (greater than 98 percent purity).

9.2.5.2 An aluminum cylinder is flushed with high-purity nitrogen gas and then evacuated to better than 25 in. Hg.

9.2.5.3 Predetermined amounts of each neat standard compound are measured using a microliter or gastight syringe and injected into the cylinder. The cylinder is equipped with a heated injection port and nitrogen flow to facilitate sample transfer.

9.2.5.4 The cylinder is pressurized to 1000 psig with zero nitrogen.

[Note: User should read all SOPs associated with generating standards in high pressure cylinders. Follow all safety requirements to minimize danger from high pressure cylinders.]

9.2.5.5 The contents of the cylinder are allowed to equilibrate (~24 hrs) prior to withdrawal of aliquots into the GC system.

9.2.5.6 If the neat standard is a gas, the cylinder concentration is determined using the following equation:

$$\text{Concentration, ppbv} = \frac{\text{Volume}_{\text{standard}}}{\text{Volume}_{\text{dilution gas}}} \times 10^9$$

[Note: Both values must be expressed in the same units.]

9.2.5.7 If the neat standard is a liquid, the gaseous concentration can be determined using the following equations:

$$V = \frac{nRT}{P}$$

and:

$$n = \frac{(\text{mL})(d)}{\text{MW}}$$

where:

- V = Gaseous volume of injected compound at EPA standard temperature (25°C) and pressure (760 mm Hg), L.
- n = Moles.
- R = Gas constant, 0.08206 L-atm/mole °K.
- T = 298°K (standard temperature).
- P = 1 standard pressure, 760 mm Hg (1 atm).
- mL = Volume of liquid injected, mL.
- d = Density of the neat standard, g/mL.
- MW = Molecular weight of the neat standard expressed, g/g-mole.

The gaseous volume of the injected compound is divided by the cylinder volume at STP and then multiplied by 10^9 to obtain the component concentration in ppb units.

9.2.6 Standard Preparation by Water Methods.

[Note: Standards may be prepared by a water purge and trap method (14) and summarized as follows].

9.2.6.1 A previously cleaned and evacuated canister is pressurized to 760 mm Hg absolute (1 atm) with zero grade air.

9.2.6.2 The air gauge is removed from the canister and the sparging vessel is connected to the canister with the short length of 1/16 in. stainless steel tubing.

[Note: Extra effort should be made to minimize possible areas of dead volume to maximize transfer of analytes from the water to the canister.]

9.2.6.3 A measured amount of the stock standard solution and the internal standard solution is spiked into 5 mL of water.

9.2.6.4 This water is transferred into the sparge vessel and purged with nitrogen for 10 mins at 100 mL/min. The sparging vessel is maintained at 40°C.

9.2.6.5 At the end of 10 mins, the sparge vessel is removed and the air gauge is re-installed, to further pressurize the canister with pure nitrogen to 1500 mm Hg absolute pressure (approximately 29 psia).

9.2.6.6 The canister is allowed to equilibrate overnight before use.

9.2.6.7 A schematic of this approach is shown in Figure 14.

9.2.7 Preparation of Standards by Permeation Tubes.

9.2.7.1 Permeation tubes can be used to provide standard concentration of a trace gas or gases. The permeation of the gas can occur from inside a permeation tube containing the trace species of interest to an air stream outside. Permeation can also occur from outside a permeable membrane tube to an air stream passing through the tube (e.g., a tube of permeable material immersed in a liquid).

9.2.7.2 The permeation system is usually held at a constant temperature to generate a constant concentration of trace gas. Commercial suppliers provide systems for generation and dilution of over 250 compounds. Some commercial suppliers of permeation tube equipment are listed in Appendix D.

9.2.8 Storage of Standards.

9.2.8.1 Working standards prepared in canisters may be stored for thirty days in an atmosphere free of potential contaminants.

9.2.8.2 It is imperative that a storage logbook be kept to document storage time.

10. GC/MS Operating Conditions

10.1 Preconcentrator

The following are typical cryogenic and adsorbent preconcentrator analytical conditions which, however, depend on the specific combination of solid sorbent and must be selected carefully by the operator. The reader is referred to Tables 1 and 2 of Compendium Method TO-17 for guidance on selection of sorbents. An example of a system using a solid adsorbent preconcentrator with a cryofocusing trap is discussed in the literature (15). Oven temperature programming starts above ambient.

10.1.1 Sample Collection Conditions

Cryogenic Trap

Adsorbent Trap

Set point	-150°C	Set point	27°C
Sample volume	- up to 100 mL	Sample volume	- up to 1,000 mL
Carrier gas purge flow	- none	Carrier gas purge flow	- selectable

[*Note: The analyst should optimize the flow rate, duration of sampling, and absolute sample volume to be used. Other preconcentration systems may be used provided performance standards (see Section 11) are realized.*]

10.1.2 Desorption Conditions

Cryogenic Trap

Desorb Temperature	120°C
Desorb Flow Rate	~ 3 mL/min He
Desorb Time	<60 sec

Adsorbent Trap

Desorb Temperature	Variable
Desorb Flow Rate	~3 mL/min He
Desorb Time	<60 sec

The adsorbent trap conditions depend on the specific solid adsorbents chosen (see manufacturers' specifications).

10.1.3 Trap Reconditioning Conditions.

Cryogenic Trap

Initial bakeout	120°C (24 hrs)
Variable (24 hrs)	
After each run	120°C (5 min)

Adsorbent Trap

Initial bakeout	
After each run	Variable (5 min)

10.2 GC/MS System

10.2.1 Optimize GC conditions for compound separation and sensitivity. Baseline separation of benzene and carbon tetrachloride on a 100% methyl polysiloxane stationary phase is an indication of acceptable chromatographic performance.

10.2.2 The following are the recommended gas chromatographic analytical conditions when using a 50-meter by 0.3-mm I.D., 1 µm film thickness fused silica column with refocusing on the column.

<u>Item</u>	<u>Condition</u>
Carrier Gas:	Helium
Flow Rate:	Generally 1-3 mL/min as recommended by manufacturer
Temperature Program:	Initial Temperature: -50°C
	Initial Hold Time: 2 min
	Ramp Rate: 8° C/min
	Final Temperature: 200°C
	Final Hold Time: Until all target compounds elute.

10.2.3 The following are the recommended mass spectrometer conditions:

<u>Item</u>	<u>Condition</u>
-------------	------------------

Electron Energy:	70 Volts (nominal)
Mass Range:	35-300 amu [the choice of 35 amu excludes the detection of some target compounds such as methanol and formaldehyde, and the quantitation of others such as ethylene oxide, ethyl carbamate, etc. (see Table 2). Lowering the mass range and using special programming features available on modern gas chromatographs will be necessary in these cases, but are not considered here.
Scan Time:	To give at least 10 scans per peak, not to exceed 1 second per scan].

A schematic for a typical GC/MS analytical system is illustrated in Figure 15.

10.3 Analytical Sequence

10.3.1 Introduction. The recommended GC/MS analytical sequence for samples during each 24-hour time period is as follows:

- Perform instrument performance check using bromofluorobenzene (BFB).
- Initiate multi-point calibration or daily calibration checks.
- Perform a laboratory method blank.
- Complete this sequence for analysis of ≤ 20 field samples.

10.4 Instrument Performance Check

10.4.1 Summary. It is necessary to establish that a given GC/MS meets tuning and standard mass spectral abundance criteria prior to initiating any data collection. The GC/MS system is set up according to the manufacturer's specifications, and the mass calibration and resolution of the GC/MS system are then verified by the analysis of the instrument performance check standard, bromofluorobenzene (BFB).

10.4.2 Frequency. Prior to the analyses of any samples, blanks, or calibration standards, the Laboratory must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check standard containing BFB. The instrument performance check solution must be analyzed initially and once per 24-hour time period of operation.

The 24-hour time period for GC/MS instrument performance check and standards calibration (initial calibration or daily calibration check criteria) begins at the injection of the BFB which the laboratory records as documentation of a compliance tune.

10.4.3 Procedure. The analysis of the instrument performance check standard is performed by trapping 50 ng of BFB under the optimized preconcentration parameters. The BFB is introduced from a cylinder into the GC/MS via a sample loop valve injection system similar to that shown in Figure 13.

The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is conducted using a single scan prior to the elution of BFB.

10.4.4 Technical Acceptance Criteria. Prior to the analysis of any samples, blanks, or calibration standards, the analyst must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check standard as specified in Table 3.

10.4.5 Corrective Action. If the BFB acceptance criteria are not met, the MS must be retuned. It may be necessary to clean the ion source, or quadrupoles, or take other necessary actions to achieve the acceptance criteria.

10.4.6 Documentation. Results of the BFB tuning are to be recorded and maintained as part of the instrumentation log.

10.5 Initial Calibration

10.5.1 Summary. Prior to the analysis of samples and blanks but after the instrument performance check standard criteria have been met, each GC/MS system must be calibrated at five concentrations that span the monitoring range of interest in an initial calibration sequence to determine instrument sensitivity and the linearity of GC/MS response for the target compounds. For example, the range of interest may be 2 to 20 ppbv, in which case the five concentrations would be 1, 2, 5, 10 and 25 ppbv.

One of the calibration points from the initial calibration curve must be at the same concentration as the daily calibration standard (e.g., 10 ppbv).

10.5.2 Frequency. Each GC/MS system must be recalibrated following corrective action (e.g., ion source cleaning or repair, column replacement, etc.) which may change or affect the initial calibration criteria or if the daily calibration acceptance criteria have not been met.

If time remains in the 24-hour time period after meeting the acceptance criteria for the initial calibration, samples may be analyzed.

If time does not remain in the 24-hour period after meeting the acceptance criteria for the initial calibration, a new analytical sequence shall commence with the analysis of the instrument performance check standard followed by analysis of a daily calibration standard.

10.5.3 Procedure. Verify that the GC/MS system meets the instrument performance criteria in Section 10.4.

The GC must be operated using temperature and flow rate parameters equivalent to those in Section 10.2.2. Calibrate the preconcentration-GC/MS system by drawing the standard into the system. Use one of the standards preparation techniques described under Section 9.2 or equivalent.

A minimum of five concentration levels are needed to determine the instrument sensitivity and linearity. One of the calibration levels should be near the detection level for the compounds of interest. The calibration range should be chosen so that linear results are obtained as defined in Sections 10.5.1 and 10.5.5.

Quantitation ions for the target compounds are shown in Table 2. The primary ion should be used unless interferences are present, in which case a secondary ion is used.

10.5.4 Calculations.

[Note: In the following calculations, an internal standard approach is used to calculate response factors. The area response used is that of the primary quantitation ion unless otherwise stated.]

10.5.4.1 Relative Response Factor (RRF). Calculate the relative response factors for each target compound relative to the appropriate internal standard (i.e., standard with the nearest retention time) using the following equation:

$$\text{RRF} = \frac{A_x C_{is}}{A_{is} C_x}$$

where: RRF = Relative response factor.
 A_x = Area of the primary ion for the compound to be measured, counts.
 A_{is} = Area of the primary ion for the internal standard, counts.
 C_{is} = Concentration of internal standard spiking mixture, ppbv.
 C_x = Concentration of the compound in the calibration standard, ppbv.

[*Note: The equation above is valid under the condition that the volume of internal standard spiking mixture added in all field and QC analyses is the same from run to run, and that the volume of field and QC sample introduced into the trap is the same for each analysis. C_{is} and C_x must be in the same units.*]

10.5.4.2 Mean Relative Response Factor. Calculate the mean RRF for each compound by averaging the values obtained at the five concentrations using the following equation:

$$\overline{RRF} = \sum_{i=1}^n \frac{x_i}{n}$$

where: \overline{RRF} = Mean relative response factor.
 x_i = RRF of the compound at concentration i.
 n = Number of concentration values, in this case 5.

10.5.4.3 Percent Relative Standard Deviation (%RSD). Using the RRFs from the initial calibration, calculate the %RSD for all target compounds using the following equations:

$$\%RSD = \frac{SD_{RRF}}{\overline{RRF}} \times 100$$

and

$$SD_{RRF} = \sqrt{\sum_{i=1}^N \frac{(RRF_i - \overline{RRF})^2}{N - 1}}$$

where: SD_{RRF} = Standard deviation of initial response factors (per compound).
 RRF_i = Relative response factor at a concentration level i.
 \overline{RRF} = Mean of initial relative response factors (per compound).

10.5.4.4 Relative Retention Times (RRT). Calculate the RRTs for each target compound over the initial calibration range using the following equation:

$$RRT = \frac{RT_c}{RT_{is}}$$

where: RT_c = Retention time of the target compound, seconds
 RT_{is} = Retention time of the internal standard, seconds.

10.5.4.5 Mean of the Relative Retention Times (\overline{RRT}). Calculate the mean of the relative retention times (\overline{RRT}) for each analyte target compound over the initial calibration range using the following equation:

$$\overline{\text{RRT}} = \sum_{i=1}^n \frac{\text{RRT}}{n}$$

where: $\overline{\text{RRT}}$ = Mean relative retention time for the target compound for each initial calibration standard.

RRT = Relative retention time for the target compound at each calibration level.

10.5.4.6 Tabulate Primary Ion Area Response (Y) for Internal Standard. Tabulate the area response (Y) of the primary ions (see Table 2) and the corresponding concentration for each compound and internal standard.

10.5.4.7 Mean Area Response (\overline{Y}) for Internal Standard. Calculate the mean area response (\overline{Y}) for each internal standard compound over the initial calibration range using the following equation:

$$\overline{Y} = \sum_{i=1}^n \frac{Y_i}{n}$$

where: \overline{Y} = Mean area response.

Y = Area response for the primary quantitation ion for the internal standard for each initial calibration standard.

10.5.4.8 Mean Retention Times ($\overline{\text{RT}}$). Calculate the mean of the retention times ($\overline{\text{RT}}$) for each internal standard over the initial calibration range using the following equation:

$$\overline{\text{RT}} = \sum_{i=1}^n \frac{\text{RT}_i}{n}$$

where: $\overline{\text{RT}}$ = Mean retention time, seconds

RT = Retention time for the internal standard for each initial calibration standard, seconds.

10.5.5 Technical Acceptance Criteria for the Initial Calibration.

10.5.5.1 The calculated %RSD for the RRF for each compound in the calibration table must be less than 30% with at most two exceptions up to a limit of 40%.

[Note: This exception may not be acceptable for all projects. Many projects may have a specific target list of compounds which would require the lower limit for all compounds.]

10.5.5.2 The RRT for each target compound at each calibration level must be within 0.06 RRT units of the mean RRT for the compound.

10.5.5.3 The area response Y of at each calibration level must be within 40% of the mean area response \overline{Y} over the initial calibration range for each internal standard.

10.5.5.4 The retention time shift for each of the internal standards at each calibration level must be within 20 s of the mean retention time over the initial calibration range for each internal standard.

10.5.6 Corrective Action.

10.5.6.1 Criteria. If the initial calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to meet the initial calibration technical acceptance criteria.

10.5.6.2 Schedule. Initial calibration acceptance criteria *must* be met before any field samples, performance evaluation (PE) samples, or blanks are analyzed.

10.6 Daily Calibration

10.6.1 Summary. Prior to the analysis of samples and blanks but after tuning criteria have been met, the initial calibration of each GC/MS system must be routinely checked by analyzing a daily calibration standard to ensure that the instrument continues to remain under control. The daily calibration standard, which is the nominal 10 ppbv level calibration standard, should contain all the target compounds.

10.6.2 Frequency. A check of the calibration curve must be performed once every 24 hours on a GC/MS system that has met the tuning criteria. The daily calibration sequence starts with the injection of the BFB. If the BFB analysis meets the ion abundance criteria for BFB, then a daily calibration standard may be analyzed.

10.6.3 Procedure. The mid-level calibration standard (10 ppbv) is analyzed in a GC/MS system that has met the tuning and mass calibration criteria following the same procedure in Section 10.5.

10.6.4 Calculations. Perform the following calculations.

[Note: As indicated earlier, the area response of the primary quantitation ion is used unless otherwise stated.]

10.6.4.1 Relative Response Factor (RRF). Calculate a relative response factor (RRF) for each target compound using the equation in Section 10.5.4.1.

10.6.4.2 Percent Difference (%D). Calculate the percent difference in the RRF of the daily RRF (24-hour) compared to the mean RRF in the most recent initial calibration. Calculate the %D for each target compound using the following equation:

$$\%D = \frac{RRF_c - \overline{RRF}_i}{\overline{RRF}_i} \times 100$$

where: RRF_c = RRF of the compound in the continuing calibration standard.

\overline{RRF}_i = Mean RRF of the compound in the most recent initial calibration.

10.6.5 Technical Acceptance Criteria. The daily calibration standard must be analyzed at the concentration level and frequency described in this Section 10.6 and on a GC/MS system meeting the BFB instrument performance check criteria (see Section 10.4).

The %D for each target compound in a daily calibration sequence must be within ± 30 percent in order to proceed with the analysis of samples and blanks. A control chart showing %D values should be maintained.

10.6.6 Corrective Action. If the daily calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to meet the daily calibration technical acceptance criteria.

Daily calibration acceptance criteria must be met before any field samples, performance evaluation (PE) samples, or blanks are analyzed. If the % D criteria are not met, it will be necessary to rerun the daily calibration sample.

10.7 Blank Analyses

10.7.1 Summary. To monitor for possible laboratory contamination, laboratory method blanks are analyzed at least once in a 24-hour analytical sequence. All steps in the analytical procedure are performed on the blank

using all reagents, standards, equipment, apparatus, glassware, and solvents that would be used for a sample analysis.

A laboratory method blank (LMB) is an unused, certified canister that has not left the laboratory. The blank canister is pressurized with humidified, ultra-pure zero air and carried through the same analytical procedure as a field sample. The injected aliquot of the blank must contain the same amount of internal standards that are added to each sample.

10.7.2 Frequency. The laboratory method blank must be analyzed after the calibration standard(s) and before any samples are analyzed.

Whenever a high concentration sample is encountered (i.e., outside the calibration range), a blank analysis should be performed immediately after the sample is completed to check for carryover effects.

10.7.3 Procedure. Fill a cleaned and evacuated canister with humidified zero air (RH >20 percent, at 25°C). Pressurize the contents to 2 atm.

The blank sample should be analyzed using the same procedure outlined under Section 10.8.

10.7.4 Calculations. The blanks are analyzed similar to a field sample and the equations in Section 10.5.4 apply.

10.7.5 Technical Acceptance Criteria. A blank canister should be analyzed daily.

The area response for each internal standard (IS) in the blank must be within ± 40 percent of the mean area response of the IS in the most recent valid calibration.

The retention time for each of the internal standards must be within ± 0.33 minutes between the blank and the most recent valid calibration.

The blank should not contain any target analyte at a concentration greater than its quantitation level (three times the MDL as defined in Section 11.2) and should not contain additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte.

10.7.6 Corrective Action. If the blanks do not meet the technical acceptance criteria, the analyst should consider the analytical system to be out of control. It is the responsibility of the analyst to ensure that contaminants in solvents, reagents, glassware, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated. If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures need to be taken and documented before further sample analysis proceeds.

If an analyte in the blank is found to be out of control (i.e., contaminated) and the analyte is also found in associated samples, those sample results should be "flagged" as possibly contaminated.

10.8 Sample Analysis

10.8.1 Summary. An aliquot of the air sample from a canister (e.g., 500 mL) is preconcentrated and analyzed by GC/MS under conditions stated in Sections 10.1 and 10.2. If using the multisorbent/dry purge approach, adjust the dry purge volume to reduce water effects in the analytical system to manageable levels.

[Note: The analyst should be aware that pressurized samples of high humidity samples will contain condensed water. As a result, the humidity of the sample released from the canister during analysis will vary

in humidity, being lower at the higher canister pressures and increasing in humidity as the canister pressures decreases. Storage integrity of water soluble compounds may also be affected.]

10.8.2 Frequency. If time remains in the 24-hour period in which an initial calibration is performed, samples may be analyzed without analysis of a daily calibration standard.

If time does not remain in the 24-hour period since the injection of the instrument performance check standard in which an initial calibration is performed, both the instrument performance check standard and the daily calibration standard should be analyzed before sample analysis may begin.

10.8.3 Procedure for Instrumental Analysis. Perform the following procedure for analysis.

10.8.3.1 All canister samples should be at temperature equilibrium with the laboratory.

10.8.3.2 Check and adjust the mass flow controllers to provide correct flow rates for the system.

10.8.3.3 Connect the sample canister to the inlet of the GC/MS analytical system, as shown in Figure 15 [Figure 16 shows an alternate two stage concentrator using multisorbent traps followed by a trap cooled by a closed cycle cooler (15)]. The desired sample flow is established through the six-port chromatographic valve and the preconcentrator to the downstream flow controller. The absolute volume of sample being pulled through the trap must be consistent from run to run.

10.8.3.4 Heat/cool the GC oven and cryogenic or adsorbent trap to their set points. Assuming a six-port valve is being used, as soon as the trap reaches its lower set point, the six-port chromatographic valve is cycled to the trap position to begin sample collection. Utilize the sample collection time which has been optimized by the analyst.

10.8.3.5 Use the arrangement shown in Figure 13, (i.e., a gastight syringe or some alternate method) introduce an internal standard during the sample collection period. Add sufficient internal standard equivalent to 10 ppbv in the sample. For example, a 0.5 mL volume of a mixture of internal standard compounds, each at 10 ppmv concentration, added to a sample volume of 500 mL, will result in 10 ppbv of each internal standard in the sample.

10.8.3.6 After the sample and internal standards are preconcentrated on the trap, the GC sampling valve is cycled to the inject position and the trap is swept with helium and heated. Assuming a focusing trap is being used, the trapped analytes are thermally desorbed onto a focusing trap and then onto the head of the capillary column and are separated on the column using the GC oven temperature program. The canister valve is closed and the canister is disconnected from the mass flow controller and capped. The trap is maintained at elevated temperature until the beginning of the next analysis.

10.8.3.7 Upon sample injection onto the column, the GC/MS system is operated so that the MS scans the atomic mass range from 35 to 300 amu. At least ten scans per eluting chromatographic peak should be acquired. Scanning also allows identification of unknown compounds in the sample through searching of library spectra.

10.8.3.8 Each analytical run must be checked for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral characteristics of that compound.

10.8.3.9 Secondary ion quantitation is allowed only when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the laboratory record book.

10.8.4 Calculations. The equation below is used for calculating concentrations.

$$C_x = \frac{A_x C_{is} DF}{A_{is} RRF}$$

where: C_x = Compound concentration, ppbv.

A_x = Area of the characteristic ion for the compound to be measured, counts.

A_{is} = Area of the characteristic ion for the specific internal standard, counts.

C_{is} = Concentration of the internal standard spiking mixture, ppbv

\overline{RRF} = Mean relative response factor from the initial calibration.

DF = Dilution factor calculated as described in section 2. If no dilution is performed, DF = 1.

[Note: The equation above is valid under the condition that the volume (~500 μ L) of internal standard spiking mixture added in all field and QC analyses is the same from run to run, and that the volume (~500 mL) of field and QC sample introduced into the trap is the same for each analysis.]

10.8.5 Technical Acceptance Criteria.

[Note: If the most recent valid calibration is an initial calibration, internal standard area responses and RTs in the sample are evaluated against the corresponding internal standard area responses and RTs in the mid level standard (10 ppbv) of the initial calibration.]

10.8.5.1 The field sample must be analyzed on a GC/MS system meeting the BFB tuning, initial calibration, and continuing calibration technical acceptance criteria at the frequency described in Sections 10.4, 10.5 and 10.6.

10.8.5.2 The field samples must be analyzed along with a laboratory method blank that met the blank technical acceptance criteria.

10.8.5.3 All of the target analyte peaks should be within the initial calibration range.

10.8.5.4 The retention time for each internal standard must be within ± 0.33 minutes of the retention time of the internal standard in the most recent valid calibration.

10.8.6 Corrective Action. If the on-column concentration of any compound in any sample exceeds the initial calibration range, an aliquot of the original sample must be diluted and reanalyzed. Guidance in performing dilutions and exceptions to this requirement are given below.

- Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.
- The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

[Note: Analysis involving dilution should be reported with a dilution factor and nature of the dilution gas.]

10.8.6.1 Internal standard responses and retention times must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 20 sec from the latest daily (24-hour) calibration standard (or mean retention time over the initial calibration range), the GC/MS system must be inspected for malfunctions, and corrections made as required.

10.8.6.2 If the area response for any internal standard changes by more than ± 40 percent between the sample and the most recent valid calibration, the GC/MS system must be inspected for malfunction and

corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

10.8.6.3 If, after reanalysis, the area responses or the RTs for all internal standards are inside the control limits, then the problem with the first analysis is considered to have been within the control of the Laboratory. Therefore, submit only data from the analysis with SICPs within the limits. This is considered the initial analysis and should be reported as such on all data deliverables.

11. Requirements for Demonstrating Method Acceptability for VOC Analysis from Canisters

11.1 Introduction

11.1.1 There are three performance criteria which must be met for a system to qualify under Compendium Method TO-15. These criteria are: the method detection limit of ≤ 0.5 ppbv, replicate precision within 25 percent, and audit accuracy within 30 percent for concentrations normally expected in contaminated ambient air (0.5 to 25 ppbv).

11.1.2 Either SIM or SCAN modes of operation can be used to achieve these criteria, and the choice of mode will depend on the number of target compounds, the decision of whether or not to determine tentatively identified compounds along with other VOCs on the target list, as well as on the analytical system characteristics.

11.1.3 Specific criteria for each Title III compound on the target compound list must be met by the analytical system. These criteria were established by examining summary data from EPA's Toxics Air Monitoring System Network and the Urban Air Toxics Monitoring Program network. Details for the determination of each of the criteria follow.

11.2 Method Detection Limit

11.2.1 The procedure chosen to define the method detection limit is that given in the *Code of Federal Regulations* (40 CFR 136 Appendix B).

11.2.2 The method detection limit is defined for each system by making seven replicate measurements of the compound of interest at a concentration near (within a factor of five) the expected detection limit, computing the standard deviation for the seven replicate concentrations, and multiplying this value by 3.14 (i.e., the Student's t value for 99 percent confidence for seven values). Employing this approach, the detection limits given in Table 4 were obtained for some of the VOCs of interest.

11.3 Replicate Precision

11.3.1 The measure of replicate precision used for this program is the absolute value of the difference between replicate measurements of the sample divided by the average value and expressed as a percentage as follows:

$$\text{percent difference} = \frac{|x_1 - x_2|}{\bar{x}} \times 100$$

where:

- x_1 = First measurement value.
- x_2 = Second measurement value.
- \bar{x} = Average of the two values.

11.3.2 There are several factors which may affect the precision of the measurement. The nature of the compound of interest itself such as molecular weight, water solubility, polarizability, etc., each have some effect on the precision, for a given sampling and analytical system. For example, styrene, which is classified as a polar VOC, generally shows slightly poorer precision than the bulk of nonpolar VOCs. A primary influence on precision is the concentration level of the compound of interest in the sample, i.e., the precision degrades as the concentration approaches the detection limit. A conservative measure was obtained from replicate analysis of "real world" canister samples from the TAMS and UATMP networks. These data are summarized in Table 5 and suggest that a replicate precision value of 25 percent can be achieved for each of the target compounds.

11.4 Audit Accuracy

11.4.1 A measure of analytical accuracy is the degree of agreement with audit standards. Audit accuracy is defined as the difference between the nominal concentration of the audit compound and the measured value divided by the audit value and expressed as a percentage, as illustrated in the following equation:

$$\text{Audit Accuracy, \%} = \frac{\text{Spiked Value} - \text{Observed Value}}{\text{Spiked Value}} \times 100$$

11.4.2 Audit accuracy results for TAMS and UATMP analyses are summarized in Table 6 and were used to form the basis for a selection of 30 percent as the performance criterion for audit accuracy.

