Analysis of Photochemical Assessment Monitoring Station (PAMS) Volatile Organic Compounds (VOCs) in Ambient Air via the Markes/Agilent Automatic Gas Chromatograph (Auto-GC) Standard Operating Procedure

By
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For the
Air Quality Program

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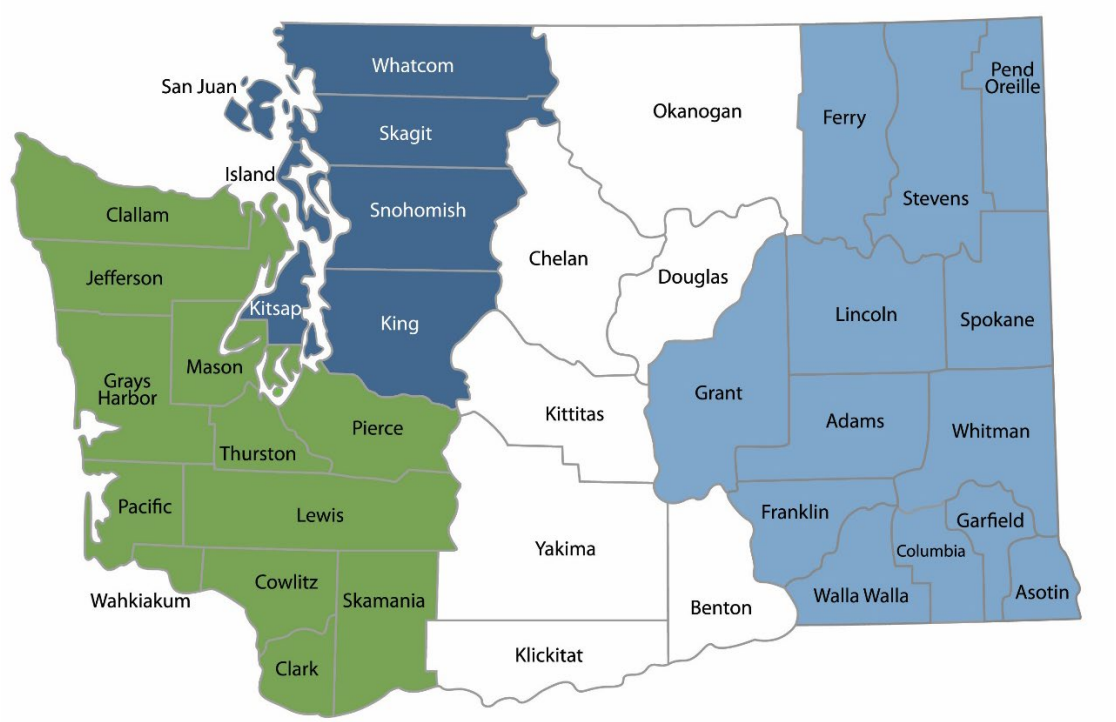

Southwest Region 360-407-6300	Northwest Region 206-594-0000	Central Region 509-575-2490	Eastern Region 509-329-3400

Region	Counties served	Mailing Address	Phone
Southwest	Clallam, Clark, Cowlitz, Grays Harbor, Jefferson, Mason, Lewis, Pacific, Pierce, Skamania, Thurston, Wahkiakum	PO Box 47775 Olympia, WA 98504	360-407-6300
Northwest	Island, King, Kitsap, San Juan, Skagit, Snohomish, Whatcom	PO Box 330316 Shoreline, WA 98133	206-594-0000
Central	Benton, Chelan, Douglas, Kittitas, Klickitat, Okanogan, Yakima	1250 W Alder St Union Gap, WA 98903	509-575-2490
Eastern	Adams, Asotin, Columbia, Ferry, Franklin, Garfield, Grant, Lincoln, Pend Oreille, Spokane, Stevens, Walla Walla, Whitman	4601 N Monroe Spokane, WA 99205	509-329-3400
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Revision History