12. References

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APPENDIX A.

LISTING OF SOME COMMERCIAL WATER
MANAGEMENT SYSTEMS USED WITH AUTOGC SYSTEMS

Tekmar Dohrman Company
7143 East Kemper Road
Post Office Box 429576
Cincinnati, Ohio 45242-9576
(513) 247-7000
(513) 247-7050 (Fax)
(800) 543-4461
[Moisture control module]

Entech Laboratory Automation
950 Enchanted Way No. 101
Simi Valley, California 93065
(805) 527-5939
(805) 527-5687 (Fax)
[Microscale Purge and Trap]

Dynatherm Analytical Instruments
Post Office Box 159
Kelton, Pennsylvania 19346
(215) 869-8702
(215) 869-3885 (Fax)
[Thermal Desorption System]

XonTech Inc.
6862 Hayenhurst Avenue
Van Nuys, CA 91406
(818) 787-7380
(818) 787-4275 (Fax)
[Multi-adsorbent trap/dry purge]

Graseby
500 Technology Ct.
Smyrna, Georgia 30082
(770) 319-9999
(770) 319-0336 (Fax)
(800) 241-6898
[Controlled Desorption Trap]

Varian Chromatography System
2700 Mitchell Drive
Walnut Creek, California 94898
(510) 945-2196
(510) 945-2335 (FAX)
[Variable Temperature Adsorption Trap]

APPENDIX B.**COMMENT ON CANISTER CLEANING PROCEDURES**

The canister cleaning procedures given in Section 8.4 require that canister pressure be reduced to <0.05 mm Hg before the cleaning process is complete. Depending on the vacuum system design (diameter of connecting tubing, valve restrictions, etc.) and the placement of the vacuum gauge, the achievement of this value may take several hours. In any case, the pressure gauge should be placed near the canisters to determine pressure. The objective of requiring a low pressure evacuation during canister cleaning is to reduce contaminants. If canisters can be routinely certified (<0.2 ppbv for target compounds) while using a higher vacuum, then this criteria can be relaxed. However, the ultimate vacuum achieved during cleaning should always be <0.2 mm Hg.

Canister cleaning as described in Section 8.4 and illustrated in Figure 10 requires components with special features. The vacuum gauge shown in Figure 10 must be capable of measuring 0.05 mm Hg with less than a 20% error. The vacuum pump used for evacuating the canister must be noncontaminating while being capable of achieving the 0.05 mm Hg vacuum as monitored near the canisters. Thermoelectric vacuum gauges and turbomolecular drag pumps are typically being used for these two components.

An alternate to achieving the canister certification requirement of <0.2 ppbv for all target compounds is the criteria used in Compendium Method TO-12 that the total carbon count be <10 ppbC. This check is less expensive and typically more exacting than the current certification requirement and can be used if proven to be equivalent to the original requirement. This equivalency must be established by comparing the total nonmethane organic carbon (TNMOC) expressed in ppbC to the requirement that individual target compounds be <0.2 ppbv for a series of analytical runs.

APPENDIX C.**LISTING OF COMMERCIAL MANUFACTURERS AND RE-SUPPLIERS OF
SPECIALLY-PREPARED CANISTERS**

BRC/Rasmussen
17010 NW Skyline Blvd.
Portland, Oregon 97321
(503) 621-1435

Meriter
1790 Potrero Drive
San Jose, CA 95124
(408) 265-6482

Restek Corporation
110 Benner Circle
Bellefonte, PA 16823-8812
(814) 353-1300
(800) 356-1688

Scientific Instrumentation Specialists
P.O. Box 8941
815 Courtney Street
Moscow, ID 83843
(208) 882-3860

Graseby
500 Technology Ct.
Smyrna, Georgia 30082
(404) 319-9999
(800) 241-6898

XonTech Inc.
6862 Hayenhurst Avenue
Van Nuys, CA 91406
(818) 787-7380

APPENDIX D.

LISTING OF COMMERCIAL SUPPLIERS OF PERMEATION TUBES AND SYSTEMS

Kin-Tek
504 Laurel St.
Lamarque, Texas 77568
(409) 938-3627
(800) 326-3627

Vici Metronics, Inc.
2991 Corvin Drive
Santa Clara, CA 95051
(408) 737-0550

Analytical Instrument Development, Inc.
Rt. 41 and Newark Rd.
Avondale, PA 19311
(215) 268-3181

Ecology Board, Inc.
9257 Independence Ave.
Chatsworth, CA 91311
(213) 882-6795

Tracor, Inc.
6500 Tracor Land
Austin, TX
(512) 926-2800

Metronics Associates, Inc.
3201 Porter Drive
Standford Industrial Park
Palo Alto, CA 94304
(415) 493-5632

TABLE 1. VOLATILE ORGANIC COMPOUNDS ON THE TITLE III CLEAN AIR AMENDMENT LIST--
MEMBERSHIP IN COMPENDIUM METHOD TO-14A LIST AND THE SOW-CLP LIST OF VOCs

Compound	CAS No.	BP (°C)	v.p. (mmHg) ¹	MW ¹	TO-14A	CLP-SOW
Methyl chloride (chloromethane); CH ₃ Cl	74-87-3	-23.7	3.8 x 10	50.5	X	X
Carbonyl sulfide; COS	463-58-1	-50.0	3.7 x 10	60.1		
Vinyl chloride (chloroethene); C ₂ H ₃ Cl	75-01-4	-14.0	3.2 x 10	62.5	X	X
Diazomethane; CH ₂ N ₂	334-88-3	-23.0	2.8 x 10	42.1		
Formaldehyde; CH ₂ O	50-00-0	-19.5	2.7 x 10	30		
1,3-Butadiene; C ₄ H ₆	106-99-0	-4.5	2.0 x 10	54		X
Methyl bromide (bromomethane); CH ₃ Br	74-83-9	3.6	1.8 x 10	94.9	X	X
Phosgene; CCl ₂ O	75-44-5	8.2	1.2 x 10	99		
Vinyl bromide (bromoethene); C ₂ H ₃ Br	593-60-2	15.8	1.1 x 10	107		
Ethylene oxide; C ₂ H ₄ O	75-21-8	10.7	1.1 x 10	44		
Ethyl chloride (chloroethane); C ₂ H ₅ Cl	75-00-3	12.5	1.0 x 10	64.5	X	X
Acetaldehyde (ethanal); C ₂ H ₄ O	75-07-0	21.0	952	44		
Vinylidene chloride (1,1-dichloroethylene); C ₂ H ₂ Cl ₂	75-35-4	31.7	500	97	X	X
Propylene oxide; C ₃ H ₆ O	75-56-9	34.2	445	58		
Methyl iodide (iodomethane); CH ₃ I	74-88-4	42.4	400	141.9		
Methylene chloride; CH ₂ Cl ₂	75-09-2	40.0	349	84.9	X	X
Methyl isocyanate; C ₂ H ₃ NO	624-83-9	59.6	348	57.1		
Allyl chloride (3-chloropropene); C ₃ H ₅ Cl	107-05-1	44.5	340	76.5	X	X
Carbon disulfide; CS ₂	75-15-0	46.5	260	76		
Methyl tert-butyl ether; C ₅ H ₁₂ O	1634-04-4	55.2	249	86		
Propionaldehyde; C ₂ H ₅ CHO	123-38-6	49.0	235	58.1		
Ethylidene dichloride (1,1-dichloroethane); C ₂ H ₄ Cl ₂	75-34-3	57.0	230	99	X	

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmHg)	MW ¹	TO-14A	CLP-SOW
Chloroprene (2-chloro-1,3-butadiene); C ₄ H ₅ Cl	126-99-8	59.4	226	88.5		
Chloromethyl methyl ether; C ₂ H ₅ ClO	107-30-2	59.0	224	80.5		
Acrolein (2-propenal); C ₃ H ₄ O	107-02-8	52.5	220	56		X
1,2-Epoxybutane (1,2-butylene oxide); C ₄ H ₈ O	106-88-7	63.0	163	72		
Chloroform; CHCl ₃	67-66-3	61.2	160	119	X	X
Ethyleneimine (aziridine); C ₂ H ₅ N	151-56-4	56	160.0	43		
1,1-Dimethylhydrazine; C ₂ H ₈ N ₂	57-14-7	63	157.0	60.0		
Hexane; C ₆ H ₁₄	110-54-3	69.0	120	86.2	X	
1,2-Propyleneimine (2-methylaziridine); C ₃ H ₇ N	75-55-8	66.0	112	57.1		
Acrylonitrile (2-propenenitrile); C ₃ H ₃ N	107-13-1	77.3	100	53	X	
Methyl chloroform (1,1,1-trichloroethane); C ₂ H ₃ Cl ₃	71-55-6	74.1	100	133.4	X	X
Methanol; CH ₄ O	67-56-1	65.0	92.0	32		X
Carbon tetrachloride; CCl ₄	56-23-5	76.7	90.0	153.8	X	X
Vinyl acetate; C ₄ H ₆ O ₂	108-05-4	72.2	83.0	86		X
Methyl ethyl ketone (2-butanone); C ₄ H ₈ O	78-93-3	79.6	77.5	72		X
Benzene; C ₆ H ₆	71-43-2	80.1	76.0	78	X	X
Acetonitrile (cyanomethane); C ₂ H ₃ N	75-05-8	82	74.0	41.0		X
Ethylene dichloride (1,2-dichloroethane); C ₂ H ₄ Cl ₂	107-06-2	83.5	61.5	99	X	X
Triethylamine; C ₆ H ₁₅ N	121-44-8	89.5	54.0	101.2		
Methylhydrazine; CH ₆ N ₂	60-34-4	87.8	49.6	46.1		
Propylene dichloride (1,2-dichloropropane); C ₃ H ₆ Cl ₂	78-87-5	97.0	42.0	113	X	X
2,2,4-Trimethyl pentane C ₈ H ₁₈	540-84-1	99.2	40.6	114		
1,4-Dioxane (1,4-Diethylene oxide); C ₄ H ₈ O ₂	123-91-1	101	37.0	88		
Bis(chloromethyl) ether; C ₂ H ₄ Cl ₂ O	542-88-1	104	30.0	115		
Ethyl acrylate; C ₅ H ₈ O ₂	140-88-5	100	29.3	100		
Methyl methacrylate; C ₅ H ₈ O ₂	80-62-6	101	28.0	100.1		

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmHg) ¹	MW ¹	TO-14A	CLP-SOW
Methyl methacrylate; C ₅ H ₈ O ₂	80-62-101	101	28.0	100.1		
1,3-Dichloropropene; C ₃ H ₄ Cl ₂ (cis)	542-75-6	112	27.8	111	X	X
Toluene; C ₇ H ₈	108-88-3	111	22.0	92	X	X
Trichloroethylene; C ₂ HCl ₃	79-01-6	87.0	20.0	131.4	X	X
1,1,2-Trichloroethane; C ₂ H ₃ Cl ₃	79-00-5	114	19.0	133.4	X	X
Tetrachloroethylene; C ₂ Cl ₄	127-18-4	121	14.0	165.8	X	X
Epichlorohydrin (1-chloro-2,3-epoxy propane); C ₃ H ₅ ClO	106-89-8	117	12.0	92.5		
Ethylene dibromide (1,2-dibromoethane); C ₂ H ₄ Br ₂	106-93-4	132	11.0	187.9	X	X
N-Nitroso-N-methylurea; C ₂ H ₅ N ₃ O ₂	684-93-5	124	10.0	103		
2-Nitropropane; C ₃ H ₇ NO ₂	79-46-9	120	10.0	89		
Chlorobenzene; C ₆ H ₅ Cl	108-90-7	132	8.8	112.6	X	X
Ethylbenzene; C ₈ H ₁₀	100-41-4	136	7.0	106	X	X
Xylenes (isomer & mixtures); C ₈ H ₁₀	1330-20-7	142	6.7	106.2	X	X
Styrene; C ₈ H ₈	100-42-5	145	6.6	104	X	X
p-Xylene; C ₈ H ₁₀	106-42-3	138	6.5	106.2	X	X
m-Xylene; C ₈ H ₁₀	108-38-3	139	6.0	106.2	X	X
Methyl isobutyl ketone (hexone); C ₆ H ₁₂ O	108-10-1	117	6.0	100.2		
Bromoform (tribromomethane); CHBr ₃	75-25-2	149	5.6	252.8		
1,1,2,2-Tetrachloroethane; C ₂ H ₂ Cl ₄	79-34-5	146	5.0	167.9	X	X
o-Xylene; C ₈ H ₁₀	95-47-6	144	5.0	106.2	X	X
Dimethylcarbamyl chloride; C ₃ H ₆ ClNO	79-44-7	166	4.9	107.6		
N-Nitrosodimethylamine; C ₂ H ₆ N ₂ O	62-75-9	152	3.7	74		
Beta-Propiolactone; C ₃ H ₄ O ₂	57-57-8	Decomposes at 162	3.4	72		
Cumene (isopropylbenzene); C ₉ H ₁₂	98-82-8	153	3.2	120		

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	V.p. (mmHg) ¹	MW ¹	TO-14A	CLP-SOW
Cumene (isopropylbenzene); C9H12	98-82-8	153	3.2	120		
Acrylic acid; C3H4O2	79-10-7	141	3.2	72		
N,N-Dimethylformamide; C3H7NO	68-12-2	153	2.7	73		
1,3-Propane sultone; C3H6O3S	1120-71-4	180/30mm	2.0	122.1		
Acetophenone; C8H8O	98-86-2	202	1.0	120		
Dimethyl sulfate; C2H6O4S	77-78-1	188	1.0	126.1		
Benzyl chloride (a-chlorotoluene); C7H7Cl	100-44-7	179	1.0	126.6	X	X
1,2-Dibromo-3-chloropropane; C3H5Br2Cl	96-12-8	196	0.80	236.4		
Bis(2-Chloroethyl)ether; C4H8Cl2O	111-44-4	178	0.71	143		
Chloroacetic acid; C2H3ClO2	79-11-8	189	0.69	94.5		
Aniline (aminobenzene); C6H7N	62-53-3	184	0.67	93		
1,4-Dichlorobenzene (p-); C6H4Cl2	106-46-7	173	0.60	147	X	X
Ethyl carbamate (urethane); C3H7NO2	51-79-6	183	0.54	89		
Acrylamide; C3H5NO	79-06-1	125/25 mm	0.53	71		
N,N-Dimethylaniline; C8H11N	121-69-7	192	0.50	121		
Hexachloroethane; C2Cl6	67-72-1	Sublimes at 186	0.40	236.7		
Hexachlorobutadiene; C4Cl6	87-68-3	215	0.40	260.8	X	X
Isophorone; C9H14O	78-59-1	215	0.38	138.2		
N-Nitrosomorpholine; C4H8N2O2	59-89-2	225	0.32	116.1		
Styrene oxide; C8H8O	96-09-3	194	0.30	120.2		
Diethyl sulfate; C4H10O4S	64-67-5	208	0.29	154		
Cresylic acid (cresol isomer mixture); C7H8O	1319-77-3	202	0.26	108		
o-Cresol; C7H8O	95-48-7	191	0.24	108		
Catechol (o-hydroxyphenol); C6H6O2	120-80-9	240	0.22	110		
Phenol; C6H6O	108-95-2	182	0.20	94		

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmHg) ¹	MW ¹	TO-14A	CLP-SOW
Catechol (o-hydroxyphenol); C6H6O2	120-80-9	240	0.22	110		
Phenol; C6H6O	108-95-2	182	0.20	94		
1,2,4-Trichlorobenzene; C6H3Cl3	120-82-1	213	0.18	181.5	X	X
nitrobenzene; C6H5NO2	98-95-3	211	0.15	123		

¹Vapor pressure (v.p.), boiling point (BP) and molecularweight (MW) data from:

- (a)D. L. Jones and J. bursey, "Simultaneous Control of PM-10 and Hazardous Air Pollutants II: Rationale for Selection of Hazardous Air Pollutants as Potential Particulate Matter," Report EPA-452/R-93/013, U. S. Environmental Protection Agency, Research Triangle Park, NC, October 1992;
- (b)R. C. Weber, P. A. Parker, and M. Bowser. Vapor Pressure Distribution of Selected Organic Chemicals, Report EPA-600/2-81-021, U. S. Environmental Protection Agency, Cincinnati, OH, February 1981; and
- (c)R. C. Weast, ed., "CRC Handbook of Chemistry and Physics," 59th edition, CRC Press, Boca Raton, 1979.

**TABLE 2. CHARACTERISTIC MASSES (M/Z) USED FOR QUANTIFYING
THE TITLE III CLEAN AIR ACT AMENDMENT COMPOUNDS**

Compound	CAS No.	Primary Ion	Secondary Ion
Methyl chloride (chloromethane); CH ₃ Cl	74-87-3	50	52
Carbonyl sulfide; COS	463-88-1	60	62
Vinyl chloride (chloroethene); C ₂ H ₃ Cl	75-01-4	62	64
Diazomethane; CH ₂ N ₂	334-88-3	42	41
Formaldehyde; CH ₂ O	50-00-0	29	30
1,3-Butadiene; C ₄ H ₆	106-99-0	39	54
Methyl bromide (bromomethane); CH ₃ Br	74-83-9	94	96
Phosgene; CCl ₂ O	75-44-5	63	65
Vinyl bromide (bromoethene); C ₂ H ₃ Br	593-60-2	106	108
Ethylene oxide; C ₂ H ₄ O	75-21-8	29	44
Ethyl chloride (chloroethane); C ₂ H ₅ Cl	75-00-3	64	66
Acetaldehyde (ethanal); C ₂ H ₄ O	75-07-0	44	29, 43
Vinylidene chloride (1,1-dichloroethylene); C ₂ H ₂ Cl ₂	75-35-4	61	96
Propylene oxide; C ₃ H ₆ O	75-56-9	58	57
Methyl iodide (iodomethane); CH ₃ I	74-88-4	142	127
Methylene chloride; CH ₂ Cl ₂	75-09-2	49	84, 86
Methyl isocyanate; C ₂ H ₃ NO	624-83-9	57	56
Allyl chloride (3-chloropropene); C ₃ H ₅ Cl	107-05-1	76	41, 78
Carbon disulfide; CS ₂	75-15-0	76	44, 78
Methyl tert-butyl ether; C ₅ H ₁₂ O	1634-04-4	73	41, 53
Propionaldehyde; C ₂ H ₅ CHO	123-38-6	58	29, 57
Ethylidene dichloride (1,1-dichloroethane); C ₂ H ₄ Cl ₂	75-34-3	63	65, 27
Chloroprene (2-chloro-1,3-butadiene); C ₄ H ₅ Cl	126-99-8	88	53, 90
Chloromethyl methyl ether; C ₂ H ₅ ClO	107-30-2	45	29, 49
Acrolein (2-propenal); C ₃ H ₄ O	107-02-8	56	55
1,2-Epoxybutane (1,2-butylene oxide); C ₄ H ₈ O	106-88-7	42	41, 72
Chloroform; CHCl ₃	67-66-3	83	85, 47
Ethyleneimine (aziridine); C ₂ H ₅ N	151-56-4	42	43
1,1-Dimethylhydrazine; C ₂ H ₈ N ₂	57-14-7	60	45, 59
Hexane; C ₆ H ₁₄	110-54-3	57	41, 43
1,2-Propyleneimine (2-methylaziridine); C ₃ H ₇ N	75-55-8	56	57, 42
Acrylonitrile (2-propenenitrile); C ₃ H ₃ N	107-13-1	53	52
Methyl chloroform (1,1,1 trichloroethane); C ₂ H ₃ Cl ₃	71-55-6	97	99, 61
Methanol; CH ₄ O	67-56-1	31	29
Carbon tetrachloride; CCl ₄	56-23-5	117	119
Vinyl acetate; C ₄ H ₆ O ₂	108-05-4	43	86
Methyl ethyl ketone (2-butanone); C ₄ H ₈ O	78-93-3	43	72

TABLE 2. (continued)

Compound	CAS No.	Primary Ion	Secondary Ion
Benzene; C ₆ H ₆	71-43-2	78	77, 50
Acetonitrile (cyanomethane); C ₂ H ₃ N	75-05-8	41	40
Ethylene dichloride (1,2-dichloroethane); C ₂ H ₄ Cl ₂	107-06-2	62	64, 27
Triethylamine; C ₆ H ₁₅ N	121-44-8	86	58, 101
Methylhydrazine; CH ₆ N ₂	60-34-4	46	31, 45
Propylene dichloride (1,2-dichloropropane); C ₃ H ₆ Cl ₂	78-87-5	63	41, 62
2,2,4-Trimethyl pentane; C ₈ H ₁₈	540-84-1	57	41, 56
1,4-Dioxane (1,4 Diethylene oxide); C ₄ H ₈ O ₂	123-91-1	88	58
Bis(chloromethyl) ether; C ₂ H ₄ Cl ₂ O	542-88-1	79	49, 81
Ethyl acrylate; C ₅ H ₈ O ₂	140-88-5	55	73
Methyl methacrylate; C ₅ H ₈ O ₂	80-62-6	41	69, 100
1,3-Dichloropropene; C ₃ H ₄ Cl ₂ (cis)	542-75-6	75	39, 77
Toluene; C ₇ H ₈	108-88-3	91	92
Trichloethylene; C ₂ HCl ₃	79-01-6	130	132, 95
1,1,2-Trichloroethane; C ₂ H ₃ Cl ₃	79-00-5	97	83, 61
Tetrachloroethylene; C ₂ Cl ₄	127-18-4	166	164, 131
Epichlorohydrin (1-chloro-2,3-epoxy propane); C ₃ H ₅ ClO	106-89-8	57	49, 62
Ethylene dibromide (1,2-dibromoethane); C ₂ H ₄ Br ₂	106-93-4	107	109
N-Nitroso-N-methylurea; C ₂ H ₅ N ₃ O ₂	684-93-5	60	44, 103
2-Nitropropane; C ₃ H ₇ NO ₂	79-46-9	43	41
Chlorobenzene; C ₆ H ₅ Cl	108-90-7	112	77, 114
Ethylbenzene; C ₈ H ₁₀	100-41-4	91	106
Xylenes (isomer & mixtures); C ₈ H ₁₀	1330-20-7	91	106
Styrene; C ₈ H ₈	100-42-5	104	78, 103
p-Xylene; C ₈ H ₁₀	106-42-3	91	106
m-Xylene; C ₈ H ₁₀	108-38-3	91	106
Methyl isobutyl ketone (hexone); C ₆ H ₁₂ O	108-10-1	43	58, 100
Bromoform (tribromomethane); CHBr ₃	75-25-2	173	171, 175
1,1,2,2-Tetrachloroethane; C ₂ H ₂ Cl ₄	79-34-5	83	85
o-Xylene; C ₈ H ₁₀	95-47-6	91	106
Dimethylcarbonyl chloride; C ₃ H ₆ ClNO	79-44-7	72	107
N-Nitrosodimethylamine; C ₂ H ₆ N ₂ O	62-75-9	74	42
Beta-Propiolactone; C ₃ H ₄ O ₂	57-57-8	42	43
Cumene (isopropylbenzene); C ₉ H ₁₂	98-82-8	105	120
Acrylic acid; C ₃ H ₄ O ₂	79-10-7	72	45, 55
N,N-Dimethylformamide; C ₃ H ₇ NO	68-12-2	73	42, 44
1,3-Propane sultone; C ₃ H ₆ O ₃ S	1120-71-4	58	65, 122

TABLE 2. (continued)

Compound	CAS No.	Primary Ion	Secondary Ion
Acetophenone; C ₈ H ₈ O	98-86-2	105	77, 120
Dimethyl sulfate; C ₂ H ₆ O ₄ S	77-78-1	95	66, 96
Benzyl chloride (a-chlorotoluene); C ₇ H ₇ Cl	100-44-7	91	126
1,2-Dibromo-3-chloropropane; C ₃ H ₅ Br ₂ Cl	96-12-8	57	155, 157
Bis(2-Chloroethyl)ether; C ₄ H ₈ Cl ₂ O	111-44-4	93	63, 95
Chloroacetic acid; C ₂ H ₃ ClO ₂	79-11-8	50	45, 60
Aniline (aminobenzene); C ₆ H ₇ N	62-53-3	93	66
1,4-Dichlorobenzene (p-); C ₆ H ₄ Cl ₂	106-46-7	146	148, 111
Ethyl carbamate (urethane); C ₃ H ₇ NO ₂	51-79-6	31	44, 62
Acrylamide; C ₃ H ₅ NO	79-06-1	44	55, 71
N,N-Dimethylaniline; C ₈ H ₁₁ N	121-69-7	120	77, 121
Hexachloroethane; C ₂ Cl ₆	67-72-1	201	199, 203
Hexachlorobutadiene; C ₄ Cl ₆	87-68-3	225	227, 223
Isophorone; C ₉ H ₁₄ O	78-59-1	82	138
N-Nitrosomorpholine; C ₄ H ₈ N ₂ O ₂	59-89-2	56	86, 116
Styrene oxide; C ₈ H ₈ O	96-09-3	91	120
Diethyl sulfate; C ₄ H ₁₀ O ₄ S	64-67-5	45	59, 139
Cresylic acid (cresol isomer mixture); C ₇ H ₈ O	1319-77-3		
o-Cresol; C ₇ H ₈ O	95-48-7	108	107
Catechol (o-hydroxyphenol); C ₆ H ₆ O ₂	120-80-9	110	64
Phenol; C ₆ H ₆ O	108-95-2	94	66
1,2,4-Trichlorobenzene; C ₆ H ₃ Cl ₃	120-82-1	180	182, 184
Nitrobenzene; C ₆ H ₅ NO ₂	98-95-3	77	51, 123

TABLE 3. REQUIRED BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria ¹
50	8.0 to 40.0 Percent of m/e 95
75	30.0 to 66.0 Percent of m/e 95
95	Base Peak, 100 Percent Relative Abundance
96	5.0 to 9.0 Percent of m/e 95 (See note)
173	Less than 2.0 Percent of m/e 174
174	50.0 to 120.0 Percent of m/e 95
175	4.0 to 9.0 Percent of m/e 174
176	93.0 to 101.0 Percent of m/e 174
177	5.0 to 9.0 Percent of m/e 176

¹All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.

TABLE 4. METHOD DETECTION LIMITS (MDL)¹

TO-14A List	Lab #1, SCAN	Lab #2, SIM
Benzene	0.34	0.29
Benzyl Chloride	--	--
Carbon tetrachloride	0.42	0.15
Chlorobenzene	0.34	0.02
Chloroform	0.25	0.07
1,3-Dichlorobenzene	0.36	0.07
1,2-Dibromoethane	--	0.05
1,4-Dichlorobenzene	0.70	0.12
1,2-Dichlorobenzene	0.44	--
1,1-Dichloroethane	0.27	0.05
1,2-Dichloroethane	0.24	--
1,1-Dichloroethene	--	0.22
cis-1,2-Dichloroethene	--	0.06
Methylene chloride	1.38	0.84
1,2-Dichloropropane	0.21	--
cis-1,3-Dichloropropene	0.36	--
trans-1,3-Dichloropropene	0.22	--
Ethylbenzene	0.27	0.05
Chloroethane	0.19	--
Trichlorofluoromethane	--	--
1,1,2-Trichloro-1,2,2-trifluoroethane	--	--
1,2-Dichloro-1,1,2,2-tetrafluoroethane	--	--
Dichlorodifluoromethane	--	--
Hexachlorobutadiene	--	--
Bromomethane	0.53	--
Chloromethane	0.40	--
Styrene	1.64	0.06
1,1,2,2-Tetrachloroethane	0.28	0.09
Tetrachloroethene	0.75	0.10
Toluene	0.99	0.20
1,2,4-Trichlorobenzene	--	--
1,1,1-Trichloroethane	0.62	0.21
1,1,2-Trichloroethane	0.50	--
Trichloroethene	0.45	0.07
1,2,4-Trimethylbenzene	--	--
1,3,5-Trimethylbenzene	--	--
Vinyl Chloride	0.33	0.48
m,p-Xylene	0.76	0.08
o-Xylene	0.57	0.28

¹Method Detection Limits (MDLs) are defined as the product of the standard deviation of seven replicate analyses and the student's "t" test value for 99% confidence. For Lab #2, the MDLs represent an average over four studies. MDLs are for MS/SCAN for Lab #1 and for MS/SIM for Lab #2.

**TABLE 5. SUMMARY OF EPA DATA ON REPLICATE PRECISION (RP)
FROM EPA NETWORK OPERATIONS¹**

Monitoring Compound Identification	EPA's Urban Air Toxics Monitoring Program (UATMP)			EPA's Toxics Air Monitoring Stations (TAMS)		
	%RP	#	ppbv	%RP	#	ppbv
Dichlorodifluoromethane	--		--	13.9	47	0.9
Methylene chloride	16.3	07	4.3	19.4	47	0.6
1,2-Dichloroethane	36.2	31	1.6	--	--	--
1,1,1-Trichloroethane	14.1	44	1.0	10.6	47	2.0
Benzene	12.3	56	1.6	4.4	47	1.5
Trichloroethene	12.8	08	1.3	--	--	--
Toluene	14.7	76	3.1	3.4	47	3.1
Tetrachloroethene	36.2	12	0.8	--	--	--
Chlorobenzene	20.3	21	0.9	--	--	--
Ethylbenzene	14.6	32	0.7	5.4	47	0.5
m-Xylene	14.7	75	4.0	5.3	47	1.5
Styrene	22.8	59 ²	1.1	8.7	47	0.2 ²
o-Xylene	--		--	6.0	47	0.5
p-Xylene	--					
1,3-Dichlorobenzene	49.1	06	0.6	--	--	--
1,4-Dichlorobenzene	14.7	14	6.5	--	--	--

¹Denotes the number of replicate or duplicate analysis used to generate the statistic. The replicate precision is defined as the mean ratio of absolute difference to the average value.

²Styrene and o-xylene coelute from the GC column used in UATMP. For the TAMS entries, both values were below detection limits for 18 of 47 replicates and were not included in the calculation.

**TABLE 6. AUDIT ACCURACY (AA) VALUES¹ FOR SELECTED
COMPENDIUM METHOD TO-14A COMPOUNDS**

Selected Compounds From TO-14A List	FY-88 TAMS AA(%), N=30	FY-88 UATMP AA(%), N=3
Vinyl chloride	4.6	17.9
Bromomethane	--	6.4
Trichlorofluoromethane	6.4	--
Methylene chloride	8.6	31.4
Chloroform	--	4.2
1,2-Dichloroethane	6.8	11.4
1,1,1-Trichloroethane	18.6	11.3
Benzene	10.3	10.1
Carbon tetrachloride	12.4	9.4
1,2-Dichloropropane	--	6.2
Trichloroethene	8.8	5.2
Toluene	8.3	12.5
Tetrachloroethene	6.2	--
Chlorobenzene	10.5	11.7
Ethylbenzene	12.4	12.4
o-Xylene	16.2	21.2

¹Audit accuracy is defined as the relative difference between the audit measurement result and its nominal value divided by the nominal value. N denotes the number of audits averaged to obtain the audit accuracy value. Information is not available for other TO-14A compounds because they were not present in the audit materials.

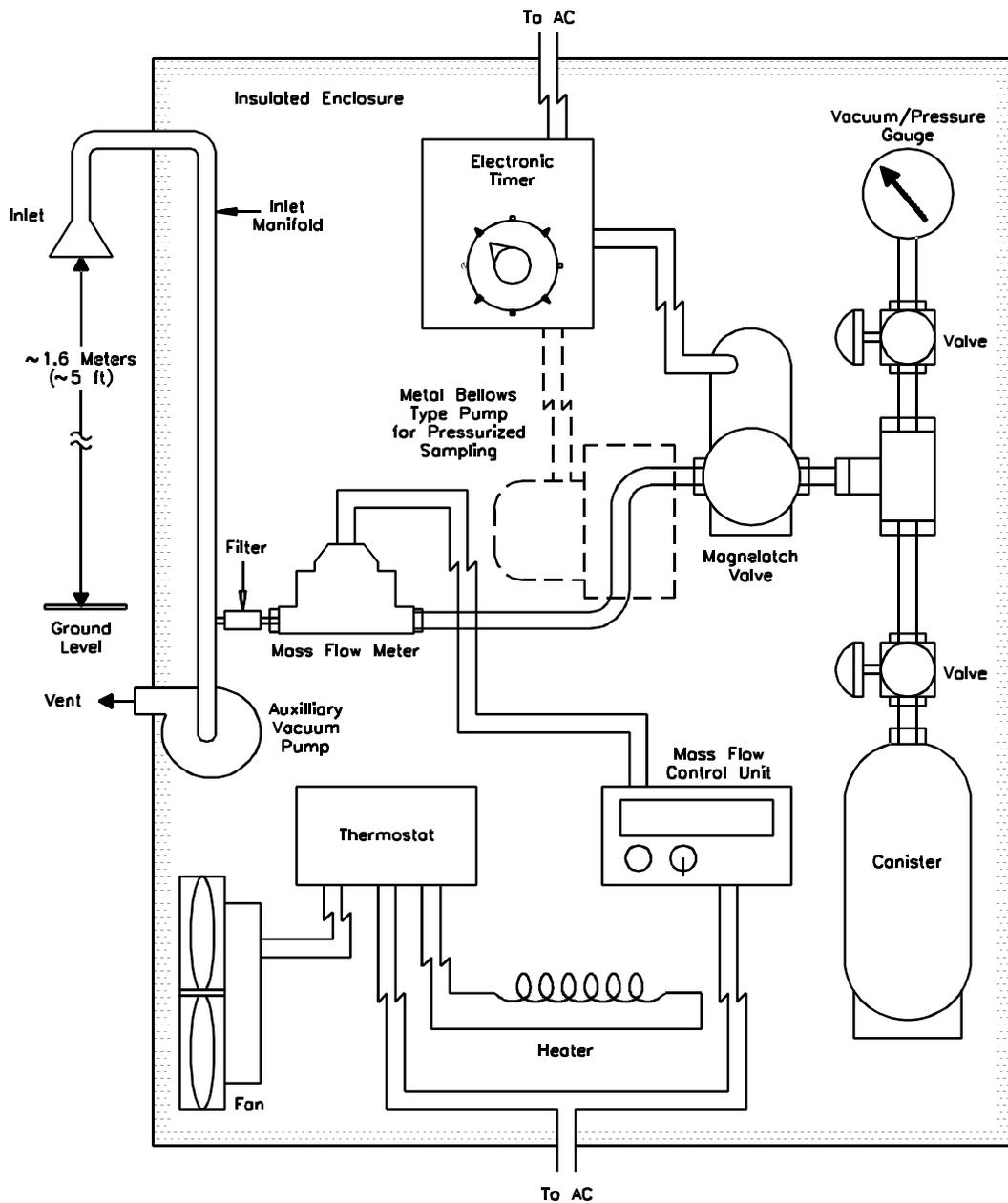
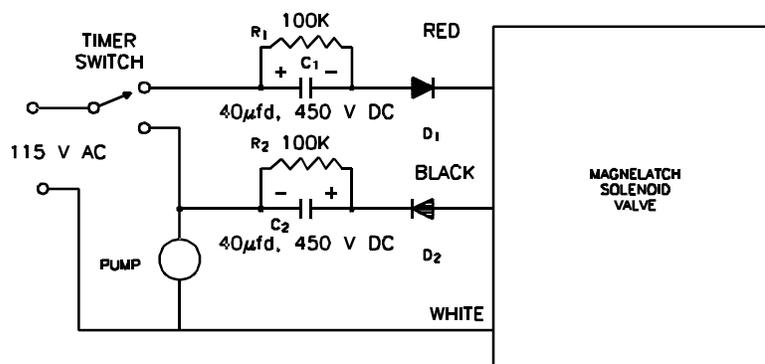
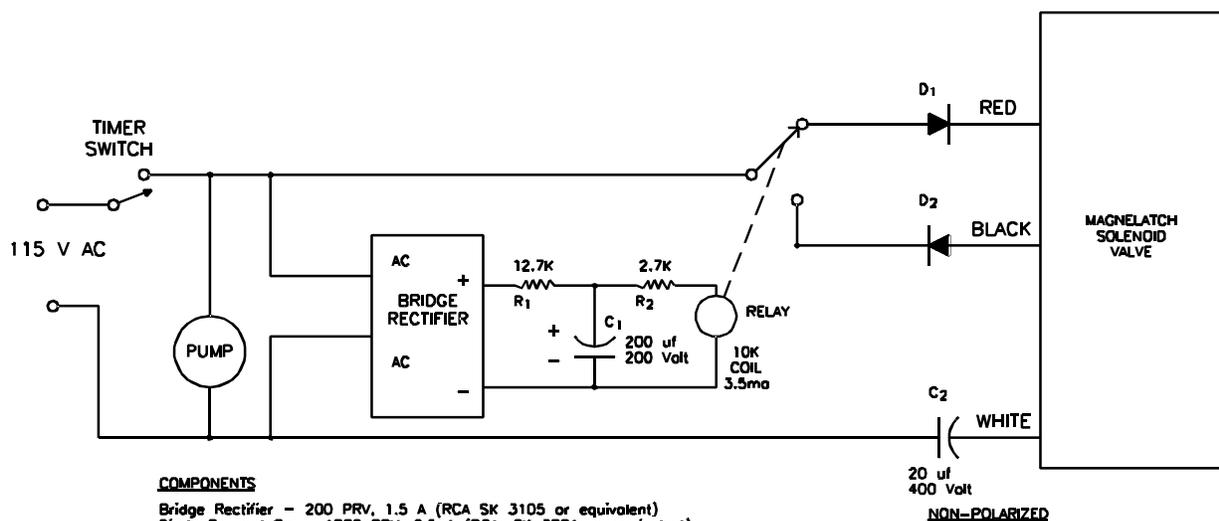


Figure 1. Sampler configuration for subatmospheric pressure or pressurized canister sampling.

**COMPONENTS**

Capacitor C₁ and C₂ - 40 µf, 450 VDC (Sprague Atom TVA 1712 or equivalent)
 Resistor R₁ and R₂ - 0.5 watt, 5% tolerance
 Diode D₁ and D₂ - 1000 PRV, 2.5 A (RCA, SK 3061 or equivalent)

(a). Simple Circuit for Operating Magnelatch Valve

**COMPONENTS**

Bridge Rectifier - 200 PRV, 1.5 A (RCA SK 3105 or equivalent)
 Diode D₁ and D₂ - 1000 PRV, 2.5 A (RCA, SK 3061 or equivalent)
 Capacitor C₁ - 200 µf, 250 VDC (Sprague Atom TVA 152B or equivalent)
 Capacitor C₂ - 20 µf, 400 VDC Non-Polarized (Sprague Atom TVAN 1652 or equivalent)
 Relay - 10,000 ohm coil, 3.5 ma (AMF Potter and Brumfield, KCP 5, or equivalent)
 Resistor R₁ and R₂ - 0.5 watt, 5% tolerance

(b). Improved Circuit Designed to Handle Power Interruptions

Figure 2. Electrical pulse circuits for driving Skinner magnelatch solenoid valve with mechanical timer.

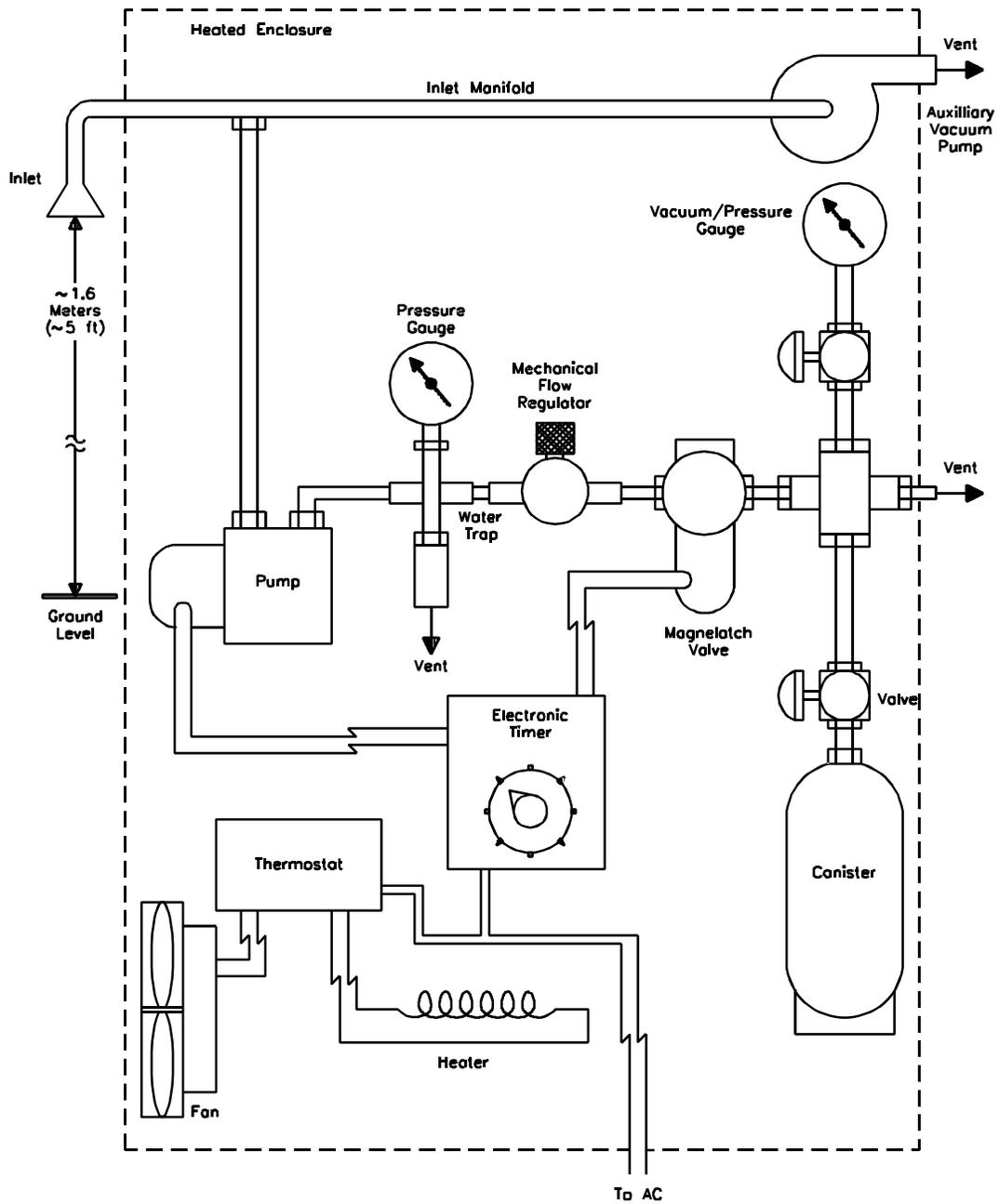


Figure 3. Alternative sampler configuration for pressurized canister sampling.

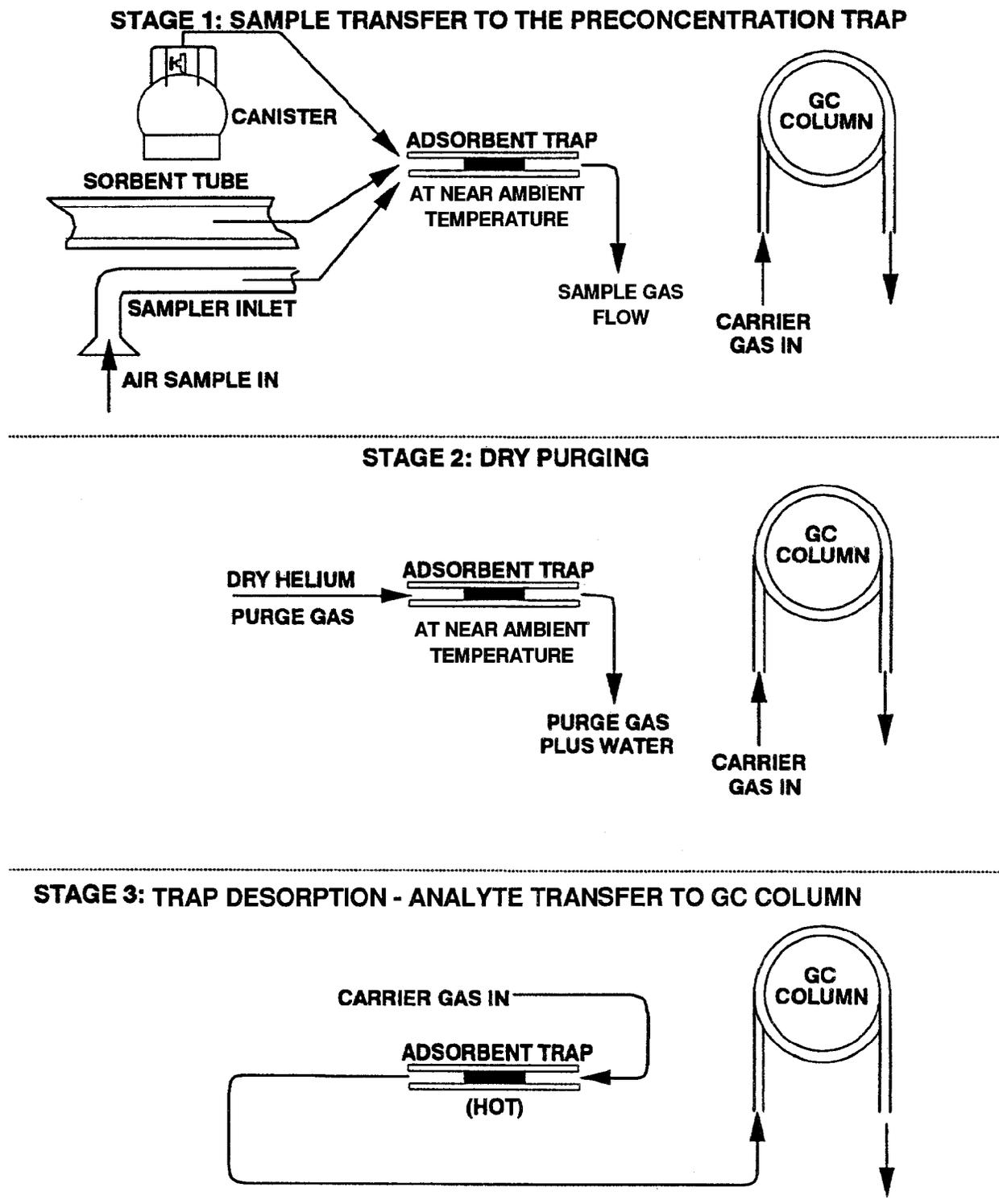


Figure 4. Illustration of three stages of dry purging of adsorbent trap.

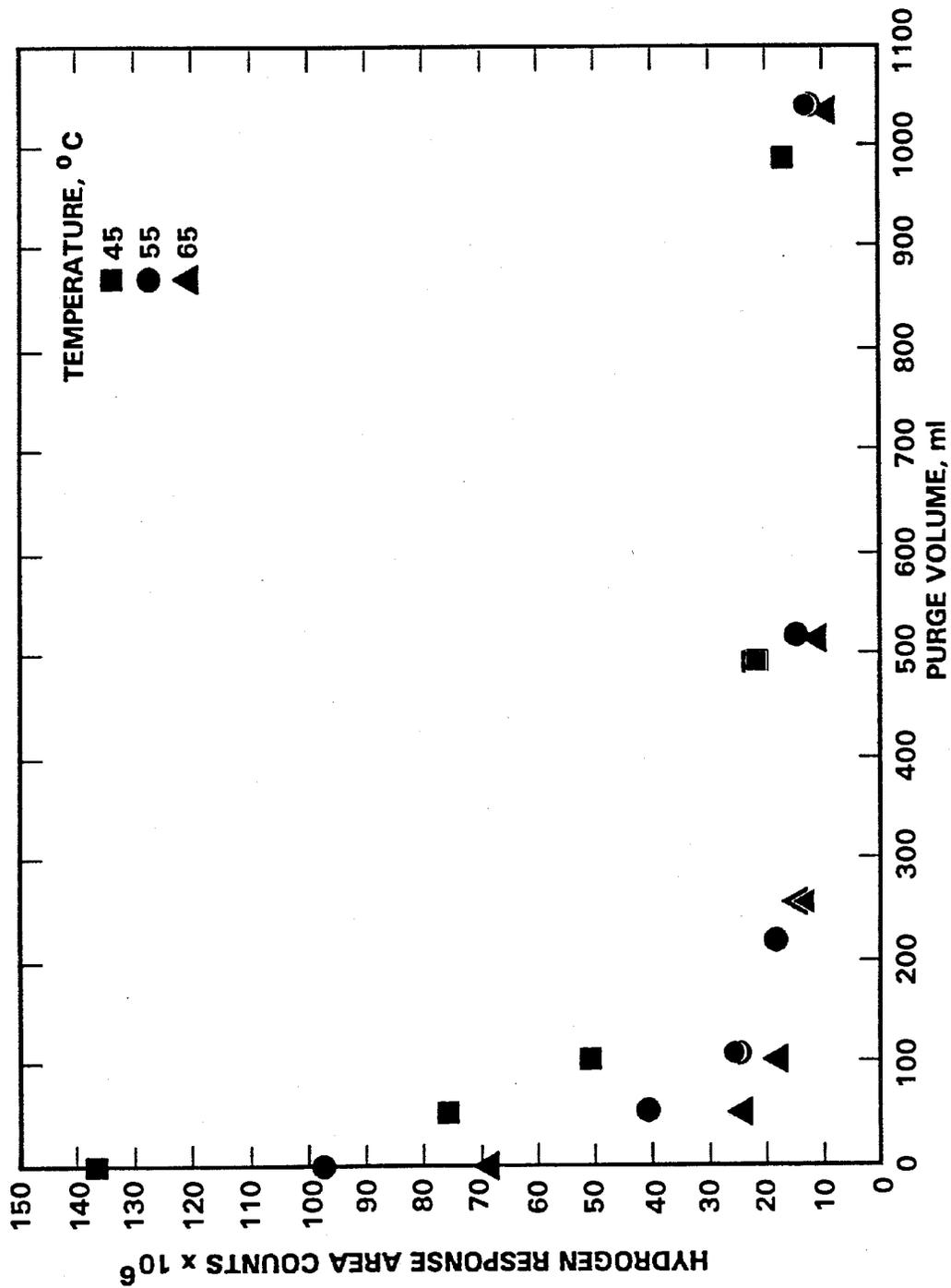


Figure 5. Residual water vapor on VOC concentrator vs. dry He purge volume.

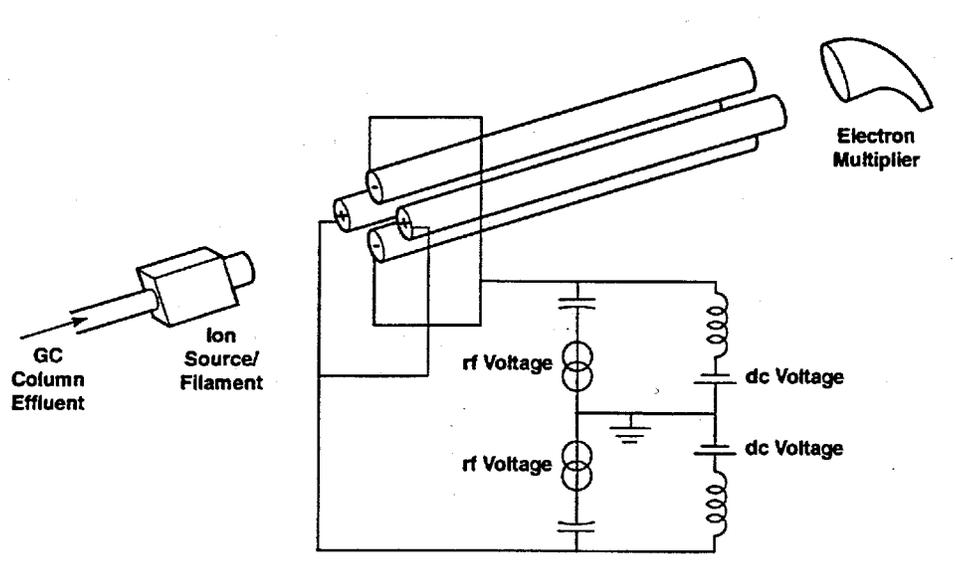


Figure 6. Simplified diagram of a quadrupole mass spectrometer.

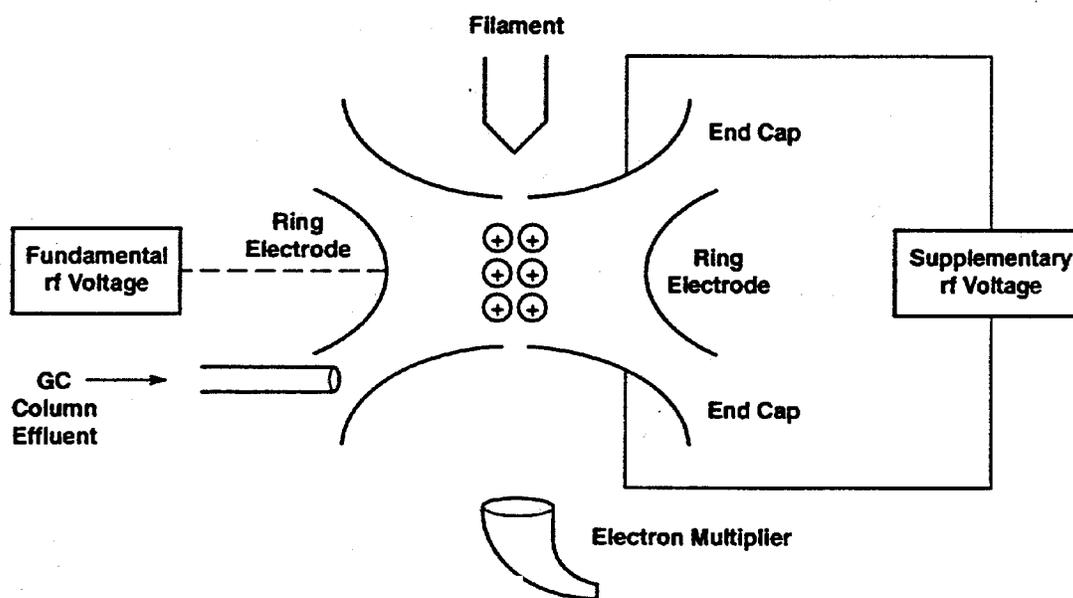


Figure 7. Simplified diagram of an ion trap mass spectrometer.