Revision Date	Revision Number	Summary of changes	Revised sections	Revised by
5/8/25	1.0	Initial publication		Jenny Li

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Definitions and Acronyms

AC	alternating current
ADQ	audit of data quality
AGL	above ground level
APD	absolute percent difference
AQS	Air Quality System
atm	atmosphere
BOA	back of analyzer
CCV	continuing calibration verification
CDS	chromatography data system
cps	counts per second
CPU	central processing unit
DF	dilution factor
DI	deionized
DQO	data quality objective
DTS	date-time stamp
EPA	Environmental Protection Agency
FEP	fluorinated ethylene propylene
FID	flame ionization detector
GC	gas chromatograph
HCF	hydrocarbon free
HVAC	heating ventilation and air conditioning
ICAL	initial calibration
ID	inner diameter
inHg	inch(es) of mercury
kPa	kilopascal(s)
MDL	method detection limit
MFC	mass flow controller

MIC	Markes Instrument Control (software)
MUR	method update rule
mL	milliliter(s)
mmHg	millimeter(s) of mercury
MQO	measurement quality objective
MUR	method update rule
mV	millivolt
NIST	National Institute of Standards and Technology
OD	outer diameter
pA	picoampere
PAMS	Photochemical Assessment Monitoring Stations
PDMS	polydimethylsiloxane
PEEK	polyetheretherketone
PFA	perfluoroalkoxy
PLOT	porous layer open tubular
ppb	part per billion
ppbC	part per billion carbon
ppbV	part per billion volume
PPE	personal protective equipment
ppmC	part per million carbon
psia	pound(s) per square inch absolute
PT	proficiency test
PTFE	polytetrafluoroethylene
QAPP	quality assurance project plan
QC	quality control
r^2	correlation coefficient
RF	response factor
RPD	relative percent difference

RSD	relative standard deviation
RT	retention time
RTS	retention time standard
SB	system blank
S:N	signal-to-noise ratio
SOP	standard operating procedure
SSCV	second source calibration verification
STP	standard temperature and pressure
TAD	technical assistance document
TD	thermal desorber
THC	total hydrocarbons
TNMOC	total non-methane organic carbon
TNMTC	total non-methane target compounds
TSA	technical systems audit
UHP	ultra-high purity
UPS	uninterrupted power supply
VOC	volatile organic compound
ZAG	zero air generator

Absolute pressure: Pressure relative to absolute vacuum, typically expressed in units of: psia, atm, mm Hg, kPa, or in Hg.

Acquisition time: Portion of the GC program during which the CDS records detector responses. To reduce data file size, the first few minutes of a chromatogram when no target analytes are eluting from the column(s) are not recorded.

Analytical sequence: List of sample analyses programmed into a sequence table within the CDS.

Auto-GC: Automatic gas chromatograph. GC capable of autonomous operation to collect an ambient air sample and to trap, separate chromatographically, identify, and quantitate the VOCs of interest.

Baseline: The instrument's detector background signal in the absence of a substance.

Carrier gas: The mobile phase in gas chromatography; the carrier gas is non-reactive to the target analytes. Carrier gas flows at a constant rate through the GC column to carry analytes to the detector. For the Markes UNITY-xr TD and Agilent 7890B GC, the carrier gas is helium. [*note: Hydrogen may be employed as a carrier gas in lieu of helium; however, such is outside the scope of this SOP.*]

Chromatogram: A graphical record of a chromatographic separation plotting detector response (generally represented in mV or pA) on the y-axis as substances elute from the separation column against elapsed time from GC injection on the x-axis.

Chromatographic peak: The portion of a chromatogram representing the increase and subsequent decrease in detector response during which a compound elutes from the separation column. To be considered a true peak for identification purposes, the signal-to-noise ratio (S:N) must be ≥ 3:1. A completely resolved peak will start and end at the baseline.