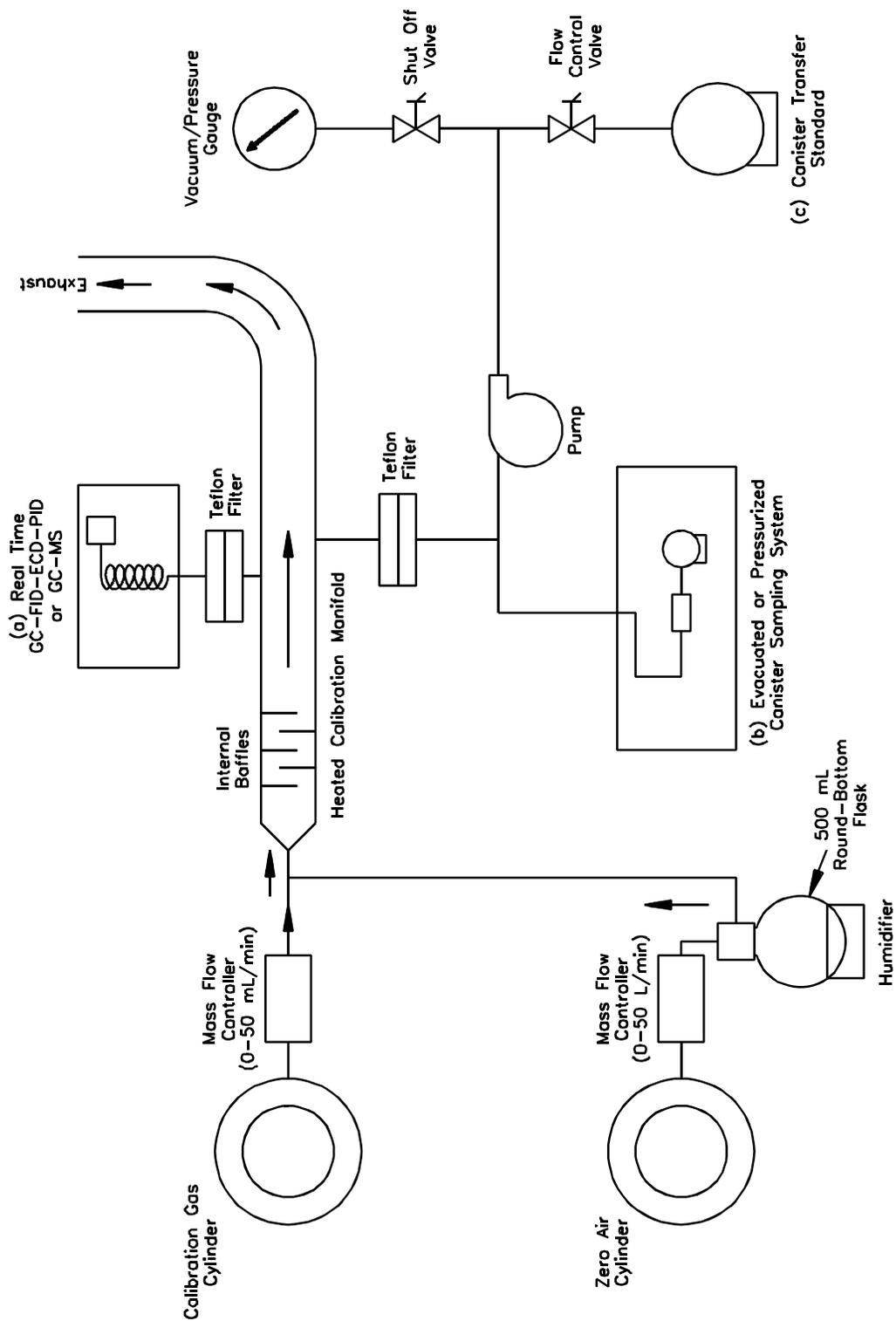


Figure 8. Schematic diagram of calibration system and manifold for (a) analytical system calibration, (b) testing canister sampling system and (c) preparing canister transfer standards.

**COMPENDIUM METHOD TO-15
CANISTER SAMPLING FIELD TEST DATA SHEET**

A. GENERAL INFORMATION

SITE LOCATION: _____
 SITE ADDRESS: _____

 SAMPLING DATE: _____

SHIPPING DATE: _____
 CANISTER SERIAL NO.: _____
 SAMPLER ID: _____
 OPERATOR: _____
 CANISTER LEAK
 CHECK DATE: _____

B. SAMPLING INFORMATION

	TEMPERATURE				PRESSURE	
	INTERIOR	AMBIENT	MAXIMUM	MINIMUM	CANISTER PRESSURE	
START						
STOP						

	SAMPLING TIMES	
	LOCAL TIME	ELAPSED TIME METER READING
START		
STOP		

FLOW RATES		
MANIFOLD FLOW RATE	CANISTER FLOW RATE	FLOW CONTROLLER READOUT

SAMPLING SYSTEM CERTIFICATION DATE: _____
 QUARTERLY RECERTIFICATION DATE: _____

C. LABORATORY INFORMATION

DATA RECEIVED: _____
 RECEIVED BY: _____
 INITIAL PRESSURE: _____
 FINAL PRESSURE: _____
 DILUTION FACTOR: _____

ANALYSIS
 GC-FID-ECD DATE: _____
 GC-MSD-SCAN DATE: _____
 GC-MSD-SIM DATE: _____

RESULTS*: _____

 GC-FID-ECD: _____
 GC-MSD-SCAN: _____
 GC-MSD-SIM: _____

 SIGNATURE/TITLE

Figure 9. Canister sampling field test data sheet (FTDS).

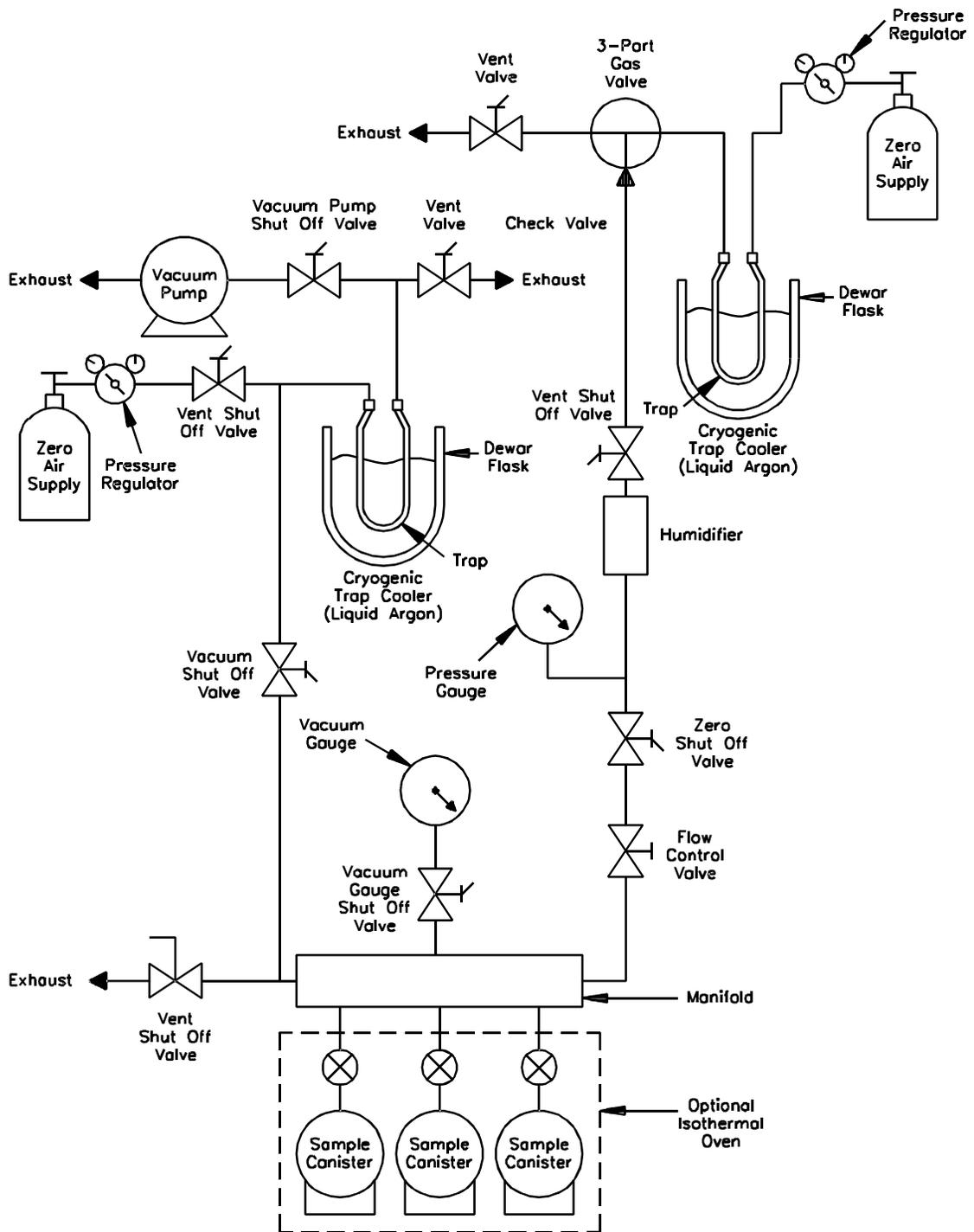


Figure 10. Canister cleaning system.

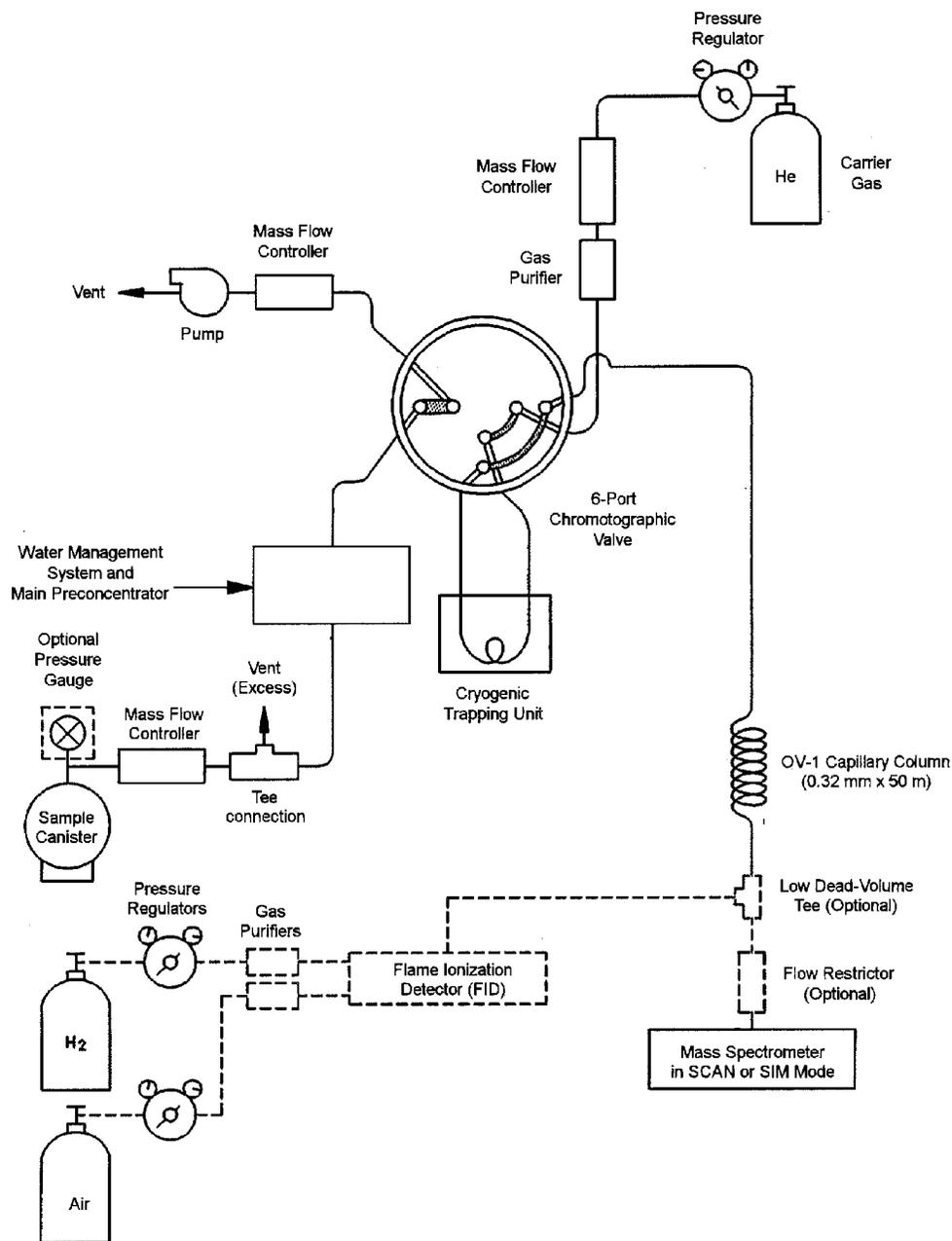
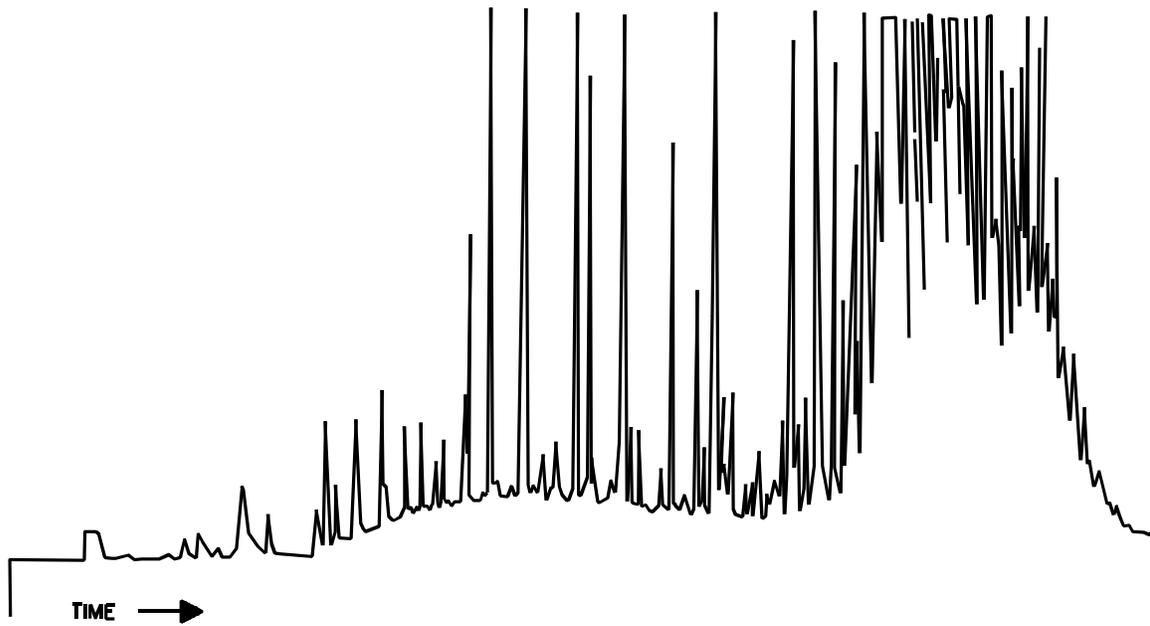


Figure 11. Canister analysis utilizing GC/MS/SCAN/SIM analytical system with optional flame ionization detector with 6-port chromatographic valve in the sample desorption mode.
[Alternative analytical system illustrated in Figure 16.]



(a). Certified Sampler



(b). Contaminated Sampler

Figure 12. Example of humid zero air test results for a clean sample canister (a) and a contaminated sample canister (b).

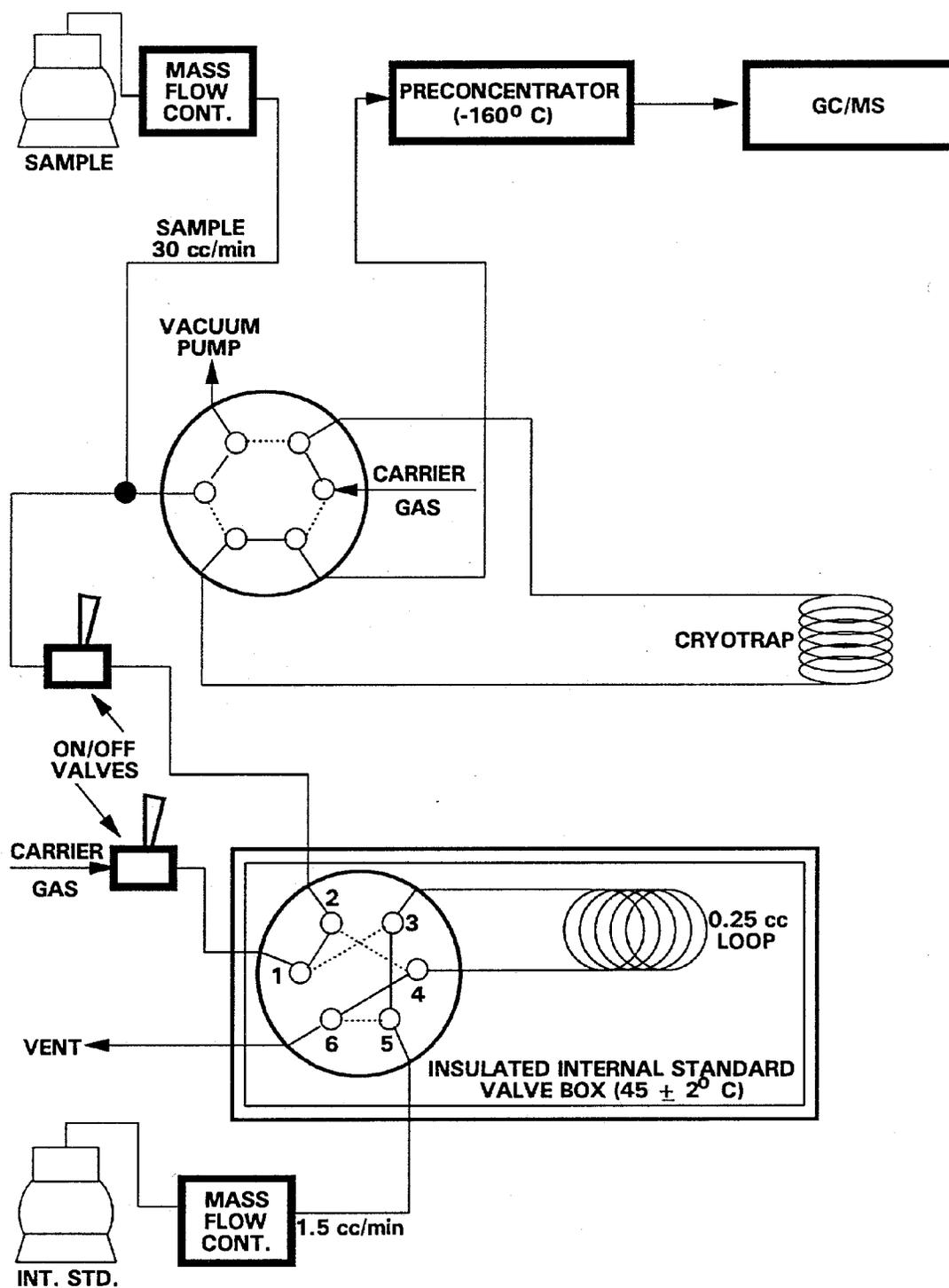


Figure 13. Diagram of design for internal standard addition.

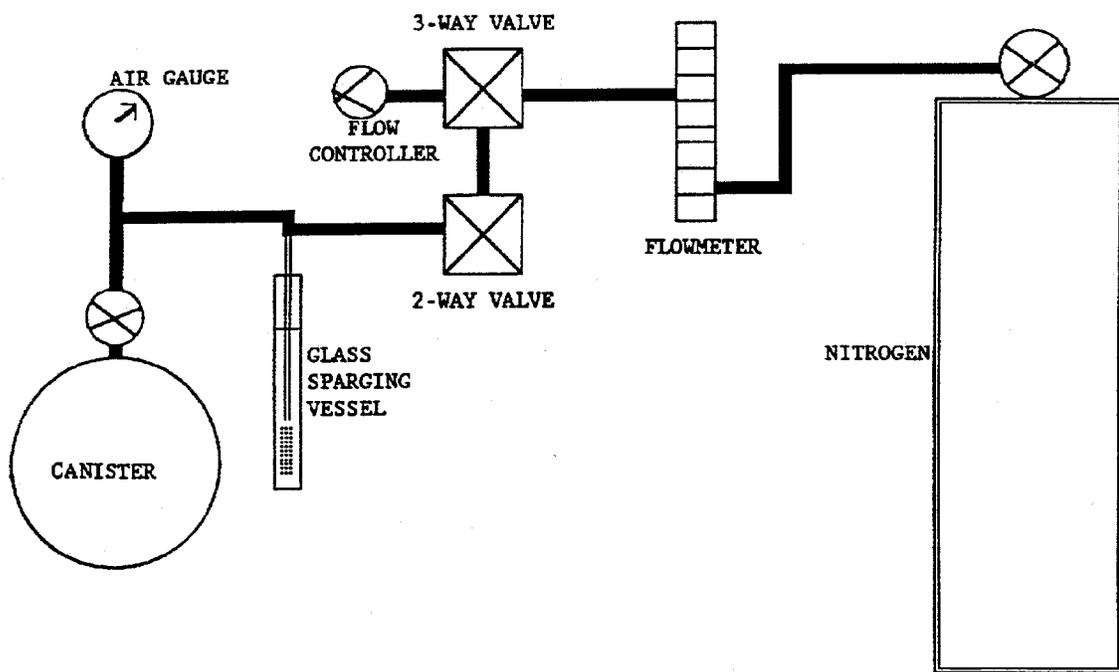


Figure 14. Water method of standard preparation in canisters.

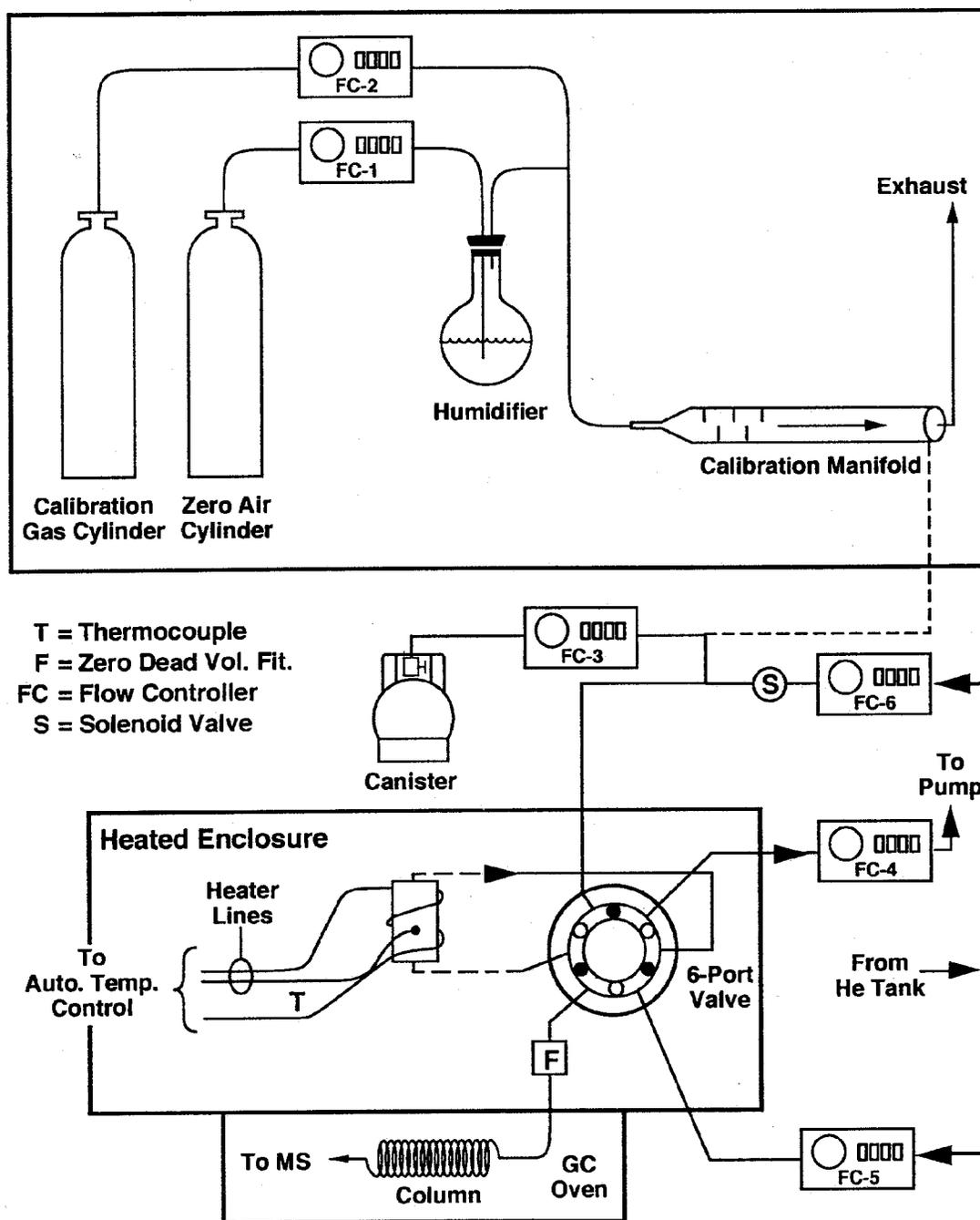


Figure 15. Diagram of the GC/MS analytical system.

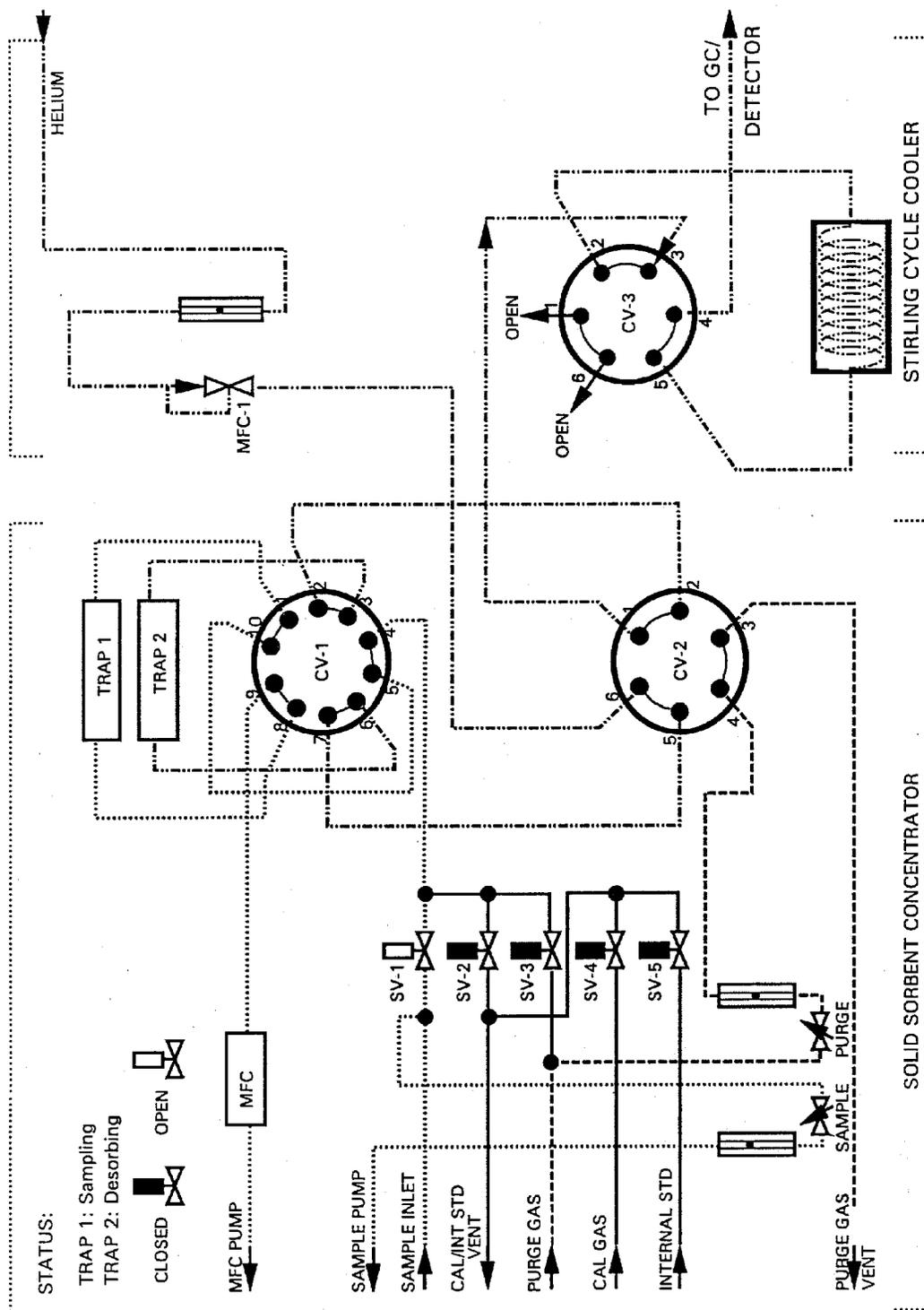


Figure 16. Sample flow diagram of a commercially available concentrator showing the combination of multisorbent tube and cooler (Trap 1 sampling; Trap 2 desorbing).



Document Information

Document Number:	Revision:
Document Title:	
Department(s):	

Date Information

Effective Date:

Notes

Document Notes:

All Dates and Times are listed in:

Signature Manifest

Document Number: ENV-SOP-MTJL-0104

Revision: 02

Title: Measurement of Volatile Organic Compounds and Gasoline Range Components in Ambient Air by Gas Chromatography/Mass Spectrometry (EPA TO-15 and EPA Method 18-Modified)

All dates and times are in Central Time Zone.

ENV-SOP-MTJL-0104

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Steven Miller (006597)	QA Director	23 Dec 2019, 03:48:01 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Heidi Ferrell (006481)	Volatiles Supervisor	24 Dec 2019, 09:41:24 AM	Approved

STANDARD OPERATING PROCEDURE

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ISSUER: Pace National – Mt. Juliet, Tennessee

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1.0 SCOPE AND APPLICATION

STATE NOTE: For samples analyzed in conjunction with the Ohio Voluntary Action Program (VAP) please utilize ENV-SOP-MTJL-0104.

CLIENT NOTE: See Attachment IV for DoD requirements.

CLIENT NOTE: For clients, whose environment laboratory quality program is administered by Environmental Standards Inc. (ESI), see controlled document QUA-25 AIR. \\FAP\NovDiskH\QAQC\Controlled Docs

1.1 This document details the procedures for analysis of volatile organic compounds (VOCs) in ambient air. The whole air samples are collected in passivated stainless steel canisters or Tedlar bags and analyzed by gas chromatography/mass spectrometry (GC/MS). The procedures describe the operational details needed to perform analysis of pressurized and sub-atmospheric air samples in the Volatiles Section of the Pace National laboratory. This procedure provides for analysis using either the SCAN or SIM modes on the Agilent GC/MS analytical systems.

1.2 The laboratory routine reporting limits for both SCAN and SIM modes are provided in the Attachment II and characteristic ions are provided in Attachment III. Reporting limits are subject to change to better meet client/project/regulatory needs or to improve laboratory method performance.

1.3 An MDL study must be completed at least annually or more frequently if major instrumentation changes occur. Method Detection Limits (MDLs) are performed based on ENV-SOP-MTJL-0016. Updated MDL records are filed and stored in a central location on the network: \\INSTSRV\Volatiles\Annual MDLs LODs and RT Studies.

1.3.1 Limit of Detection (LOD) and Limit of Quantitation (LOQ) studies are completed at the frequency required by the TNI standard per the procedure identified in the ENV-SOP-MTJL-0016, *Method Detection Limits (MDL), Limits of Detection (LOD) and Limits of Quantitation (LOQ)*. Should the procedure be utilized for DOD support; then the frequency of these studies must meet the requirements of the current DOD QSM (see Attachment IV).

2.0 METHOD SUMMARY AND DEFINITIONS

2.1 Whole air is collected into Tedlar bags or evacuated canisters using passive or pump-assisted air sampling techniques. The sample of air is drawn through a sampling device that removes particulates, regulates sampling flow rate and duration, controls sample start and end times, and monitors start and end pressures. The canisters are cleaned, evacuated and certified prior to sample collection. The available instruments may be used to collect and analyze both sub-atmospheric pressure and pressurized samples.

2.2 During analysis in the laboratory, the sample canister or Tedlar bag is attached to an autosampler where typically 1 to 400cc of the air sample is pumped out of the canister and collected on a cryogen-cooled glass bead trap. Internal standard (IS) and tuning compounds are also collected on the trap with the sample. The sample and IS compounds are then transferred to a second stage Tenax trap, effectively removing most of the water and CO₂. The VOC compounds are then transferred to a third stage where they are cryogenically focused prior to injection onto the GC column. The detector used in the analysis is a quadrupole mass spectrometer.

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- 2.3 The VOC compounds are separated *via* gas chromatography and detected using a mass spectrometer, which provides both qualitative and quantitative information. The described method is based on TO-15 in the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition* (EPA/625/R-96/010b). The procedures described here are designed to meet or exceed the criteria from both of these EPA quantitative methods. The TO-14A and TO-15 methods are sufficiently similar to permit the analysis of all compounds in the TO-14A list and a subset of the TO-15 compound list using a single procedure. The compounds in Method TO-15 tend to be more polar than those in Method TO-14A, requiring special consideration to address water management. Please refer to these EPA guidance documents for additional details.
- 2.4 Absolute Pressure - Pressure measured with reference to absolute zero pressure expressed in psia. An absolute pressure value of zero is indicative of an evacuated system (vacuum).
- 2.5 Gauge Pressure - Pressure measured with reference to the surrounding atmospheric pressure expressed in units of psi. A gauge pressure value of zero is equal to atmospheric pressure.
- 2.6 Dynamic Calibration - Calibration of the analytical system with gas standard concentrations at similar concentrations, in a form identical and through the same analytical path as in the real samples.
- 2.7 Dynamic Dilution – Preparation of calibration mixtures in which concentrated standard gas are continually blended with zero air in a manifold and introduced at the inlet of the analytical system or a receiving canister.
- 2.8 Sub-atmospheric Sampling - Collection of ambient air into an evacuated canister with a final canister pressure below atmospheric pressure. This is the normal practice when collecting air with passive sampling devices since the sample collection must be stopped prior to completely filling the canister.
- 2.9 GC/MS Scan Mode – A GC/MS system in Full Scan mode will monitor a range of masses known as mass to charge ratio (abbreviated m/z). A typical mass scan range will cover from 35-500 m/z four times per second and will detect compound fragments within that range over a set time period. The Full Scan mode is quite useful when identifying unknown compounds in a sample and providing confirmation of results from GC using other types of detectors.
- 2.10 GC/MS SIM Mode – (Gas Chromatography/Mass Spectroscopy- Selective Ion Monitoring) Operation of a GC/MS in SIM mode allows for detection of specific analytes with increased sensitivity relative to full scan mode. In SIM mode the MS gathers data for masses of interest rather than looking for all masses over a wide range. Because the instrument is set to look for only masses of interest it can be specific for particular analytes of interest. Typically two to four ions are monitored per compound and the ratios of those ions are unique to the analyte of interest. In order to increase sensitivity, the mass scan rate and dwell times (the time spent looking at each mass) are adjusted. When properly setup and calibrated, GC/MS SIM can increase sensitivity by a factor of 10 to 100 times that of GC/MS Full Scan.
- 2.11 See the current Quality Assurance Manual for definitions associated with other terms found in this document.

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3.0 HEALTH AND SAFETY

- 3.1 The toxicity or carcinogenicity of each reagent used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds must be as low as reasonably achievable. A reference file of safety data sheets (SDSs) is made available on Pace National's intranet to all personnel. Use hazardous reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing and observe proper mixing protocols.
- 3.2 Glycol ethers are suspected carcinogens. All solvent handling should be done in a hood while using proper protective equipment to minimize exposure to liquid and vapor. Minimum personal protection includes the use of laboratory safety glasses, a lab coat or apron, and protective gloves.
- 3.3 The following analytes have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichloroethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds must be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

4.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

- 4.1 All samples must have been collected using a sampling plan that addresses the considerations of this method.
- 4.2 The sampling process begins with the preparation of the canisters or purchase of Tedlar bags used to collect the sample. The canisters are provided by the laboratory and are prepared based on the sample requests received on a weekly basis. Please refer to ENV-SOP-MTJL-0108 for canister cleaning and certification information.

STATE NOTE: When analyzing samples from MN and AZ, samples should not be collected in Tedlar bags. Samples received from these states in Tedlar bags must be qualified as having an improper container.

CLIENT NOTE: When analyzing samples from Environmental Standards clients, samples should not be collected in Tedlar bags. Samples received from these clients in Tedlar bags must be transferred to a summa canister or bottle vac and qualified as having an improper container.

4.3 Sample Collection

- 4.3.1 Samples are collected with either a passive critical orifice sampler or an active pump sampler with a mass flow controller. The canisters and sampling unit must be certified clean prior to collecting samples. All sampling procedures are the responsibility of the client.

4.4 Sample Storage

- 4.4.1 Under conditions of normal usage for sampling ambient air, most VOCs can be recovered from summa canisters near their original concentrations after storage times of up to thirty days from the date of collection to analysis.

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STATE NOTE: When analyzing samples from MN and NJ, canister samples must be analyzed within 14 days from the time of collection.

The holding time for Tedlar bags is generally five (5) days from collection to analysis. Shorter hold times may apply depending on regulatory agency requirements.

STATE NOTE: Samples received in a Tedlar bag from FL and AZ have a three (3) day holding time from collection.

CLIENT NOTE: Samples received in a Tedlar bag from Environmental Standards clients have a three (3) day holding time from collection. Samples can be transferred to a summa canister or bottle vac in which the holding times extends to thirty (30) days from collection.

4.4.2 Air samples are maintained in the AIR laboratory where they are secure and at ambient temperature.

4.5 Sample Preparation

4.5.1 Each canister or Tedlar bag must be visually inspected for damaged or missing parts. This includes but is not limited to valves and loose stems. Any problems found are to be communicated with the Project Manager via e-mail so that the proper instructions on how to proceed are communicated from the client to the laboratory.

4.5.2 The canister pressure is checked upon arrival into the lab. That pressure is compared to the client pressures when available. The pressure must read +/- 4"Hg from clients final sample pressure reading. If the canister pressure does not meet the criteria, the TSR is informed and communicates the information to the client requesting their guidance.

The pressure is documented on the canister label as well as in the Air Tracking software program.

Note: If there is no final vacuum documented by the client and the canister reads zero or if the field documentation of the summa pressure does not indicate zero, but the summa is received at zero, then Project Managers will be notified via e-mail of the situation to communicate with the client for guidance.

4.5.3 Connect each sample canister or Tedlar bag to an autosampler position, but leave the valve closed

4.5.4 Flush and leak check each of the autosampler positions using the SmartLab software for the autosampler.

4.5.5 Once the autopositions are leak tight, open the valves on the canisters or Tedlar bags.

4.5.6 The internal standard and surrogate compounds are automatically added to each sample by the sample concentrator

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5.0 INTERFERENCES

- 5.1 Moisture and carbon dioxide are two of the primary interferences encountered in whole air measurements due to the normally high concentration of these compounds in ambient air. The sample concentrator unit used to isolate the volatile organic compounds from whole air is designed to effectively remove water and carbon dioxide prior to sample introduction into the gas chromatograph. Elevated levels of water or carbon dioxide may severely restrict the sample size that can be measured. Compendium Method TO-15 provides guidance for water management systems as it pertains to the analysis of polar organic compounds.
- 5.2 Contamination may occur in the sampling and concentrator systems if the equipment is improperly cleaned before each use. All sampling and analysis equipment contacting the sample must be thoroughly cleaned and tested on a regular basis.
- 5.3 The potential for overlap of eluting compounds in the chromatography is significant when dealing with such an extensive compound list from two air analysis methods. The potential for encountering interferences is significantly reduced by using cryogenic focusing, a smaller ID capillary column and a mass spectrometer detector. Cryogen focusing and the small ID capillary column used in this method give enhanced compound separation such that overlapping compounds are minimized. The mass spectrometer can effectively resolve many of the remaining overlapped compounds based on the mass spectra of the compounds.

6.0 EQUIPMENT AND SUPPLIES

The operation, cleaning and scheduled maintenance procedures prescribed by the equipment manufacturer are followed as provided in the Operator's Manuals. Maintenance contracts, provided by the manufacture, are purchased for the Gas Chromatograph/Mass Spectrometer Systems. Documentation of cleaning, maintenance or system modification is recorded in a maintenance logbook that accompanies each instrument system.

6.1 Sample Containers

- 6.1.1 6L Restek Silcoan canister with fused silica lining in the can and valve
- 6.1.2 6L Entech Silonite canister with fused silica lining in the can and valve
- 6.1.3 1L Entech Silonite canister with fused silica lining in the can and valve
- 6.1.4 1L Restek Silcoan canister with fused silica lining in the can and valve
- 6.1.5 1L Tedlar bags
- 6.1.6 1.4L Entech Silonite canister with fused silica lining in the can and MicroQT

6.2 IsoTemp Forced-Air Oven

6.3 Gas Chromatograph/Mass Spectrometer System

- 6.3.1 Agilent 6890 Gas Chromatograph or equivalent
- 6.3.2 Agilent 5973 Quadrupole Detector or equivalent
- 6.3.3 Entech 7200 Preconcentrator or equivalent

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- 6.3.4 Entech 7016CA Autosampler or equivalent
- 6.3.5 Entech 7032A-LB Tedlar Bag Autosampler or equivalent
- 6.3.6 IBM-compatible Pentium personal computer
- 6.3.7 Agilent Computer Software
- 6.3.8 LIMS Network Software
- 6.3.9 J&W Scientific DB-5MS, 60m x 0.25mm ID capillary column, 0.25µm film thickness or equivalent
- 6.3.10 Compendium Method TO-15 Calibration Standard Cylinder with dedicated regulator and transfer line

6.4 Equipment Cleaning and Certification Procedures

The equipment used for sample collection and analysis must be clean and certified before use. For information regarding the canister cleaning and certification process, see ENV-SOP-MTJL-0108, *Canister Cleaning, Certification and Storage*.

7.0 REAGENTS AND STANDARDS

Working with volatile compounds presents a number of challenges not normally confronted in the handling of most other chemicals. Volatile compounds may escape from sample containers or, when present in the laboratory environment, can contaminate analytical equipment.

Sources of the reagents and chemicals are given, but may change based on availability, quality and cost. The use of a different source is acceptable without modification of the procedures provided the products are equivalent.

All reagents and standards must be recorded in the appropriate preparation log and assigned a unique number. See ENV-SOP-MTJL-0041, *Standards Logger – Tree Operation*.

- 7.1 Laboratory Reagent Water: DI water VOC free or equivalent
- 7.2 Helium, Nitrogen and Air: Ultra-high purity grade in gas cylinders of Nitrogen and breathing grade Air. Helium is used as the carrier gas in the GC/MS.
- 7.3 Internal Standard, Surrogate, and Tuning Standard
 - 7.3.1 1ppmv Internal Standard and Tune Standard Mixture
 - 7.3.1.1 The internal standard and tune standard mixture is purchased in a 3395L (2A) cylinder from Spectra Gases at a concentration of 1ppmv. The internal standard compounds are:

- Bromochloromethane
 - 1,4-Difluorobenzene
 - Chlorobenzene-d₅
 - 1,4-Bromofluorobenzene

The compounds in this mixture are typically prepared in nitrogen at a final cylinder pressure of approximately 2000psig. The standard mixture is certified by Spectra Gases for one year from preparation.

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- 7.3.1.2 The mass spectrometer tune standard and surrogate compound is 4-bromofluorobenzene.
- 7.3.2 Preparation
 - 7.3.2.1 Inject 1800cc of 1ppmv standard into a 15L Canister for TO-15 (routine scan) or 300cc of 1ppmv standard for SIM.
 - 7.3.2.2 Using an airtight syringe, add 0.20mL of laboratory reagent water (VOC free).
 - 7.3.2.3 Bring to a final volume of 20psig with nitrogen.
 - 7.3.2.4 Final concentration equals 20ppbv per component.
 - 7.3.2.5 Place canister on autosampler.
 - 7.3.2.6 Autosampler will inject 50cc of standard per sample.
 - 7.3.2.7 50cc of injected standard will result in a concentration of 4ppbv per component for TO-15 or 1.25ppbv per component for SIM.
- 7.4 Calibration Standards
 - 7.4.1 The TO-15 calibration standard is purchased as a custom mix in a 3395L (2A) cylinder from Spectra Gases at a concentration of 0.100ppmv, production number 1475123 or equivalent. The compounds in this mixture are balanced with nitrogen at a final cylinder pressure of 2000psig. The standard mixture is certified by Spectra Gases for 12 months from preparation.
 - 7.4.2 Preparation of Calibration Curve
 - 7.4.2.1 Prepare an intermediate standard(s) using the Dynamic Diluter. Bring summa to a final volume of 20psig.

Dynamic Diluter Software Settings		
Final Concentration (ppbv)	Nitrogen (cc)	Standard (cc)
0.5	3980	20
5	950	50
25	150	50

- 7.4.2.2 Using the standard mix prepared in 7.4.2.1, prepare the following calibration concentrations for routine SCAN analysis:

Standard Level (ppbv)*	Volume of 2.5ppbv Standard Used (cc)	Volume of 25ppbv Standard Used (cc)
0.19	15	-
0.3125	25	-
0.625	50	-

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Standard Level (ppbv)*	Volume of 2.5ppbv Standard Used (cc)	Volume of 25ppbv Standard Used (cc)
1.25	100	-
2.5	200	-
3.75	300	-
10	-	80
25	-	200
50	-	400
100	-	800

All compounds are calibrated with these concentrations except for: m&p Xylene = 0.31, 0.625, 1.25, 2.5, 5.0, 7.5, 10, 20, 40, 100; and TPH:

TPH Calibration Standards								
Std. Vol (cc):	50	100	200	300	400	800	1600 (400)	4000 (800)
Final Conc. (ppm):	34.02	67.5	135	202.5	270	540	1350	2700

For GC/MS SIM analysis for the compounds identified in Attachment II(b), reduce the Standard Levels and the volume of standards in the above table by 10x as presented in the following table:

Standard Level (ppbv)*	Volume of 0.5ppbv Standard Used (cc)	Volume of 25ppbv Standard Used (cc)
0.019	15	-
0.03125	25	-
0.0625	50	-
0.125	100	-
0.25	200	-
0.375	300	-
0.5	400	-
1	-	16
5	-	80
10	-	160

7.4.2.3 The low standard must be at or below the RL.

7.4.2.4 The daily initial calibration verification standard analyzed in lieu of a full initial calibration to verify the on-going stability of the existing calibration curve is prepared using the process for the 3.75ppbv calibration standard for SCAN analysis and 0.50ppbv for SIM analysis.

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7.5 Laboratory Control Standard - Stock

7.5.1 0.100ppmv TO-15 Calibration Standard Mixture

- 7.5.1.1 The TO-15 calibration standard is purchased as a custom mix in a 3395L (2A) cylinder from Spectra Gases at a concentration of 0.100ppmv, production #1433041 or equivalent.
- 7.5.1.2 The compounds in this mixture are balance with nitrogen at a final cylinder pressure of 2000psig.
- 7.5.1.3 The standard mixture is certified by Spectra Gases for 12 months from preparation.

7.5.2 Prepare an intermediate standard for GC/MS Scan analysis using the Dynamic Diluter. Bring to a final volume of 20psig with nitrogen.

Dynamic Diluter Software Settings		
Final Concentration (ppbv)	Nitrogen (cc)	Standard (cc)
0.5	3980	20
5	950	50
25	150	50

7.5.3 Second Source LCS is available upon the request of the client.

8.0 PROCEDURE

Suggested instrument conditions are presented below. Specific instrument conditions may vary slightly, depending on analysis being performed.

8.1 INSTRUMENT OPERATIONS

8.1.1 Entech Concentrator and Autosampler Settings (typical):

Line Temp	100°C	Module 2 Desorb	180°C
Bulk Head 1	30°C	Module 2 Bake	190°C
Bulk Head 2	30°C	Module 2 Desorb Tim	3.5 min
Module 1 Trap	-150°C	Module 3 Trap	-180°C
Module 1 Preheat	20°C	Module 3 Inject	2 min
Module 1 Desorb	20°C	Module 3 Bake Time	2 min
Module 1 Bake	130°C	Module 3 Event	3
Module 1 Bake Time	5 min	Module 3 Wait Time	25 min
Module 2 Trap	-30°C	Pressure Comp Factor	14
Module 2 Preheat	off	Loop Flush	30 seconds

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8.1.2 Agilent GC/MS Conditions (typical):

Initial temperature = 35°C
Hold time= 3 min.
Ramp rate = 8°C/min. to 200°C
Ramp rate = 30° C/min to 230°C
Final time = 25.63 min

8.1.3 GC/MS instrument file names are generated using the following naming convention **MMDD_##.D**

where:

M Month: (01 = January, 02 = February, 03 = March, 04 = April, 05 = May, 06 = June, 07 = July, 08 =August, 09 = September, 10 = October, 11 = November, 12 = December)

DD Day: (01-31)

##: Sequential sample numbers from 01-99.

8.1.4 Pre-Analysis Checklist for the GC/MS Run Sequence

- 8.1.4.1 Check the autosampler program.
- 8.1.4.2 Check the quantity of internal standard.
- 8.1.4.3 Check the air cylinder pressure.
- 8.1.4.4 Check the Entech 7200 or equivalent concentrator settings.
- 8.1.4.5 Check the LIMS lab comments for any special instructions.
- 8.1.4.6 Setup the acquisition sequence in the instrument log and in the computer acquisition program.
- 8.1.4.7 Check the acquisition parameters in the computer program.
- 8.1.4.8 Arrange the canisters on the autosampler.
- 8.1.4.9 Double check the order of the sample cylinders to ensure that it is consistent with the computer acquisition and the instrument log.
- 8.1.4.10 Flush and pressure test the cylinder connections on the autosampler.
- 8.1.4.11 Open the valves on the sample cylinders.

8.1.5 Analytical Sequence

The analysis sequence should be similar to the following:

- 8.1.5.1 BFB tune check (the nitrogen blank and tune check or CCV and tune check can be analyzed together), every 24 hours
- 8.1.5.2 3.75ppbv Initial Calibration Verification Standard every 24 hours for SCAN mode or 0.50ppb

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- 8.1.5.3 Replicate laboratory control samples (LCS and LCSD)
- 8.1.5.4 Daily method blank
- 8.2 GC/MS Tuning: The GC/MS system must be checked to ensure that acceptable performance criteria are achieved for the tuning compound bromofluorobenzene (BFB) at the beginning of each day and every 24 hours thereafter for as long as analysis are to be performed. This performance test must be successfully completed before any samples are analyzed.

8.2.1 The tune analysis must meet the criteria listed in EPA Method TO-15 for a 25-ng injection of BFB (4-bromofluorobenzene).

- Once the data is acquired, either select the mass spectrum at the peak apex for evaluation, or use an averaged mass spectrum (e.g., three highest abundance spectra, or across entire BFB peak). Background subtraction is conducted using a single scan prior to the elution of BFB. No part of the BFB peak or any other discrete peak should be subtracted.
- If the criteria are not achieved, the operator must retune the mass spectrometer, either automatically or manually, and the test must be repeated until all criteria are achieved.

Table 8 - BFB m/z Abundance Criteria

Mass	m/z Abundance Criteria
50	8-40 % of mass 95
75	30-66 % of mass 95
95	Base peak, 100 %
96	5-9 % of mass 95
173	<2 % of mass 174
174	50-120 % of mass 95
175	4-9 % of mass 174
176	93-101 % of mass 174
177	5-9 % of mass 176

- 8.2.2 The internal standard and surrogate mixture are added automatically by the sample concentrator and contain BFB. Analysis of a nitrogen blank will serve as a GC/MS performance test. The standard mixture is added at a rate of 50cc per sample.
- 8.3 Initial Calibration
 - 8.3.1 Calibration Standards
 - Each instrument is calibrated according to the procedures specified within EPA Method TO-15.
 - Clarification of the calibration requirements and practices of this laboratory are discussed below. Calculations can be found in section 9.
 - Refer to the EPA method protocols for additional detail.

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- Initial calibration of the GC/MS is performed before sample analysis, with the assistance of the preconcentrator calibration system.
- The preconcentrator draws standard gas from cylinders purchased at a concentration of 0.1ppmv.
- The standard gas flow into the preconcentrator is regulated by a mass flow controller or electronic flow controller that is set through the system software.
- See section 9.1 for calculation of RSD for calibration response factors and for linear fit equations. See section 10.6 for required acceptance criteria for the initial calibration.

STATE NOTE: When analyzing samples from Minnesota, the reporting limit must be verified with each calibration or at least monthly. Verification can be performed by re-quantitation of the low calibration standards using the newly updated calibration curve or by analyze a separate reporting level standard following calibration curve update. This standard must recover $\pm 40\%$ of the expected concentration. If the criterion is not met, a higher level standard may be re-quantitated or analyzed; however the reporting limit must be amended to reflect the increased concentration of the standard utilized. Analytes known to be poor performers are dealt with on a case-by-case basis.

8.3.2 Reference Spectra: A reference mass spectrum library must be generated for all the target compounds.

8.3.2.1 The reference spectra can be extracted the calibration data, provided that the target compounds do not co-elute.

8.3.2.2 In the case of co-elution, an individual compound standard analyzed using the same method conditions will be required to produce the reference mass spectra.

8.3.2.3 The reference spectra will be used for qualitative and quantitative analysis as described later in this section

8.3.3 Internal Standard Retention Time and Internal Standard Response

8.3.3.1 The internal standard responses and retention times of each standard and sample analyzed are evaluated after data acquisition.

8.3.3.2 See section 10.11 for internal standard acceptance criteria.

8.4 ROUTINE CONTINUING CALIBRATION

Daily verification of the calibration curve can be used in lieu of a full initial calibration.

8.4.1 For routine analysis, a single point initial calibration verification sample or ICV is evaluated daily to insure on-going calibration stability. See section 10.7 for required acceptance criteria.