Chromatography data system (CDS): The software program that controls the operation of the GC, acquires raw instrument data, and permits processing of collected data. The CDS allows programming of analytical sampling sequences, generation of instrument calibration curves for target analytes, calculation of target analyte concentrations, and post-collection processing of raw instrument data. The CDS for the Agilent 7890B system is Agilent OpenLab EZChrom or OpenLab ChemStation. The Markes UNITY-xr TD is operated through the Markes Instrument Control (MIC) software.

Co-elution: Simultaneous elution of two or more substances from the separation column whereby their chromatographic peaks overlap, and the chromatogram does not return to baseline between the substances. Co-elutions can be partial or complete and can interfere with the ability of the CDS and/or analyst to properly identify and/or integrate the peak(s).

Continuing calibration verification (CCV): QC sample consisting of a known concentration of target analytes analyzed to assess the ongoing suitability of the instrument calibration. CCVs are prepared by diluting a stock standard gas to a concentration within the calibration curve range (preferably within the lower one-third of the calibration curve range) and analyzed approximately every 24 hours of analysis. The CCV must demonstrate the measured concentrations for propane and benzene, each of which is separately detected on the two different FID channels, are within ±30% of their theoretical concentrations. The CCV is to be sourced from a certified standard.

Date-timestamp (DTS): The date-time stamp is appended to a digital file as a result of saving the contents of the file. The DTS will change each time the file is changed or accessed.

Data quality objective (DQO): Metric defined for a project or program that describes or quantifies the desired acceptance criteria for collected data.

Deans switch: Gas routing device that operates by controlling the flows of subject gas (e.g., column effluent) by adjusting flows of said gas through increasing or decreasing the flow rate of an auxiliary gas.

Dilution factor (DF): The ratio of a standard gas to the corresponding diluent. Such is needed to calculate the concentration of diluted standard gases.

Dynamic dilution: Dilution of a standard gas or gases with a diluent gas by mixing gases together at known flow rates in an inert plenum.

Flame ionization detector (FID): Detection device that responds to ions formed during combustion of organic compounds in a hydrogen flame. The production of ions and associated response within the FID is proportional to the concentration of carbon atoms in the sample gas stream introduced to the detector. FIDs require a source of both hydrogen (fuel) and oxygen to produce the hydrogen flame.

Gas chromatograph (GC): Analytical instrument utilized to separate vaporized compounds according to physical or chemical properties by passing the sample through a separation column, which serves as the stationary phase, with a carrier gas acting as the mobile phase.

Gauge pressure: Pressure relative to ambient atmospheric pressure. Typically expressed in pounds per square inch gauge (psig). A measurement of 0 psig indicates ambient atmospheric pressure.

Initial calibration (ICAL): Standardization of the instrument response to known concentrations of a target analyte. Generation of an ICAL typically involves fitting response factors of analyses of several concentration levels via linear regression. The concentration of the target analyte can then be determined by translating its measured chromatographic peak area response into a concentration via inversion of the linear regression equation determined from the ICAL.

Inlet probe: The opening of the analytical system inlet to the ambient atmosphere. The materials comprising, siting, and configuration of the inlet probe must comply with 40 CFR Part 58 Appendix E.

Make-up gas: Inert gas (such as nitrogen or helium) added to the FID to maintain the linear velocity of column eluent and maintain appropriate chromatographic response.

Mass flow controller (MFC): Device that controls the flow of a specific gas by adjusting a flow control valve based on thermal differences within a capillary tube between

temperature sensors upstream and downstream from a heater. The difference in temperature between the sensors is translated to set the gas flow to a calibrated known flow rate via the flow control valve.

Measurement quality objective (MQO): Acceptance criteria prescribed for a given data quality indicator such as bias, precision, completeness, frequency, and sensitivity.

NCore: EPA's National Core ambient air monitoring network.

PAMS hydrocarbons (PAMSHC): Those priority and optional compounds listed in the PAMS target list.

Part per billion carbon (ppbC): Concentration unit of measurement equivalent to a ppbv (defined below) multiplied by the number of carbon atoms in the molecule.