8.5 Blank Analysis

8.5.1 Daily method blank - Analyze a summa canister containing ultra high purity nitrogen after the calibration standard and before the samples to demonstrate that the analytical system is clean and will not impart target analytes to the field

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- samples. This sample serves as the method blank for the analytical sequence. See acceptance criteria in section 10.8 for the method blank.
- 8.5.2 A blank check may also be interspersed throughout the analytical sequence to demonstrate that there is no carryover contamination from previous high concentration samples.
- 8.5.3 Nitrogen filled blanks are also used when cleaning canisters to verify the cleanliness prior to use for sampling. See ENV-SOP-MTJL-0107, *Cleaning, Certification and Storage of Air Sampling Equipment*. These canisters can be used as the daily method blank.
- 8.6 Sample Analysis
- 8.6.1 Sample Introduction
- 8.6.1.1 Sample canisters are connected to the 7016CA/D autosampler inlet ports and the canister valves are opened. Entech 7032A-LB Autosampler is only used for Tedlar Bags.
- 8.6.1.2 The sample information is recorded into the sequence log for that system, including such information as sample name, laboratory identification number, analysis file name, calibration method used, canister number, dilution factor, and volume of sample loaded.
- 8.6.1.3 While the GC oven is cooling, the pre-concentrator collects the specified volume of a single sample (up to 400cc) out of the specified sample container (canister or Tedlar bag) along with 50cc of the BFB/internal standard (IS)/Surrogate mixture and concentrates the sample volume a 3-stage trapping system.
- 8.6.1.4 The trapped sample is then thermally desorbed onto the head of the GC column, and the GC begins the temperature program.
- 8.6.2 Quantitative Compound Identification – Individual Target Analytes
- 8.6.2.1 IS peak areas for each analysis completed in the 24-hour GC/MS analysis period must be compared to the mean area response for each IS in the most recent calibration. See section 10.11 for acceptance criteria for internal standards.
- 8.6.2.2 The ID of each compound in the sample must be verified by retention time and relative abundances of the primary and secondary ions. See Attachment II for characteristic masses.
- 8.6.2.3 Each compound spectrum is compared against a reference spectrum from the spectral library.
- 8.6.3 Quantitative Compound Identification – TPH
- 8.6.3.1 Quantitation is performed using an internal standard method.
- 8.6.3.1.1 The concentration of volatile petroleum products in the sample is determined from a summation of the total response within a specified range.
- 8.6.3.1.2 The retention time window must, at a minimum, include the area immediately prior to MTBE through the conclusion of the 1,2,4-Trimethylbenzene peak and must be verified daily, using the initial calibration verification standard.

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- 8.6.3.1.3 No area other than that relating to the internal standard or surrogate may be subtracted from the retention time window in calculating results.
- 8.6.3.1.4 For the calculation of response factors for total petroleum hydrocarbons, see the equations in section 9.0.
- 8.6.3.2 Integration must be “baseline to baseline” as opposed to “valley to valley”.
 - 8.6.3.2.1 Baseline to baseline is defined here as a flat baseline drawn parallel to the x-axis of the chromatogram that includes all responses within the retention time window.
 - 8.6.3.2.2 The correct baseline coincides with a horizontal line drawn through the lowest point in the chromatogram before the end of the window, or before the solvent front.
 - 8.6.3.2.3 Baseline to baseline integration does not include the solvent peak.
 - 8.6.3.2.4 Placement of the baseline is determined for each sample.
- 8.6.4 Any manual integration performed must be documented with the exception of TPH. When manual integration is performed on a peak, the “before” and “after” integrations must be printed out and included in the data package. All manual integrations performed must be done so in accordance to ENV-SOP-MTJL-0024, *Manual Integration*.
- 8.6.5 Sample Dilutions

If any target analytes are detected that exceed the upper calibration range of the instrument, the sample is re-analyzed at a dilution if enough sample permits.

Autosampler Dilution:

- Dilutions on summa canisters can be performed one of three ways, depending on the degree of dilution needed.
- First, a smaller sample volume can be analyzed using the capabilities of the Entech autosampler. For example, for a standard sample volume of 200cc, if 20cc were analyzed, that would be equivalent to a 10 fold dilution.
- The smallest sample volume that can be accurately analyzed using the autosampler method is 1cc (or a 200x).

Pressurized Manual Dilution:

- Sometimes, a 200X dilution is not sufficient to bring the concentration of a target analyte within the calibration range. In those cases, the sample canister is pressurized resulting in a dilution of the target analytes present.
- The act of introducing more pure air into the canister performs a dilution.
- The canister can then be analyzed at 200cc or diluted using a lesser autosampler volume if necessary.

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Secondary Manual Dilution:

- In extreme cases, the canister may need to be diluted into a second evacuated canister.
- This is accomplished by using a gas tight syringe to remove an aliquot of sample (1-10mL) from the initial canister then injecting it into a clean evacuated second canister.
- The second canister is then analyzed and quantified taking into account the dilution based on the amount of sample injected and the total volume of the canister utilized.

Tedlar Bag Dilutions/1L Glass Bottle Vac:

- Dilutions on Tedlar bags or 1L bottle vacs can be performed in much the same manner as summa canisters using either the autosampler dilution or the secondary manual dilution using a second Tedlar bag or 1L bottle vac and filling it with ultra-pure helium then adding an aliquot of field sample using a gas tight syringe.

8.6.6 Qualitative Compound Identification

Qualitative identification of each compound is based on retention time and comparison of the sample mass spectrum with characteristic ions in the reference mass spectrum. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest intensity or any ions over 30% relative intensity. Compounds are identified as present when the following criteria are met:

8.6.6.1 The characteristic ions of a compound maximize in the same scan or within one scan of each other.

8.6.6.2 The retention time of the compound is within ± 0.2 seconds of the retention time of the standard component.

8.6.6.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. The presence of co-eluting compounds may alter the relative intensities and complicate the compound identification. Examination of extracted ion current profiles can aid in the selection of spectra and in qualitative identification of compounds.

8.6.6.4 Structural isomers that produce similar mass spectra and are sufficiently resolved are identified as individual isomers. If the height of the valley between two close eluting isomers is more than 25% of the sum of the two peak heights, then the structural isomers must be identified as isomeric pairs.

8.6.6.5 A library search must be performed for unknown chromatographic peaks when the total ion chromatogram of the sample contains unknown peaks larger than the internal standard peaks. A tentative identification can be assigned provided that relative intensities of major ions in the library reference spectrum are present in the sample spectrum and the relative intensities agree within 20%. Molecular ions must also be present.

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8.7 Post-Analysis Checklist

The results of each analytical run must be examined promptly upon completion. The instruments are designed to create an electronic file for each sample analyzed. The following items must be checked following each batch analysis:

8.7.1 Check all tunes for compliance with tuning requirements.

8.7.2 Check to make sure the internal standards are in the retention time window and their mass spectra are correct.

8.7.3 Review the method blank for acceptance criteria.

8.7.4 Review the LCS/LCSD pair for acceptable recovery and precision as listed in section 10.

8.8 For acceptance criteria and corrective actions regarding calibration, QC and sample analysis, refer to sections 10.0 & 11.0.

8.9 TIC's – Tentatively Identified Compounds

Periodically, clients may request additional identification of compounds that are not normally calibrated. This identification is limited to the compounds in the current mass spectral library employed by Pace National.

For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification is determined by the type of analyses being conducted. At the client request, when serving the role of QA (or referee) laboratory, tentatively identified compounds (TICs) must always be reported. Guidelines for making tentative identification are:

- (1) Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.
- (2) The relative intensities of the major ions should agree within 15% to be consistent with target compound list identification. (Example: For an ion with an abundance of 50% in the standard spectrum the corresponding sample ion abundance must be between 20 and 80%).
- (3) Molecular ions present in the reference spectrum should be present in the sample spectrum.
- (4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.
- (5) Ions present in the reference spectrum but not in the sample spectrum must be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each

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other. Only after visual comparison of sample with the nearest library searches does the mass spectral interpretation specialist assign a tentative identification.

Routinely, Pace National employs a minimum Q value of 85% for tentative identifications and a minimum concentration of 10ppb. Peaks below a Q value of 85% but above 10ppb may be reported as “Unknown”. Any identified peaks below 10ppb are removed as these could result from baseline noise or other interferences, not necessarily attributable to the field sample or reliably quantifiable using GCMS technology. Additionally, any peaks that are attributable to instrument contamination (e.g., siloxanes) are also removed.

If multiple TICs, with same exact name, exist for a sample, the LIMS will only display the TIC with the highest quality match per sample.

TIC names assigned as “Unknown” may initially have the same name as another “Unknown” until parsed and displayed in LIMS where it is given a hyphen and incremental number which then becomes a unique TIC (e.g., Unknown-1).

When reporting “Total TIC” for any client sample, only concentrations per above requirements will be used to sum the Total TIC concentration.

9.0 DATA ANALYSIS AND CALCULATIONS

9.1 TPH Calculations: The total area must be measured, from the beginning to the end marker, will be used in conjunction with the concentration to calculate the response factor.

$$RF = \frac{(\text{Total TPH Area}) \times (\text{Concentration of Internal Standard})}{(\text{Area of Internal Standard}) \times (\text{Concentration of Total TPH})}$$

$$\text{Total Sample TPH} = \frac{(\text{Area of Sample}) \times (\text{Concentration of Internal Standard})}{(\text{Area of Internal Standard}) \times (\text{Avg. RF of Total TPH})}$$

9.2 Sample Concentration: Target compound concentrations in units of ppbv are calculated using the RRFs obtained in the initial calibration. The abundance of the primary ion is used for quantitation unless there is an interference with the primary ion; in case of interference with the primary ion, a secondary ion can be used.

$$C_t = \frac{(A_t) (C_{is}) (DF)}{(A_{is}) (MRRF)}$$

Where:

- A_t = area count of the primary ion for the target compound to be measured
- A_{is} = area count of the primary ion for the ISTD
- C_t = concentration of the target compound (ppbv)
- C_{is} = concentration of the internal standard (ppbv)
- $MRRF$ = mean RRF from initial calibration
- DF = dilution factor. $DF = 1$, if no dilution.

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9.3 Concentration Conversions

$$\text{ppmv} = \text{ppbv}/1000$$

$$\text{mg}/\text{m}^3 = \frac{(\text{compound molecular weight})(\text{ppmv})}{(\text{molar volume})}$$

$$\mu\text{g}/\text{m}^3 = \frac{(\text{compound molecular weight})(\text{ppbv})}{(\text{molar volume})}$$

$$\mu\text{g}/\text{L} = \frac{(\mu\text{g}/\text{m}^3)}{1000}$$

$$\mu\text{g} = \frac{\mu\text{g}/\text{L}}{\text{sample size analyzed}}$$

$$\text{ng} = \mu\text{g} \times 1000$$

9.4 See the current Quality Assurance Manual for equations associated with common calculations.

10.0 QUALITY CONTROL AND METHOD PERFORMANCE

- 10.1 All analysts must meet the qualifications specified in ENV-SOP-MTJL-0015, *Technical Training and Personnel Qualifications* before approval to perform this method. Analysts must complete an initial demonstration of proficiency before being approved to perform this method. Continuing proficiency must be demonstrated using proficiency testing, laboratory control sample analysis and/or MDL studies. Method performance is assessed per analyst. Updated method performance records are filed and stored in a central location within the department.
- 10.2 Use the designated Run log to record batch order and standards/reagents used during analysis. See ENV-SOP-MTJL-0014, *Data Handling and Reporting*.
- 10.3 Batches are defined as sets of 1 - 20 samples. Batch analysis must include the following: 1 method blank, 1 Laboratory Control Sample (LCS) and 1 Laboratory Control Sample Duplicate (LCSD). All batch information must be maintained in the preparation documentation assigned to the department.
- 10.4 Detector Tuning - The BFB must be analyzed daily prior to any calibration or field sample analysis (once/24 hours). The acceptance criteria must meet the specifications found in Table 8.
- 10.5 Retention Time - Evaluation of retention time windows to ensure that all compounds are detected within their respective time windows. The retention time of the target analytes in

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each calibration standard must agree within +/-0.06 RRT Units. Late-eluting compounds usually have much better agreement.

- 10.6 Initial Calibration - There must be an initial calibration of the GC/MS system as described in Section 8.3. A calibration curve of at least five (5) points must be established that brackets the expected range of sample concentrations and remains within the analytical range of the instrument. The Relative Standard Deviation (RSD) for any one of the compounds must be <30% for sample analysis to proceed with two compounds being allowed to be <40%. If the RSD for any analyte is beyond the required criteria, any of the curve fits listed below may be used for calibration if the correlation coefficient is ≥ 0.990 . Establishment of a successful calibration curve occurs when analysis of continuing calibration standards indicate that a new calibration curve is required or when there has been a major change, repair, or maintenance performed on the instrument. The recalibration period does not exceed three (3) months. The most appropriate curve fitting mode is used from among the following choices below (given in order of preference):

- Average Response Factor
- Linear – No Weighting
- Linear – 1/x Weighting
- Linear – 1/x² Weighting
- Quadratic

When second order (quadratic) curves are evaluated, acceptability must include an assessment of a graphic representation of the curve to confirm that this fit type is not being used to mask detector saturation and that the curve (which defines a parabola) does not result in two concentration for one response. High order polynomial curves (i.e., third-order and greater) are not allowed at Pace National.

- 10.7 ICV - On the days that an initial calibration of the instrument is not needed, a mid-level standard is analyzed daily to verify the stability of the original calibration curve. The deviations of the response factor for the target analytes in this standard must be <30% from those of the initial calibration curve. The GC/MS system must meet the calibration criteria each 24 hours of instrument operation as described in Section 8.3. If the Percent Difference for the compounds in the single point initial calibration verification sample are <30%, then analysis of field samples may continue.
- 10.8 Method Blank – One each day of analysis, a nitrogen filled summa (method blank) must be analyzed before the samples in the analytical batch. The method blank must be analyzed following the BFB tune and calibration verification standard (ICV) and prior to any field sample analysis. This method blank verifies that the instrument is free from target analytes prior to the analysis of field samples. The acceptance criteria for target analytes in the method blank is < the MDL.
- 10.9 LCS/LCSD - On days of field sample analysis, an LCS/LCSD pair must be analyzed. The recoveries for the target analytes must be within 70-130% for accuracy and the RPD must be <25% for most commonly analyzed target in this method. Marginal exceedence limits for these analytes are 60-140%. Some analytes that are routinely quantitated by this method do not respond well due to various factors. These analytes are considered poor performers in the analytical sequence and utilize control limits based on historical data that may be updated per laboratory policy. The analytes noted in this method as poor performing are included in the table below. See LIMS for the current acceptance limits of these poor performing compounds.

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Poor Performing Compound Name
1,2,4-TRICHLOROBENZENE
1,4-DIOXANE
2-PROPANOL
4-METHYL-2-PENTANONE (MIBK)
BENZYL CHLORIDE
DICHLORODIFLUOROMETHANE
ETHANOL
HEXACHLORO-1,3-BUTADIENE
METHYL BUTYL KETONE
NAPHTHALENE
PROPENE
TETRAHYDROFURAN
TERT-BUTYL ALCOHOL
2-METHYLNAPHTHALENE

- 10.10 Surrogate (1,4-Bromofluorobenzene) - The surrogate is automatically added to each standard, QC and field sample by the autosampler. The surrogate must recovery within 60-140% of the expected value.
- 10.11 Internal Standards - In each QC and field sample, the autosampler automatically adds internal standard, along with the surrogate. The internal standard area response for each QC and field sample must be $\pm 40\%$ of the mean area response for each of the ISTDs in the multipoint calibration. The retention time of the ISTD compounds in each QC and field sample must also be within $\pm 0.06RRT$ units of the same internal standard in the multipoint calibration.
- 10.12 Manual Integration – All manual integrations must comply with the requirements found in ENV-SOP-MTJL-0024, *Manual Integration Procedure*. Before and after integrations must be available for review by the secondary data reviewer.
- 10.13 Reporting Limit Verification (RLV) – RL checks are evaluated but are currently applicable to Minnesota samples only. See State Note in Section 8.3.1 above for details.
- 10.14 Any sample analyte responses that are beyond the linear range of the calibration curve must be diluted and re-analyzed.
- 10.15 For corrective actions, see section 11.0.
- 11.0 DATA VALIDATION AND CORRECTIVE ACTION
- 11.1 BFB Instrument Tune - If the acceptance criteria are not met, the analyst can attempt a second tune injection. If the second tune also fails, the analyst must perform corrective action. Corrective actions can include: instrument autotuning, source cleaning, manual adjustment of the mass spectrometer parameters. Analysis of field sample cannot occur until a successful tune is achieved.

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- 11.2 Initial Calibration - If a calibration curve does not meet the acceptance criteria, review the points of the curve to determine if an individual point requires reanalysis, if so, re-analyze the suspect point and re-process the curve. If all calibration points analyzed appear acceptable and the calibration still does not pass criteria, perform instrument maintenance, if suspected as the cause, prepare new calibration standards, and repeat the calibration curve.
- 11.3 Initial Calibration Verification - If this criterion is not met, the ICV can be re-analyzed once. If the re-analysis continues to fail the acceptance criteria, the full calibration curve must be re-analyzed. Instrument maintenance may be necessary prior to re-calibration.
- 11.4 LCS/LCSD - If these criteria are not met, repeat the LCS and/or LCSD analysis once and if the criteria is still not met then a new standard is prepped and analyzed. If the failure persists, re-calibrate the instrument and re-analyze the LCS/LCSD and any additional sample injections that may have occurred with the previous failing LCS/LCSD pair.
- 11.5 Surrogate Recovery - If the acceptance criteria are not met, re-analyze any failing sample, method blank and/or LCS/LCSD sample. If the failure occurs in the method blank or LCS/LCSD sample, re-analyze once. If the failure persists, corrective action is needed. Corrective action can include instrument maintenance and/or re-calibration. Failures of method blanks and LCS/LCSD samples are routinely noted and addressed prior to the analysis of field samples; however if the failure occurs in the method blank or LCS/LCSD sample during an analytical sequence, then any samples analyzed in conjunction with the failure must be re-analyzed. If the failure occurs in the field sample, unless gross contamination or high target analyte levels are present, all re-analyses should be performed at the same dilution as the original analysis to determine the cause of the original failure. If the failure persists in the re-analysis, flag the data with explanation to the client.
- 11.6 Method Blank Analysis - If the method blank does not meet criteria, the analysis must be repeated with a different nitrogen filled canister. If the method blank is still not valid, the pre-concentrator/GC/MS system must be checked for leaks and/or contamination. Canister cleaning batch nitrogen blanks can be used for clean method blanks since one canister of each cleaned batch must be analyzed by GC/MS for the batch to be certified as clean. An acceptable method blank must be achieved prior to any field sample analysis.
- NOTE:** Tedlar bags have, in some cases, been shown to contain analytes above the values listed on the certificates of cleanliness. This has not been experienced at Pace National; however should a new manufacturer be chosen as the supplier of Tedlar bags, a method blank Tedlar may be necessary to demonstrate acceptable cleanliness.
- 11.7 Internal Standard Recovery - If the area response for any ISTD changes by more than $\pm 40\%$ between the sample and the most recent calibration, the GC/MS system must be inspected for malfunction and corrections made as appropriate. When corrections are made, an initial calibration verification sample must be analyzed to determine whether the multipoint calibration remains valid. If acceptance criteria are not met, recalibration is necessary. Re-analysis of all samples analyzed while the GC/MS system was malfunctioning is necessary.
- 11.8 Reporting Limit Verification (RLV) – RL checks are evaluated but are currently applicable to Minnesota samples only. See State Note in Section 8.3.1 above for details.

STANDARD OPERATING PROCEDURE

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- 11.9 All data must undergo a primary review by the analyst. The analyst must check the performance of the initial calibration and continuing calibrations to ensure that they meet the criteria of the method. The analyst should review any sample that has quantifiable compounds and make sure that they have been confirmed, if needed. The analyst must also verify that reported results are derived from quantitation between the MDL and the highest standard of the initial calibration curve. All calculations must be checked (any dilutions, re-analyses, etc.). Data must be checked for the presence or absence of appropriate flags. Comments should be noted when data is flagged.
- 11.10 All data must undergo a second analyst review. The analyst checking the data must check the performance of the initial calibration and calibration verifications to ensure that they meet the criteria of the method.
- 11.10.1 The analyst should look at any sample that has quantifiable compounds and check the integration.
- 11.10.2 All surrogate recoveries must be checked to see if they are within limits.
- 11.10.3 Method Blanks must be clean of all interfering peaks.
- 11.10.4 Quality control criteria should be checked for the ISTDs, LCS, and LCSD.
- 11.10.5 Data must be checked for the presence or absence of appropriate flags. Comments should be noted when data is flagged.
- 11.10.6 See ENV-SOP-MTJL-0014, *Data Handling and Reporting*.
- 11.10.7 See ENV-SOP-MTJL-0018, *Corrective and Preventive Action*.
- 11.11 LCS/LCSD: The laboratory control sample and laboratory control sample duplicate, recoveries must be evaluated against the limits listed in this procedure. The LCS/LCSD are spiked with the same list of compounds for which the instrument is calibrated. Due to the large number of compounds analyzed using these methods, it is statistically likely that accuracy and precision failures will occur.

LCS or LCSD samples that do not pass the acceptable QC criteria must be re-analyzed. LCS/LCSD failures must meet the marginal exceedance criteria below. Allowable marginal exceedance outliers are based on the number of compounds being analyzed and must be random events.

Upper and lower marginal exceedance (ME) limits are established by ± 4 times the standard deviation of historical accuracy data.

Number of allowable marginal exceedances:

90+ analytes,	5 analytes allowed in the ME limit
71 – 90 analytes,	4 analytes allowed in the ME limit.
51 – 70 analytes,	3 analytes allowed in the ME limit.
31 – 50 analytes,	2 analytes allowed in the ME limit.
11 – 30 analytes,	1 analyte allowed in the ME limit.
< 11 analytes,	no analyte allowed in the ME limit.

STATE NOTE: For South Carolina, marginal exceedances do not apply. All outliers in QC require corrective action when possible and the data must be flagged when necessary.

STANDARD OPERATING PROCEDURE

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12.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

- 12.1 The EPA requires that laboratory waste management practice to be conducted consistent with all applicable federal and state laws and regulations. Excess reagents, samples and method process wastes must be characterized and disposed of in an acceptable manner. See *ENV-SOP-MTJL-0051, Waste Management Plan*.
- 12.2 See ENV-SOP-MTJL-0046, *Environmental Sustainability & Pollution Prevention*.

13.0 METHOD MODIFICATIONS/CLARIFICATIONS

- 13.1 Modifications to this method are noted in the body of the text as state notes. Compliance analyses performed in conjunction with specific state requirements must be performed as noted within the specific state(s) note listed.
- 13.2 Provisions have been added to this procedure for the analysis of gasoline range organics and additional analytes from those listed specifically in the EPA TO-14A and TO-15 Compendium Methods. Sufficient supporting data is maintained by the laboratory to demonstrate accurate identification and adequate sensitivity for quantitation of these analytes using this procedure.
- 13.3 Adjustments to the concentrations of standards/spiking solutions, standards providers, and quality control are subject to change to better meet client/project/regulatory needs or to improve laboratory method performance.

14.0 REFERENCES

- 14.1 *Ambient Air*: Method TO-14A, Second Edition, U.S. Environmental Protection Agency, Research Triangle Park, NC, EPA 600/625/R-96/010b, January 1999.
- 14.2 *Compendium of Method for the Determination of Toxic Organic Compounds in Ambient Air*: Method TO-15, Second Edition, U.S. Environmental Protection Agency, Research Triangle Park, NC, EPA 600/625/R-96/010b, January 1999.
- 14.3 Entech 7100 Operators Manual, Version 2.0, Entech Instruments Inc., Simi Valley, CA, 1999.
- 14.4 Entech 3100 Operators Manual, Version 1.0, Entech Instruments Inc., Simi Valley, CA, 1999.
- 14.5 Method 18 – Measurement of Gaseous Organic Compound Emissions by Gas Chromatography, 40 CFR 60, Appendix A-6.
- 14.6 Markes Unity-xr User Manual, QUI-1119, Version 1.0 – July 2016, Markes International Ltd.
- 14.7 Markes CIA Advantage Operator Manual, QUI-1078, Version 1.1 – Markes International Ltd.

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Attachment I: Revision History

Current Version (Pace National):

Date	Description of Revisions
12/23/2019	Added corporate header and footer. Added Client Note in Sections 4.2 and 4.4.1. Deleted Section 4.5.1, 6.3.3, 6.3.7, 6.3.8, and renumbered as appropriate. Added Section 6.1.6. Revised Sections 4.5.2, 6.0, 7.4.2.2, 8.6.1.1, and 8.6.5.

Superseded Versions (ESC Lab Sciences SOP#330367):

Version	Date	Description of Revisions
0	3/26/04	Origination
1	3/24/05	
2	6/15/05	
3	12/5/05	
4	4/21/06	
5	4/30/07	Corrected format errors and sequential numbering, expanded on process discussion in response to Ohio VAP review.
6	2/3/09	Technical and Quality Review and update. Inclusion of sections 12.1-12.2 & 13.1; Clarification of holding times; Addition of State Notes for Ohio VAP and MN; Ohio VAP approval 2/3/09.
7	7/13/11	Technical and Quality Review and update. Revised sections 7.3.2, 7.4, Table 7.4, 7.5, 8.1 through 8.5, 9.1 through 9.5, 11.6 through 11.11, 12.1 and 13.2; Added sections 1.2, 2.9 through 2.23, 10.4 through 10.14, 13.3 and Attachments II and III.
8	9/19/11	Technical and Quality Review and update. Revised sections 8.7.4 and 10.9
9	11/17/11	Technical and Quality Review and update. Revised sections 7.3.1, 7.4.2, 8.3.1, 8.3.3, 8.4, 8.6.2, 8.6.3, 8.6.4, 8.7, 10.5, 10.8, 10.14, 11.5, and 11.7; Added sections 7.4.2.4, 8.1.4, 8.1.5, and 8.5; Removed sections 8.2.3, 8.2.6, 8.4, and 8.6; Reconciled Ohio VAP approval with changes from Rev. 7, 8 and 9 - 11/17/11.
10	1/29/13	Technical and Quality Review and update. Revised sections 4.2 (including state note), 8.2.1, and 10.9; Added state note in section 1.0 and sections 1.3.1, 2.24, 2.25, and 6.3.4.
	3/19/14	Reviewed with no changes per D. Ramey/D. Marlin
11	11/6/14	Technical and Quality Review and update. Revised Attachments II and II and Table 7.4, Revised sections 1.1, 1.2, 4.5.3, 7.4.2.2, 7.4.2.4, 8.1.5.2, 10.9 and 11.4; Added sections 2.26, 2.27, 4.5.4, and 7.5.3.
12	11/25/2015	Technical and quality review and update. Header and signature block re-formatting. Revised Sections 1.3.1, 4.4.2, 4.5.4, 6.1.4, 7.1, 7.2, 7.3.1.1, 7.4.1, Table 7.4, 7.5.4, 8.0, 8.1.5.1, 8.2.2, 8.5, 8.6.5, 8.7.5, 8.7.6, 10.8, 11.6, 11.9.8, 12.2, Attachment IIa, and Attachment IIIa. Removed Sections 7.3.1.2 and 7.3.1.3. Added Attachment IV.

STANDARD OPERATING PROCEDURE

TITLE: ENV-SOP-MTJL-0104 Measurement of Volatile Organic Compounds and Gasoline Range Components in Ambient Air by Gas Chromatography/Mass Spectrometry (EPA TO-15 and EPA Method 18-Modified)

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Version	Date	Description of Revisions
13	11/9/2016	Technical and quality review and update. Header and signature block re-formatting. Revised Sections 2.9, 2.10, 2.11, 7.3.1.1, 7.3.2.1, 7.3.2.2, 7.3.2.7, 7.4.1, 7.4.2.1.1, 7.4.2.1.4, 7.5.1.3, 7.5.2.1, 7.5.2.2, 7.5.2.4, 8.1.4.5, 8.1.5.3, 8.3.1, 8.5, 8.6.1, 8.6.2, 8.6.4, 8.6.5, 8.7.5, 10.3, 10.6, 10.8, 11.7, 11.10, 11.11.1, and Attachment IV Table 2. Deleted Sections 2.9 through 2.25, 7.3.2.5, 7.5.3 and all subsections, 9.1, 9.2, 9.4, and 9.5. Added Section 9.4.
14	4/10/2017	Technical and quality review and update. Revised SOP title and Sections 1.3, 4.5.2, 4.5.3, 7.3.1.1, 7.4.2.2, 8.1.4.9, 8.1.5.1, 8.1.5.3, 8.2, 8.6.5, 10.9, 10.10, and 10.11. Deleted Section 4.5.2 and 8.1.4.1. Added Section 6.3.7, 6.3.8, 14.5, 14.6, and 14.7.
15	11/30/2017	Update in response to A2LA audit finding CAR2872. Revised Sections 1.0, 1.3, 3.1, and Attachment IV Table 4.

Superseded Versions (Pace National):

Date	Description of Revisions
1/19/2019	Technical and quality review and update. Deleted header, footer and signature bar. Revised sections 1.0, 1.1, 1.3, 1.3.1, 3.1, 4.2, 4.3, 4.4, 4.4.1, 4.5, 4.5.1, 4.5.2, 4.5.3, 6.1, 6.1.1, 6.1.2, 6.1.3, 6.1.4, 6.1.5, 6.3, 6.3.9, 6.3.12, 6.4, 7.0, 7.1, 7.3.2.2, 7.4.1, 7.4.2.2, 7.5, 7.5.1, 7.5.1.1, 7.5.2, 8.1.4, 8.1.4.4, 8.1.5, 8.1.5.1, 8.1.5.2, 8.2.1, 8.2.2, 8.3, 8.6, 8.6.4, 8.7, 8.9, 10.1, 10.2, 10.3, 10.6, 10.9, 10.10, 10.12, 11.6, 12.1, 12.2 and 14.7. Deleted Table 7.4. Deleted sections 7.4.2.1, 7.4.2.1.1, 7.4.2.1.2, 7.4.2.1.3, 7.4.2.1.4, 7.5.1.2, 7.5.2.1, 7.5.2.2, 7.5.2.3, 7.5.2.4, 8.7.5, 8.7.6, 11.9.2, 11.11, 11.11.1, 11.11.2 and renumbered as necessary. Added sections 7.4.2.1, 8.9, 10.13, 11.8 and renumbered as necessary. Added State Note to section 8.3.1. Added sub-section numbers to sections 8.3.2, 8.3.3, 8.4, 8.5, 8.6.1, 8.6.2, 8.6.3.1 and 8.6.3.2. Revised sections 8.5.1, 8.5.3, 8.6.1.3, 11.10.6 and 11.10.7. Revised Attachments I, IIa and IIIa.

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Attachment IIa: Routine Analytes and Reporting Limits for Scan Mode (* See section 13.3)

Compound*	RL ppbv*
1,1,1-Trichloroethane	0.2
1,1,2,2-Tetrachloroethane	0.2
1,1,2-Trichloroethane	0.2
1,1,2-Trichlorotrifluoroethane	0.2
1,1-Dichloroethane	0.2
1,1-Dichloroethylene	0.2
1,2,4-Trichlorobenzene	0.63
1,2,4-Trimethylbenzene	0.2
1,2-Dibromoethane	0.2
1,2-Dichlorobenzene	0.2
1,2-Dichloroethane	0.2
1,2-Dichloropropane	0.2
1,2-Dichlorotetrafluoroethane	0.2
1,3,5-Trimethylbenzene	0.2
1,3-Butadiene	2.0
1,3-Dichlorobenzene	0.2
1,4-dichlorobenzene	0.2
1,4-Dioxane	0.2
2,2,4-Trimethylpentane	0.2
2-Butanone	1.25
2-Chlorotoluene	0.2
2-propanol	1.25
4-Ethyltoluene	0.2
4-Methyl-2-Pentanone	1.25
Acetone	1.25
Allyl Chloride	0.2
Benzene	0.2
Benzyl Chloride	0.2
Bromodichloromethane	0.2
Bromoform	0.6
Bromomethane	0.2
Carbon Disulfide	0.2
Carbon Tetrachloride	0.2
Chlorobenzene	0.2
Chloroethane	0.2
Chloroform	0.2
n-Propylbenzene	0.2
sec-Butylbenzene	0.2
1,2,3-Trimethylbenzene	0.2
Tert-butyl alcohol	1.25
Dicyclopentadiene	0.2
Ethyl Acetate	0.2
Butane	0.2
Acrolein	0.31
2-Methylnaphthalene	1.0
Acetonitrile	0.2

Compound*	RL ppbv*
Chloromethane	0.2
cis-1,2-Dichloroethene	0.2
cis-1,3-Dichloropropene	0.2
Cyclohexane	0.2
Dibromochloromethane	0.2
Dichlorodifluoromethane	0.2
Ethanol	0.63
Ethylbenzene	0.2
Heptane	0.2
Hexachloro-1,3-Butadiene	0.63
Isopropyl benzene	0.2
m&p-Xylene	0.4
Methyl Butyl Ketone	1.25
Methyl Methacrylate	0.2
Methylene Chloride	0.2
MTBE	0.2
Naphthalene	0.63
n-Hexane	0.2
o-Xylene	0.2
Propene	2
Styrene	0.2
Tetrachloroethylene	0.2
Tetrahydrofuran	0.2
Toluene	0.2
TPH	50
Trans-1,2-Dichloroethene	0.2
trans-1,3-Dichloropropene	0.2
Trichloroethylene	0.2
Trichlorofluoromethane	0.2
Vinyl Acetate	0.2
Vinyl Bromide	0.2
Vinyl Chloride	0.2
1,4-Bromofluorobenzene (surrogate)	0.2
1,4-Difluorobenzene (internal standard)	0.2
Bromochloromethane (internal standard)	0.2
Chlorobenzene-d5 (internal standard)	0.2
tert-Butylbenzene	0.2
n-Butylbenzene	0.2
1,1-Difluoroethane	0.2
Tert-Amyl Ethyl Ether	0.2
Chlorodifluoromethane	0.2
Methyl Cyclohexane	0.2
Pentane	0.2
Acrylonitrile	0.2
Bromoethane	0.2
Nonane	0.2

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Attachment IIb: Routine Analytes and Reporting Limits for SIM Mode (* See section 13.3)

Compound*	RL ppbv*
1,1,1-Trichloroethane	0.02
1,1,1,2-Tetrachloroethane	0.02
1,1,2-Trichloroethane	0.03
1,1-Dichloroethane	0.02
1,1-Dichloroethylene	0.02
1,2-Dibromoethane	0.02
1,2-Dichloropropane	0.03
1,4-Dichlorobenzene	0.02
Benzene	0.02
Carbon Tetrachloride	0.02
Chloroethane	0.04
Chloroform	0.02
Chloromethane	0.03

Compound*	RL ppbv*
cis-1,2-Dichloroethene	0.02
cis-1,3-Dichloropropene	0.03
Ethylbenzene	0.03
Tetrachloroethylene	0.02
trans-1,2-Dichloroethene	0.02
trans-1,3-Dichloropropene	0.03
Trichloroethylene	0.02
Vinyl Acetate	0.02
Vinyl Chloride	0.02
1,4-Bromofluorobenzene (surrogate)	0.02
1,4-Difluorobenzene (ISTD)	0.02
Bromochloromethane (ISTD)	0.02
Chlorobenzene-d5 (ISTD)	0.02

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Attachment IIIa: Characteristic Ions for SCAN mode

Compound	1° Ion	2° Ion	Compound	1° Ion	2° Ion
1,1,1-Trichloroethane	97	99, 61	Chloromethane	50	52
1,1,2,2-Tetrachloroethane	83	85	cis-1,2-Dichloroethene	96	61, 98
1,1,2-Trichloroethane	97	83, 61	cis-1,3-Dichloropropene	75	39, 77
1,1,2-Trichlorotrifluoroethane	101	151, 85	Cyclohexane	56	84, 41
1,1-Dichloroethane	63	65	Dibromochloromethane	129	127, 131
1,1-Dichloroethylene	96	98, 61	Dichlorodifluoromethane	85	87, 101
1,2,4-Trichlorobenzene	105	122	Ethanol	31	45, 27, 46
1,2,4-Trimethylbenzene	105	120	Ethylbenzene	91	106
1,2-Dibromoethane	107	109	Heptane	43	71, 57
1,2-Dichlorobenzene	146	148, 111	Hexachloro-1,3-Butadiene	225	227, 223
1,2-Dichloroethane	62	64	Isopropyl benzene	105	120
1,2-Dichloropropane	63	62, 41	m&p-Xylene	91	106
1,2-Dichlorotetrafluoroethane	85	135, 87	Methyl Butyl Ketone	43	58, 57, 100
1,3,5-Trimethylbenzene	105	120	Methyl Methacrylate	41	69, 100
1,3-Butadiene	54	53, 39	Methylene Chloride	84	49
1,3-Dichlorobenzene	146	148, 111	MTBE	73	57
1,4-Dichlorobenzene	146	148, 111	Naphthalene	128	-
1,4-Dioxane	88	58	n-Hexane	57	41, 43
2,2,4-Trimethylpentane	57	41, 56	o-Xylene	91	106
2-Butanone	43	72	Propene	41	39, 42
2-Chlorotoluene	91	126	Styrene	104	78, 103
2-propanol	45	43	Tetrachloroethylene	166	164, 131
4-Ethyltoluene	105	120	Tetrahydrofuran	42	41, 72, 71
4-Methyl-2-Pentanone	43	58, 100	Toluene	91	92
Acetone	43	58	TPH	NA	NA
Allyl Chloride	76	41, 78	trans-1,2-Dichloroethene	96	98, 61
Benzene	78	77, 50	trans-1,3-Dichloropropene	75	39, 77
Benzyl Chloride	91	126	Trichloroethylene	130	132, 95
Bromodichloromethane	83	85, 129	Trichlorofluoromethane	101	103, 105
Bromoform	173	171, 175, 252	Vinyl Acetate	43	86
Bromomethane	94	96	Vinyl Bromide	106	108
Carbon Disulfide	76	44, 78	Vinyl Chloride	62	64
Carbon Tetrachloride	117	119	1,4-Bromofluorobenzene (surr.)	95	174, 176
Chlorobenzene	112	77, 114	1,4-Difluorobenzene (ISTD)	114	-
Chloroethane	64	66	Bromochloromethane (ISTD)	51	131
Chloroform	83	85	Chlorobenzene-d5 (ISTD)	117	-
n-Propylbenzene	91	120	tert-Butylbenzene	119	91, 134
sec-Butylbenzene	105	134	n-Butylbenzene	91	92, 134
1,2,3-Trimethylbenzene	105	120	Tert-butyl alcohol	59	-
Dicyclopentadiene	66	132	Tert-amyl ethyl ether	73	55, 87, 43
1,1-Difluoroethane	51	-	chlorodifluoromethane	51	67
Ethyl acetate	43	45, 70	Methyl Cyclohexane	83	55, 41
Butane	43	58	Pentane	43	57, 72
Acrolein	56	55	Acrylonitrile	53	52, 51
2-Methylnaphthalene	142	141, 115	Bromoethane	108	110

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Compound	1° Ion	2° Ion	Compound	1° Ion	2° Ion
Acetonitrile	41	40, 39	Nonane	43	57, 71, 128

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Attachment IIIb: Characteristic Ions for SIM mode

Compound	1° Ion	2° Ion	Compound	1° Ion	2° Ion
1,1,1-Trichloroethane	97	99, 61	cis-1,2-Dichloroethene	96	61, 98
1,1,2,2-Tetrachloroethane	83	85	cis-1,3-Dichloropropene	75	39, 77
1,1,2-Trichloroethane	97	83, 61	Ethylbenzene	91	106
1,1-Dichloroethane	63	65	Tetrachloroethylene	166	164, 131
1,1-Dichloroethylene	96	98, 61	trans-1,2-Dichloroethene	96	98, 61
1,2-Dibromoethane	107	109	trans-1,3-Dichloropropene	75	39, 77
1,2-Dichloropropane	63	62, 41	Trichloroethylene	130	132, 95
1,4-Dichlorobenzene	146	148, 111	Vinyl Acetate	43	86
Benzene	78	77, 50	Vinyl Chloride	62	64
Carbon Tetrachloride	117	119	1,4-Bromofluorobenzene (surr.)	95	174, 176
Chloroethane	64	66	1,4-Difluorobenzene (ISTD)	114	-
Chloroform	83	85	Bromochloromethane (ISTD)	51	131
Chloromethane	50	52	Chlorobenzene-d5 (ISTD)	117	-

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Attachment IV: DoD Requirements

1.0 Equipment/Instrument Maintenance

Instrument maintenance must be performed routinely to optimize instrument performance and improve chromatography. Commonly performed maintenance includes baking traps and columns, cleaning inlet, replacing valves, etc. A new calibration curve must be analyzed following any major maintenance performed on the analytical system.

2.0 Computer Hardware and Software

Software name and version: MSD Chemstation E.02.01.1177 or equivalent

3.0 Troubleshooting

Table 1. GCMS Troubleshooting Guide		
Problem	Cause	Treatment
Peaks broaden and tail	Poor column installation causing dead volume in the injector	Reinstall column in injector. Check seal at ferrule. Check insertion depth. Ensure a good column cut.
	Solvent flashing in hot injector	Reduce injection speed on hot injectors and if possible reduce injector temperature
	Injector not being purged properly after splitless injection	For splitless injection, the vent flow should be 70 ml/min, and the injector should be switched to the split mode 0.5_1.5 min after injection.
Tailing sample peaks for active components	Active sites in the injector insert or liner	Change or clean the injector insert
	Active sites or degraded phase in column	Remove the front 15 cm of the column and reinstall. If retention times are changing or cutting the column does not help, replace the column.
	Injector not hot enough for higher boiling compounds	Increase the injector temperature and lower the injection speed. Check that the graphite ferrule is free of cracks and the septum support is tight.
Low response and tailing of high boiling point compounds	Injector is not hot enough to vaporize high boilers	Increase injector temperature
	Interface/ion source not getting to adequate temperature	Change the manifold heater
Leading sample peaks	Column overload due to excess amount of component injected	Dilute the sample or do split injection
	Degradation of stationary phase	Change the column
	Carrier gas velocity too low	Increase carrier gas flow rate
Poor chromatographic resolution	Column temperature or program not optimized	Modify method by changing temperature ramp segment slopes

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Table 1. GCMS Troubleshooting Guide		
Problem	Cause	Treatment
	Carrier gas flow rate not optimized	Decrease carrier gas linear velocity
	Stationary phase has degraded	Replace the column
Peak splitting, especially low boilers	Sample is flashing in the injector simulating two injections	Lower injector temperature
Retention times shift in chromatogram	Unstable carrier gas flow controller/regulator	Check pneumatics for leaks. Replace flow controller/ regulator if necessary.
	Column contamination or degradation	Condition or replace column
	Leaks at septum or column to injector connection	Replace septum regularly and check that the septum nut and the capillary column nut are tight
Cannot reach operating vacuum	Analyzer contaminated by diffusion pump oil	Shut down and clean mass spec
	Major air leak around column fitting into interface	Replace column ferrule and reseal compression fitting
No tuning peaks	Cal gas valve not open	Open cal gas valve
	Calibration gas solenoid valve stuck open. All PFTBA has evaporated.	Have solenoid replaced. Put fresh PFTBA in the cal gas vial.
Analysis sensitivity has decreased	Background has increased	Check column bleed, septum bleed, pump oil, and ion source contamination
	Detector needs replacement	Replace detector
	Defective syringe	Try a new or proven syringe
	“Blown” septum or other massive leaks at the inlet or with carrier gas flow. Poor peak shapes usually result from bad leaks.	Find and fix leaks and adjust gas flow.
	Purge flow or split ratio too high	Adjust gas flow rates

4.0 Other Requirements

- 4.1 All hardcopy laboratory notebooks must be reviewed by the Supervisor, or their designee, on a monthly basis.
- 4.2 If not self-explanatory (e.g., a typo or transposed number), corrections to technical and quality records shall also include a justification for the change.
- 4.3 A storage blank must be stored with all volatile organic samples, regardless of suspected concentration levels.
- 4.4 A person performing a manual integration must sign and date each manually integrated chromatogram and record the rationale for performing manual integration. Electronic signatures are acceptable.

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4.5 The results of calibration and verification of support equipment must be within the specifications required of the application for which this equipment is used or the equipment must be removed from service until repaired. Calibration and verification records, including those of established correction factors, must be maintained. In the absence of method-specific requirements, the minimum requirements are as follows:

Table 2. Support Equipment Checks		
Performance Check	Frequency	Acceptance Criteria
Balance calibration check [Using two standard weights that bracket the expected mass]	Daily prior to use	Top-loading balance: $\pm 2\%$ or $\pm 0.02\text{g}$, whichever is greater Analytical balance: $\pm 0.1\%$ or $\pm 0.5\text{mg}$, whichever is greater
Verification of standard mass [Using weights traceable to the International System of Units (SI) through a NMI]	Every 5 years	Certificate of Calibration from ISO/IEC 17025 accredited calibration laboratory
Monitoring of refrigerator/freezer temperatures	Daily (i.e. 7 days per week) [use MIN/MAX thermometers or data loggers equipped with notification of out of control event capabilities if personnel not available to record daily]	Refrigerators: 0°C to 6°C Freezers: $\leq -10^{\circ}\text{C}$
Thermometer verification check [Using a thermometer traceable to the SI through an NMI] [Performed at two temperatures that bracket the target temperature(s). Assume linearity between the two bracketing temperatures.] [If only a single temperature is used, at the temperature of use]	Liquid in glass: Before first use and annually Electronic: Before first use and quarterly	Apply correction factors or replace thermometer
Volumetric labware	Class B: By lot before first use Class A and B: Upon evidence of deterioration	Bias: Mean within $\pm 2\%$ of nominal volume Precision: $\text{RSD} \leq 1\%$ of nominal volume (based on 10 replicate measurements)
Non-volumetric labware [Applicable only when used for measuring initial sample volume and final extract/ digestates volume]	By lot before first use or upon evidence of deterioration	Bias: Mean within $\pm 3\%$ of nominal volume Precision: $\text{RSD} \leq 3\%$ of nominal volume (based on 10 replicate measurements)
Mechanical volumetric pipette	Quarterly	Bias: Mean within $\pm 2\%$ of nominal volume Precision: $\text{RSD} \leq 1\%$ of nominal volume (based on minimum of 3 replicate measurements) [Note: for variable volume pipettes, the nominal volume is the volume of use]

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Performance Check	Frequency	Acceptance Criteria
Glass microliter syringe	Upon receipt and upon evidence of deterioration	General Certificate of Bias & Precision upon receipt Replace if deterioration is evident
Drying oven temperature check	Daily prior to and after use	Within ±5% of set temperature
Water purification system	Daily prior to use	See method blank criteria given in Section 4.20 of this addendum

- 4.6 The expiration date of the prepared standard shall not exceed the expiration date of the primary standard. All containers must bear a preparation date.
- 4.7 To avoid preparing non-representative samples, the laboratory shall not “target” within a relatively small mass range (e.g., 1.00 ± 0.01g) because such targeting will produce non-representative subsamples if the sample has high heterogeneity. The laboratory shall not manipulate the sample material so the sample aliquot weighs exactly 1.00g ± 0.01g, as an example.
- 4.8 In the absence of project-specific requirements, the minimum standard data qualifiers to be used are:
- U Analyte was not detected and is reported as less than the LOD or as defined by the customer. The LOD has been adjusted for any dilution or concentration of the sample.
 - J The reported result is an estimated value (e.g., matrix interference was observed or the analyte was detected at a concentration outside the quantitation range).
 - B Blank contamination. The recorded result is associated with a contaminated blank.
 - N Non-target analyte. The analyte is a tentatively identified compound using mass spectrometry or any non-customer requested compounds that are tentatively identified.
 - Q One or more quality control criteria failed (e.g., LCS recovery, surrogate spike recovery, or CCV recovery).
- Additional data qualifiers may be used, or different letters or symbols to denote the qualifiers listed above, as long as they are appropriately defined and their use is consistent with project-specific requirements (e.g., QSM 5.0, the contract, and project-planning documents).
- 4.9 If the time of the sample collection is not provided, assume the most conservative time of day. For the purpose of batch processing, the start and stop dates and times of the batch preparation shall be recorded.
- 4.10 Each preparation method listed on the scope of accreditation must have quarterly LOD/LOQ verifications. However, not all possible combinations of preparation and cleanup techniques are required to have LOD/LOQ verifications. If LOD/LOQ verifications are not performed on all combinations, the laboratory must base the LOD/LOQ verifications on the worst case basis (preparation method with all applicable cleanup steps).
- 4.11 After each MDL determination, the laboratory must establish the LOD by spiking a quality system matrix at a concentration of at least 2 times but no greater than four times the MDL. This spike concentration establishes the LOD and the concentration at which the LOD shall be verified. It is specific to each suite of analyte, matrix, and method (including sample preparation). The following requirements apply to the initial LOD establishment and to the LOD verifications:

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- The apparent signal to noise (S/N) ratio at the LOD must be at least three and the results must meet all method requirements for analyte identification (e.g., ion abundance, second column confirmation, or pattern recognition). For data systems that do not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least three standard deviations greater than the mean method blank concentration. This is initially estimated based on a minimum of four method blank analyses and later established with a minimum of 20 method blank results.
 - If the LOD verification fails, then the laboratory must repeat the MDL determination and LOD verification or perform and pass two consecutive LOD verifications at a higher spike concentration and set the LOD at the higher concentration.
 - The laboratory shall maintain documentation for all MDL determinations and LOD verifications.
 - The DL and LOD must be reported for all analyte-matrix-methods suites, unless it is not applicable to the test or specifically excluded by project requirements.
- 4.12 The LOD shall be verified quarterly. In situations where methods are setup and used on an infrequent basis, the laboratory may choose to perform LOD verifications on a one per batch basis. All verification data will be in compliance, reported, and available for review.
- 4.13 For DoD, at a minimum, the LOQ shall be verified quarterly. In situations where methods are setup and used on an infrequent basis, the laboratory may choose to perform LOQ verifications on a one per batch basis.
- 4.14 All initial instrument calibrations must be verified with a standard obtained from a second manufacturer prior to analyzing any samples. The use of a standard from a second lot obtained from the same manufacturer (independently prepared from different source materials) is acceptable for use as a second source standard. The concentration of the second source standard shall be at or near the midpoint of the calibration range. The acceptance criteria for the initial calibration verification must be at least as stringent as those for the continuing calibration verification.
- 4.15 Exclusion of calibration points without documented scientifically valid technical justification is not permitted.
- 4.16 The concentration of the CCV standard shall be greater than the low calibration standard and less than or equal to the midpoint of the calibration range.
- 4.17 All CCVs analyzed must be evaluated and reported. If a CCV fails, reanalysis or corrective actions must be taken.
- If a CCV fails, the laboratory can immediately analyze two additional consecutive CCVs (immediately is defined as starting a consecutive pair within one hour; no samples can be run between the failed CCV and the two additional CCVs). This approach allows for spurious failures of analytes to be reported without reanalysis of samples. Any corrective actions that change the dynamics of the system (e.g., clip column, clean injection port, run blanks) requires that all samples since the last acceptable CCV be reanalyzed.
 - Both of these CCVs must meet acceptance criteria in order for the samples to be reported without reanalysis.

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- If either of these two CCVs fail or if the laboratory cannot immediately analyze two CCVs, the associated samples cannot be reported and must be reanalyzed.
 - Corrective action(s) and recalibration must occur if the above scenario fails. All affected samples since the last acceptable CCV must be reanalyzed.
 - Flagging of data for a failed CCV is only appropriate when the affected samples cannot be reanalyzed. The laboratory must notify the client prior to reporting data associated with a failed CCV.
- 4.18 The results of all MS/MSDs must be evaluated using the same acceptance criteria used for the DoD LCS limits (see Addendum Table 3) or project limits, if specified. If the specific analyte(s) are not available in the Addendum Table 3, the laboratory shall use their LCS in-house limits (see the LIMS) as a means of evaluating MS/MSDs. The MS and MSD must be spiked with all reported analytes.
- 4.19 Surrogate spike results shall be compared with DoD LCS limits (see Addendum Table 3) or acceptance criteria specified by the client. If these criteria are not available, the laboratory shall compare the results with its in-house statistically established LCS criteria (see the LIMS).
- 4.20 The method blank shall be considered to be contaminated if:
- The concentration of any target analyte (chemical of concern) in the blank exceeds 1/2 the LOQ and is greater than 1/10th the amount measured in any associated sample, or 1/0th the regulatory limit, whichever is greater;
 - The concentration of any common laboratory contaminant in the blank exceeds the LOQ;
 - If a method blank is contaminated as described above, then the laboratory shall reprocess affected samples in a subsequent preparation batch, except when sample results are below the LOD. If insufficient sample volume remains for reprocessing, the results shall be reported with appropriate data qualifiers.
- 4.21 Sporadic Marginal Exceedances are not allowed for target analytes (chemicals of concern as identified by a project) without project-specific approval. Target analytes are considered those few analytes that are critical for the success of a project (such as risk drivers) where sporadic marginal exceedances cannot be allowed. Laboratories should consult with clients whenever long lists of analytes are requested for analysis to determine if marginal exceedances will not be allowed.
- 4.22 DoD considers the same analyte exceeding the LCS control limit two (2) out of three (3) consecutive LCS to be indicative of non-random behavior, which requires corrective action and reanalysis of the LCS.

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Table 3. LCS Control Limits – Method TO-15 Gas Matrix

CAS ID	Analyte	N Records	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit
630-20-6	1,1,1,2-Tetrachloroethane	1344	97.9	10.5	67	129
71-55-6	1,1,1-Trichloroethane	5436	96.7	9.5	68	125
79-34-5	1,1,2,2-Tetrachloroethane	5273	95.9	10.4	65	127
79-00-5	1,1,2-Trichloroethane	5332	95.9	7.7	73	119
76-13-1	1,1,2-Trifluoro-1,2,2-trichloroethane [Freon-113]	5351	96.1	10	66	126
75-34-3	1,1-Dichloroethane	5422	97	9.7	68	126
75-35-4	1,1-Dichloroethene	3503	97.3	11.9	61	133
96-18-4	1,2,3-Trichloropropane	465	99.6	8	76	124
120-82-1	1,2,4-Trichlorobenzene	4545	98.5	14.5	55	142
95-63-6	1,2,4-Trimethylbenzene	4699	99.2	11.1	66	132
106-93-4	1,2-Dibromoethane	4655	98.2	7.9	74	122
76-14-2	1,2-Dichloro-1,1,2,2-tetrafluoroethane	4572	92.4	9.7	63	121
95-50-1	1,2-Dichlorobenzene	4739	95.7	11	63	129
107-06-2	1,2-Dichloroethane	5467	96.8	10.5	65	128
78-87-5	1,2-Dichloropropane	4729	95.7	8.9	69	123
108-67-8	1,3,5-Trimethylbenzene	4679	98.3	10.4	67	130
106-99-0	1,3-Butadiene	3167	99.8	11.4	66	134
541-73-1	1,3-Dichlorobenzene	4737	97.1	10.9	65	130
142-28-9	1,3-Dichloropropane	165	105.2	14.4	62	148
542-75-6	1,3-Dichloropropene	560	100.7	8.1	77	125
106-46-7	1,4-Dichlorobenzene	4719	95.8	11.8	60	131
123-91-1	1,4-Dioxane	2656	96.5	8.6	71	122
540-84-1	2,2,4-Trimethylpentane [Isooctane]	3008	94.3	8.8	68	121
78-93-3	2-Butanone [MEK]	4635	98.4	10.4	67	130
95-49-8	2-Chlorotoluene	1092	101.9	9.2	74	130
591-78-6	2-Hexanone	4600	95.4	11	62	128
67-63-0	2-Propanol [Isopropyl alcohol]	3069	88.4	12.3	52	125
622-96-8	4-Ethyltoluene	4673	97.9	10.3	67	129
108-10-1	4-Methyl-2-pentanone [MIBK]	4646	98.5	10.5	67	130
67-64-1	Acetone	4600	92.7	11.6	58	128
75-05-8	Acetonitrile	1999	97.3	11.6	63	132
107-02-8	Acrolein [Propenal]	2469	93.8	10.6	62	126
107-13-1	Acrylonitrile	2105	103.7	10.9	71	137
107-05-1	Allyl chloride	2980	101.1	10.1	71	131
98-83-9	alpha-Methylstyrene	1976	97.3	10.2	67	128
71-43-2	Benzene	5436	93.8	8.4	69	119
100-44-7	Benzyl chloride	4419	98.7	16.2	50	147
75-27-4	Bromodichloromethane	4682	99.9	9.3	72	128
75-25-2	Bromoform	4638	102.3	12.1	66	139
74-83-9	Bromomethane	2657	98.6	11.8	63	134
106-97-8	Butane	587	96.2	10.9	64	129
75-15-0	Carbon disulfide	4756	95.6	12.7	57	134

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Table 3. LCS Control Limits – Method TO-15 Gas Matrix

CAS ID	Analyte	N Records	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit
56-23-5	Carbon tetrachloride	4202	99.6	10.7	68	132
108-90-7	Chlorobenzene	4652	94.5	8	70	119
124-48-1	Chlorodibromomethane	4628	99.9	10	70	130
75-45-6	Chlorodifluoromethane	559	102.1	14.3	59	145
75-00-3	Chloroethane	5370	94.7	10.6	63	127
67-66-3	Chloroform	5481	95.3	9.3	68	123
74-87-3	Chloromethane	4540	95.2	12.2	59	132
156-59-2	cis-1,2-Dichloroethene	5320	95.6	8.4	70	121
10061-01-5	cis-1,3-Dichloropropene	4691	98.8	9.7	70	128
110-82-7	Cyclohexane	3178	93.5	7.7	70	117
124-18-5	Decane	1982	93.8	7.9	70	118
75-71-8	Dichlorodifluoromethane [Freon-12]	5307	93.6	11.5	59	128
108-20-3	Diisopropyl ether	2309	93.5	8	70	117
64-17-5	Ethanol	2981	91.8	11.1	59	125
141-78-6	Ethyl acetate	2835	96.4	10.5	65	128
100-41-4	Ethylbenzene	5420	96.8	9	70	124
142-82-5	Heptane	3163	95.7	8.9	69	123
87-68-3	Hexachlorobutadiene	4551	96.7	13.7	56	138
110-54-3	Hexane	3150	91.6	9.5	63	120
98-82-8	Isopropylbenzene	3022	95.6	9.3	68	124
179601-23-1	m/p-Xylene [3/4-Xylene]	5019	97.3	12.3	61	134
80-62-6	Methyl methacrylate	3037	98.9	9.7	70	128
1634-04-4	Methyl tert-butyl ether [MTBE]	4681	95.5	10	66	126
75-09-2	Methylene chloride	5314	88.8	8.9	62	115
71-36-3	n-Butyl alcohol	1981	97.5	11.7	62	133
104-51-8	n-Butylbenzene	2656	97.7	10.6	66	130
112-40-3	n-Dodecane	1932	104.4	14.1	62	147
103-65-1	n-Propylbenzene	2570	95.7	9	69	123
91-20-3	Naphthalene	2439	97.5	13.4	57	138
111-84-2	Nonane	2617	95.4	10.8	63	128
95-47-6	o-Xylene	5334	96.3	9.7	67	125
111-65-9	Octane	2514	95	8.7	69	121
99-87-6	p-Isopropyltoluene [p-Cymene]	2694	98.1	10.5	67	130
109-66-0	Pentane	712	96.7	11.3	63	131
115-07-1	Propene	3193	96.6	13.3	57	136
135-98-8	sec-Butylbenzene	2665	96.4	9.6	68	125
100-42-5	Styrene	4735	100.1	9	73	127
75-65-0	tert-Butyl alcohol	2997	86.8	20.9	24	150
98-06-6	tert-Butylbenzene	2710	94.3	9.8	65	124
127-18-4	Tetrachloroethene	5432	95.2	9.7	66	124
109-99-9	Tetrahydrofuran	3192	93.7	9.8	64	123
108-88-3	Toluene	5406	92.7	8.8	66	119
156-60-5	trans-1,2-Dichloroethene	5411	95.5	9.5	67	124

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Table 3. LCS Control Limits – Method TO-15 Gas Matrix

CAS ID	Analyte	N Records	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit
10061-02-6	trans-1,3-Dichloropropene	4621	104	9.6	75	133
79-01-6	Trichloroethene	5478	96.7	8.7	71	123
75-69-4	Trichlorofluoromethane [Freon-11]	5376	93.7	10.6	62	126
1120-21-4	Undecane	1976	96.1	9	69	123
108-05-4	Vinyl acetate	4599	97.4	13.7	56	139
593-60-2	Vinyl bromide	1054	98.4	9.2	71	126
75-01-4	Vinyl chloride	5445	95.1	10.4	64	127

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Table 4. Quality Control Requirements – GC/MS Analysis of Air Samples

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Canister Cleanliness Check	Each canister prior to shipment.	No reported analytes detected > ½ LOQ.	Correct problem, then repeat cleaning of canister and recertify.	Flagging is not appropriate.	Applicable only when laboratory supplies sampling canisters to client.
Tune Check	Prior to ICAL and prior to each 24-hour period of sample analysis.	Specific ion abundance criteria of BFB from method.	Retune instrument and verify.	Flagging is not appropriate.	No samples shall be analyzed without a valid tune.
Initial calibration (ICAL) for all analytes	At instrument set-up, prior to sample analysis	Calculated %RSD for the RRF of each analyte in the calibration must be less than 30%; Or Linear least squares regression for each analyte: r2 ≥ 0.99; Or Non-linear least squares regression (quadratic) for each analyte: r2 ≥ 0.99.	Correct problem then repeat ICAL.	Flagging is not appropriate.	Minimum 5 levels for linear and 6 levels for quadratic with one calibration point at the same concentration as the daily CCV. The lowest calibration standard concentration at or below the LOQ. No samples shall be analyzed until ICAL has passed.
Retention Time window position establishment	Once per ICAL and at the beginning of the analytical sequence.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA.	NA.	Calculated for each analyte.

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STANDARD OPERATING PROCEDURE

TITLE: ENV-SOP-MTJL-0104 Measurement of Volatile Organic Compounds and Gasoline Range Components in Ambient Air by Gas Chromatography/Mass Spectrometry (EPA TO-15 and EPA Method 18-Modified)

ISSUER: Pace National – Mt. Juliet, Tennessee

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Table 4. Quality Control Requirements – GC/MS Analysis of Air Samples

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Evaluation of Relative Retention Times(RRT)	With each sample.	RRT of each reported analyte within ± 0.06 RRT units of the mean RRT of the calibration standards. RRTs may be updated based on the daily CCV	Correct problem, then rerun ICAL.	NA	RRTs shall be compared with the most recently updated RRTs. After maintenance is performed which may affect retention times, RRTs may be updated based on the daily CCV.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis	All reported analytes within $\pm 30\%$ of true value.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Continuing Calibration Verification (CCV)	Daily before sample analysis; after every 24 hours of analysis time; and at the end of the analytical batch run.	Concentration the same as the mid-point calibration standard (or lower). All reported analytes and surrogates within $\pm 30\%$ of true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or if two consecutive CCVs cannot be run, perform corrective action(s) until a passing CCV is attained, and r then reanalyze all affected samples since the last acceptable CCV. Alternatively, perform an ICAL (including appropriate instrument QC) if necessary; then reanalyze all associated samples since the last acceptable CCV	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since last acceptable calibration verification.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed. If the specific version of a method requires additional evaluation (e.g., average RFs) these additional requirements must also be met.

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Table 4. Quality Control Requirements – GC/MS Analysis of Air Samples

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Internal standards (IS)	Every field sample, standard and QC sample.	<p><u>ICAL Standards</u> The area response for each internal standard must be within 40% of the mean area response of the calibration standards for each internal standard. The retention time shift for each internal standard at each calibration level must be within 20 seconds of the mean retention time of the calibration standards for each internal standard.</p> <p><u>Field Samples, Blanks & QC</u> RT of each IS must be within +/-0.33 minutes of the most recent initial calibration.</p>	Inspect mass spectrometer and GC for malfunctions and correct problem. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	If corrective action fails in field samples, data must be qualified and explained in the case narrative. Apply Q-flag to analytes associated with the non-compliant IS. Flagging is not appropriate for failed standards.	Must include at a minimum bromochloromethane, Chlorobenzene-d5, and 1, 4-difluorobenzene.

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Table 4. Quality Control Requirements – GC/MS Analysis of Air Samples

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Method Blank (MB)	One per analytical batch (after the first CCV), prior to analysis of any field samples.	No analytes detected > ½ LOQ or > 1/10 the amount measured in any sample or 1/10 the regulatory limit, whichever is greater. Common contaminants must not be detected > LOQ.	Conduct investigation to determine the source of the contamination and take appropriate corrective actions. Rerun MB and all associated samples. If required, reprep and reanalyze MB and all QC samples and field samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch. Flagging is only appropriate in cases where the samples cannot be reanalyzed	The MB is a certified clean canister of the same type as the sample that has not left the laboratory. The blank has been pressurized with humidified zero air and carried through the same analytical procedures as a field sample. Results may not be reported without a valid method blank. If a TIC search is required for any samples, then a TIC search is also required for the associated Method Blank.

STANDARD OPERATING PROCEDURE

TITLE: ENV-SOP-MTJL-0104 Measurement of Volatile Organic Compounds and Gasoline Range Components in Ambient Air by Gas Chromatography/Mass Spectrometry (EPA TO-15 and EPA Method 18-Modified)

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Table 4. Quality Control Requirements – GC/MS Analysis of Air Samples

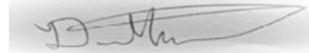
QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Laboratory Control Sample (LCS)	One per preparatory batch.	One canister standard is analyzed two times in the analytical run. A laboratory must use the limits in Table 3 for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits (see the LIMS) if project limits are not specified. RPD between the LCS and LCS Replicate for each target analyte must be < 30%.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated analytical batch for failed analytes, if sufficient sample material is available	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Must contain all surrogates and all analytes to be reported. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed. If the daily CCV is prepared in a canister, then the initial and closing CCVs can serve as the LCS and LCS Replicate as well. Both the CCV and LCS acceptance criteria would apply.

APPENDIX C

 <p>CRESTONE PEAK RESOURCES</p>	<p>Continuous Emissions Monitoring Data Evaluation and Response Procedure</p>	<p>Page 1 of 9</p>
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DATE OF ISSUE:	SUPERSEDES:	Control Number: 13.11200
EFFECTIVE DATE: DRAFT	EXECUTIVE OWNER: Taryn Weiner	

ENDORSEMENTS:

NAME	TITLE	SIGNATURE	DATE
David Stewart	VP of EHS&R		12/11/20
Taryn Weiner	Air Quality Supervisor		12/11/20

1.0 PURPOSE

This Procedure has been developed to establish a consistent process for evaluating Canary S™ continuous emissions data (CEM) and defining Crestone Peak Resources (Crestone) response thresholds. Additionally, this Procedure will be used and updated for the purposes of utilizing CEM data to augment and replace Crestone’s LDAR program and use of Canary S™ as an Alternative Instrument Monitoring Method (AIMM).

2.0 SCOPE AND APPLICATION

This Procedure lays out how Crestone will implement and evaluate the Canary continuous emission monitoring program and data in tandem with Crestone’s LDAR program defined by CDPHE Regulation No. 7.

3.0 ACRONYMS AND DEFINITIONS:

AIMM	Alternative Instrument Monitoring Method
APCD	Air Pollution Control Division
AVO	Audio, visual and olfactometry
CDPHE	Colorado Department of Public Health and Environment
CEM	Continuous emissions monitoring
Cygnnet	Crestone’s automation tracking system
PM	Particulate matter



NO _x	Nitrogen oxides
VOC	Volatile Organic Compound
FLIR	Forward Looking Infrared
LDAR	Leak detection and repair
ppm	Parts per million

4.0 RESPONSIBILITIES AND AUTHORITY

Executive Owner – Taryn Weiner

The Vice President of Environmental, Health, Safety & Regulatory (EHS&R), or designee(s) is accountable for ensuring that all Crestone employees and contractors working under direction of Crestone are trained to this Procedure prior to participation in the CEM program.

5.0 PROCEDURE REQUIREMENTS

Individuals executing this Procedure must have completed general awareness training on the Crestone EHS&R management system.

6.0 HEALTH AND SAFETY

6.1 Field Safety Requirements

- a. Personal protective equipment requirements:
 - i. Hard hat
 - ii. Steel toe shoes
 - iii. Safety glasses
 - iv. Fire resistant clothing (outer most layer)
 - v. Hearing protection (when conditions warrant)
 - vi. Four-gas monitors
- b. Driving: Operating a motor vehicle will be conducted according to the Crestone “Safe Vehicle Usage Practice” document.
- c. Respiratory Hazards: Condensate storage tank thief hatch repair and maintenance subjects the LDAR Technician to the greatest risk of an inhalation hazard. Any thief hatch work should be conducted as safely as possible and in accordance with the, “Thief Hatch Repair and Maintenance” Standard Operating Procedure.



7.0 QUALITY ASSURANCE AND CONTROLS

This controlled document is subject to an annual review by the Executive Owner (see Section 7.1 of Procedure **53.10Aa** for details).

This controlled document is subject to a formal triannual update by the subject matter expert assigned to this document (see Section 7.2 of Procedure **53.10Aa** (Controlled Documents Procedure) for details).

8.0 PROCEDURE REQUIREMENTS

8.1 Field Monitoring Setup

a. Equipment:

i. Canary STM monitoring equipment will include:

1. Anemometer
2. Total hydrocarbon sensor
3. NO_x sensor (if installed)
4. PM sensors (if installed)
5. Modem and cloud connection
6. Solar power equipment

ii. FLIR Camera

iii. Apple iPad

b. Technology:

i. Canary-provided website:

<https://dashboard.projectcanary.io/dashboard/global/devices/overview>

1. Data will be continually received from the field

ii. Intelex ACTs database:

<https://crestone.acts.intelex.com/Default.aspx>

1. Stores LDAR inspection information

iii. Prontoforms iOS App

1. Logs LDAR inspections

c. Canary STM Alarm Thresholds

i. 5-minute average threshold set at 3 ppm

ii. Instantaneous spike threshold set at 10 ppm

iii. 24-hour average threshold set at 1 ppm

d. Crestone Canary Team (Team)



- i. LDAR technician(s)
- ii. Air Quality Supervisor
- iii. Vice President of EHS&R

8.2 Canary S™ Field Monitoring Procedure

- a. The Canary S™ website and database will notify the Team based on the 5-minute average and 24-hour averages or the instantaneous spike threshold.
- b. Alarm event is less than 45 minutes from initial alarm timestamp:
 - i. The Canary S™ graph will be evaluated to determine if the ppm levels have returned to pre-alarm threshold.
 - 1. If readings have returned to near-normal levels (within 0.5 ppm of monthly pre-alarm average) for 20 minutes following the 45 minute window, the alarm is considered resolved.
 - 2. If the readings are below the alarm threshold but not returned to near-normal levels for 20 minutes following the 45 minute window the site will be monitored for 24 hours.
 - a. If levels do not increase, then the alarm will be considered resolved.
 - b. If levels increase to above any alarm threshold, an LDAR technician will be dispatched on the next business day to perform a FLIR camera site inspection.
- c. Alarm events that persist more than 45 minutes on a business day.
 - i. The lease operator and/or Cygnet will be utilized to determine if normal facility operations are occurring.
 - 1. If normal operations or maintenance are being performed, then the alarms will be monitored to ensure the site readings return to normal.
 - a. If normal operations are occurring, the alarm timestamp, type of operation (i.e. water hauling, drip pot cleaning, etc.), and start time of operational activity will be recorded in Log of Operational Events and Canary S™ Alarms (CPRO - Operational Canary S Alarms.csv spreadsheet).



Continuous Emissions Monitoring Data Evaluation and Response Procedure

2. If normal operations or maintenance are not being performed or the lease operator does not respond to the call within 15 minutes, an LDAR technician will be dispatched to the site as soon as possible but no later than the next business day to perform a FLIR camera site inspection.
 - c. If the LDAR technician is enroute and the cause is determined by correlating alarm timestamp to start of normal operations, an inspection will not be performed.
 - d. If normal operations are occurring, the alarm timestamp, type of operation (i.e. water hauling, drip pot cleaning, etc.), and start time of operational activity will be recorded in Log of Operational Events and Canary S™ Alarms (CPRO - Operational Canary S Alarms.csv spreadsheet).
- d. Any alarm events that occur outside of Crestone business hours (evenings, weekends, holidays) will be evaluated on the next business day.
 - i. For durations of less than 3 hours, the process defined in 5.b will be followed.
 - ii. For alarm events greater than 3 hours but not still alarming the lease operator and Cygnet will be consulted.
 1. If the cause of the alarm can be identified, then the cause will be noted, and ppm readings will be evaluated to confirm levels have returned to normal.
 - a. If normal operations are occurring, the alarm timestamp, type of operation (i.e. water hauling, drip pot cleaning, etc.), and start time of operational activity will be recorded in Log of Operational Events and Canary S™ Alarms (CPRO - Operational Canary S Alarms.csv spreadsheet).
 2. If the cause is unknown or levels have not returned to normal, an LDAR technician will perform a FLIR camera site inspection on the next business day.
- e. For alarm events that have not concluded, a lease operator will be dispatched to conduct an AVO inspection to try and identify the



issue. If the issue is not identified, an LDAR technician will be dispatched within 12 hours.

- f. If an alert led to the deployment of an LDAR team, the alarm timestamp will be recorded in Log of Canary STM Alarms and LDAR inspection (Canary STM compared to LDAR.xlsx spreadsheet) .

8.3 Regulation No. 7 LDAR Inspection Comparison

- a. Crestone will complete LDAR inspections per the frequency defined in APCD Regulation No. 7, Part D, Section II.E.4.d (Reg. 7).
- b. After an inspection has been completed, an evaluation of Canary STM versus the LDAR inspection results will be performed. Data that will be evaluated and entered into Canary STM vs LDAR.xls spreadsheet:
 - i. Number of leaks identified by FLIR camera.
 - ii. Leak information: Opinion on leak size, large, medium or small leak. (This will not include leak quantification but only a judgement call by the LDAR technician.)
 - iii. Number of Canary STM alarms, includes all three alarm types (3 ppm and 1ppm averages, and 10 ppm instantaneous).
 - iv. Average Canary STM Reading in ppm since last inspections.
 - v. Analyze Canary STM data since last inspection.
- 3. Evaluate ppm for increase that indicates if moderate to large leaks were visible with the Canary STM:
 - i. Enter ppm increase;
 - ii. Include comments; and
 - iii. Link screenshot of Canary STM graph.

8.4 Decrease Regular Inspection Frequency

dependent on CDPHE/EPA Approval

- a. Crestone will follow sections 8.2 and 8.3 for three inspection frequencies as defined by Reg. 7.
- b. After three inspections, the Canary STM information and LDAR results will be evaluated to:
 - i. Confirm Canary STM sensors are functioning as expected;
 - ii. Confirm Canary STM alarms are functioning; and



**Continuous Emissions Monitoring
Data Evaluation and Response
Procedure**

- iii. Confirm Canary S™ data matches the LDAR inspection results, and that no moderate to large leaks were occurring that the Canary S™ should have caught.
- c. If every point is confirmed in section 8.4.b, then Crestone will step down Regulation 7 inspections to the next lower inspection frequency.
 - i. Refer to Table 1 and 2 for reference.
- d. Following two additional inspection frequencies, the Canary S™ information and LDAR results will be evaluated again.
 - i. following a successful evaluation, the frequency will be decreased again.
- e. After one third and final evaluation frequency, any sites not yet on an annual LDAR inspection frequency will be evaluated
 - i. following a successful evaluation, the frequency will be decreased to an annual LDAR inspection frequency.
- f. If frequency is decreased in 8.4.c, Crestone will still complete regular LDAR inspections no less than annually.

Table 1

Initial Inspection Frequency	Inspection Frequency Following <u>Successful</u> initial Review	Inspection Frequency Following <u>Successful</u> Second Review	Inspection Frequency Following <u>Successful</u> Third Review
Monthly	Quarterly	Semiannually	Annually
Quarterly	Semiannually	Annually	Annually
Semiannually	Annually	Annually	Annually
Annually	Annually	Annually	Annually

Table 2

	Monthly Inspection	Quarterly Inspection	Semiannual Inspection
Time from SOP implementation to initial review (3 inspection Frequencies)	3 months	9 months	18 months
Time from first to second review (2 inspection Frequencies)	6 months	12 months	NA
Time from second to third review (1 inspection frequency)	6 months	NA	NA
Total time to move to annual review	15 months	21 Months	18 Months



8.5 Increased Evaluation Conditions Upon Unsuccessful Evaluation

dependent on CDPHE/EPA Approval

- a. Crestone will follow sections 8.4 above to evaluate a site in order to reduce the inspection frequencies as defined by Reg. 7.
- b. Upon an unsuccessful evaluation, the site will undergo one more inspection frequency at its current frequency level (monthly, quarterly, or semiaannually) and will then be reevaluated according to section 8.4.b.
 - i. Refer to table 3 for reference.

Table 3

If site does not meet standards after initial review	If site does not meet standards after second review	If site does not meet standards after third review	If site does not meet standards after review on annual basis
perform one more inspection frequency and reevaluate	perform one more inspection frequency and reevaluate	perform one more inspection frequency and reevaluate	Site is bumped back to semiannual review for 3 inspection frequencies

8.6 Record Keeping Requirements

- a. Reg. 7 and NSPS 40 CFR Subpart OOOOa LDAR inspections maintained in ACTs.
- b. Log of Canary S™ Alarms and LDAR inspection (Canary S™ compared to LDAR.xlsx spreadsheet) maintained on Crestone’s network.
- c. Log of Operational Events and Canary S™ Alarms (CPRO - Operational Canary S Alarms.csv spreadsheet) Maintained on Crestone’s network.

9.0 MANAGEMENT OF CHANGE

This document is subject to Crestone Management of Change Procedure.

10.0 VIOLATIONS



Violations of this Procedure and related policies and procedures by employees may result in disciplinary action up to and including termination. Violations of this Procedure by contractors and other authorized third parties may result in the revocation of such party’s access to Crestone’s premises and/or electronic access to its systems, and the termination of such party’s contract for services.

11.0 REFERENCES

- Management of Change Practice (52.10Aa).
- EHS&R Master List of Controlled Documents (<https://www.envstd.info/crestonepeak>).
- Crestone Brand Standard Guide.

12.0 REVISION HISTORY AND EXPIRATION

Note: Revision # should be listed in descending order starting with most recent version at the top

REV. #	DATE	Description/Modification	Revision Section (s)	Author(s)

13.0 ATTACHMENTS

- Log of locations with Canary S™ continuous emission monitoring equipment, including:
 - Equipment installation date; and
 - Sensor technology installed.

APPENDIX D

1. The Principle

The Canary monitoring system is designed to meet CPRO's goal of:

1. Detecting, evaluating, and reducing as necessary hazardous air pollutant emissions
2. Detecting, evaluating, and reducing as necessary methane emissions.

2. Data System

Project Canary JSON dictionary v1.0

JSON packages are relayed as they are received, without alteration. They will typically flow at a rate of 1 per minute per unit. A customer is able to specify the full URL for a webhook target in the Project Canary Portal v1.0. The JSON packages will then be relayed as they are received. To date, only one target per customer has requested raw JSON payloads via the Portal, additional needs will require some custom development. Below is the body of a typical JSON package. Green text has been added for explanation. **File names do not contain any identifying data other than timestamp when generated (example 2019-11-26T16-51-01.925Z).**

Green text not part of JSON payload, used to clarify reading information

```
{
"public": "false",
"fw_version": "v0",
"userid": "Project Canary",
"published_at": "2019-11-26T16:51:01.720Z",
"coreid": "2f001f001550483553353620", - UID of the Canary Unit, this is the UID Project Canary
uses
"data": {
"ICCID": "2f001f001550483553353620", - Unique ID of the Canary Unit, same as coreid
"Time": "2019-11-26T16:50:00Z", - Timestamp of data collection, this should be the time you
use
"Sig": "-67", - signal strength, used for internal diagnostics
"WD": "-1", - Wind Direction in degrees if applicable, '-1' denotes null
"WS": "-1", - Wind Speed in meters/sec if applicable, '-1' denotes null
"Long": "Longitude", -unit Longitude, '-1' denotes null. Project Canary doesn't transmit this every
time
"Lat": "Latitude", - unit Latitude, '-1' denotes null. Project Canary doesn't transmit this every time
"IH": "65.8", - unit internal humidity, '-1' denotes null
"IT": "28.6", - unit internal temperature, in Fahrenheit '-1' denotes null
"P": "832.76", - unit internal pressure in mb/hPa
"PM10": "1.15", -Particulate Matter in micrograms per cubic meter, '-1' denotes null
"PM2_5": "1.15", -Particulate Matter in micrograms per cubic meter, '-1' denotes null
"PM1_0": "0.57", -Particulate Matter in micrograms per cubic meter, '-1' denotes null
"CH4": "0", -Methane in parts per million
"TVOC": "0.347" – TVOC in parts per million
},
```

"event": "telemetry",
"timestamp": "2019-11-26T16:51:01.925Z"

3. Electrical Requirements

Operational time without solar was tested during the Wyoming winter with average temperatures below freezing for prolonged periods of time. This test, conducted with a completely detached solar panel connection, generated the 6-day figure mentioned. Very cold weather can impact the battery energy storage capacity so this was a test case that exceeds the vast majority of Colorado conditions (i.e. worst-case test)

Battery		Charging	
Chemistry	Lithium-Ion	Solar Panel	12V DC (20W)
Capacity	8000 mAh	Solar Charge Controller	12V DC
		Wall Charger	120V AC (US std) input to 12V DC output (24W)

4. Calibration Procedures

Every Canary S unit individually undergoes lab calibration with a variety of NIST traceable scientific gases with specifically known concentrations. This allows every unit to have an adjustment applied to it to compensate for any manufacturing differences. The in-field baseline setting is then conducted once the units are deployed to adjust for site-specific conditions. Distinct algorithms are utilized to account for temperature, humidity and atmospheric pressure impacts on sensor readings. Such ambient condition adjustment algorithms were developed after extensive testing in climate control temperatures capable of a wide range of temperatures and humidity levels.

Calibration Process

1. Field Technician will directly work with the internal components of the device to begin the “calibration test” process
2. Field Technician exposes the VOC sensor to scientific grade gas premixture, with extremely accurate known concentration levels
3. Project Canary staff monitor the readings coming from the VOC sensors in real-time
4. Input gas type & contractions used, calibrate based on live readings
5. Re-expose the VOC sensor to scientific grades gas(es)

6. Ensure the readings come back accurate and precise – .5ppm, 1ppm, and 3ppm gases utilized) following recalibration
7. If the Canary S unit’s readings do not match the premixture, the Field Technician will replace the existing unit with a new unit.
 - A. Field Tech will take existing unit back to the lab for further calibration and testing

5. Schematic Diagram



Due to the Intellectual Property Agreement with Lunar Outpost, we cannot share internal schematics of the units, as that could compromise the sensor layout and manufacturer’s design.

Dimension Value	Value
Width	8.6 in
Height	10 in
Depth	6.7 in
Weight	~4.3 lbs