Part per billion volume (ppbv): Concentration unit of measurement equivalent to a mixing ratio of 10^{-9} L (or moles) of a trace gas in 1 L (or mole) of diluent. One ppbv is equivalent to $2.46 \cdot 10^{10}$ molecules cm^{-3} at 760 mm Hg pressure and 25°C.

Precision: The reproducibility of a measurement. Auto-GC precision is determined by evaluating the similarity of the measured concentrations of successive analyses of a CCV on a weekly basis. The relative percent difference of the measurement pair is calculated by taking the absolute difference of the two measurements and dividing by the measurement pair average, expressed as a percentage.

Raw instrument data: Time-based signals generated and recorded by the instrument in the process of making measurements. Such data may include instrument detector responses, time stamps, flow rates, and other associated recorded instrument events such as valve switching, temperature changes, etc.

Recovery: The measured concentration of a target analyte divided by its theoretical nominal concentration, expressed as a percentage.

Relative standard deviation (RSD): The standard deviation of a given number of measurements divided by the mean of the measurements, expressed as a percentage.

Response factor (RF): The ratio of the instrument response in area units to a known concentration of a target analyte. The concentration of a given unknown target analyte can be calculated by multiplying or dividing (as appropriate) the measured area response by the RF determined in the initial calibration.

Retention time (RT): Duration of time it takes for a given target analyte to reach the detector following initiation of the desorption of the VOCs on the sorbent trap onto the GC column. RTs are assigned as the apex of the chromatographic peak.

Retention time window: Assigned time range during which a given target analyte is expected to elute from the separation column and reach the detector. Compound identification is determined by whether it elutes within a specified RT window, which is set by analysis of a known standard of the target analyte.

Retention time standard (RTS): A 56- to 59-component VOC mixture containing target analytes. This standard is analyzed to establish and confirm the RT of target analytes.

Sample: Aliquot of atmosphere introduced to the inlet of the GC system that is trapped for subsequent separation by the GC. The volume of sample is determined by multiplying the sampling flow rate by the duration of sample collection.

Second source calibration verification (SSCV) standard: A standard gas purchased from a supplier different than the primary standard from which the ICAL is prepared (a different lot from the same supplier as the primary standard is acceptable if the standard is unavailable from a different supplier). The SSCV standard gas is diluted to within the calibration curve and analyzed immediately following the establishment of the ICAL. The SSCV independently verifies the quality of the calibration curve(s).

Signal-to-noise: The ratio of the peak height or integrated area of the detector responses to a known substance to that of the detector response in the absence of the substance.

Standard temperature and pressure (STP): 25ºC and 760 mm Hg absolute pressure.

Static dilution: Preparation of a standard gas dilution by addition of a standard gas or gases and diluent gas to an evacuated vessel. The absolute pressure of the vessel is measured before and after the addition of each gas and the dilution factor calculated by dividing the final vessel pressure by the partial pressure of each standard gas.

System blank (SB): Analysis of a humidified zero air blank provided to the instrument through the instrument sampling inlet to ensure the instrument is sufficiently free of contamination. This

Theoretical nominal concentration: The concentration of a target analyte sourced from a certified concentration standard gas after adjustment for dilution, as applicable.

Thermal desorption (TD): The freeing of molecules from a sorbent by heating the sorbent to a temperature sufficient to release the molecules of interest from the sorbent.

Total non-methane organic carbon (TNMOC): Sum of carbon species responses on both FIDs eluting between ethane and dodecane.

Total non-methane target compounds (TNMTC): Total of the speciated, identified, and quantitated compounds in the FID analyses.

Ultra-high purity (UHP): Gas purity ≥ 99.999%.

Volatile organic compound (VOC): Carbon-containing compounds with vapor pressure greater than 10^{-1} Torr at 25ºC and 1 atmosphere pressure.

Wetted surfaces: Interior surfaces of the sampling flow path that contact the sample gas.

Zero air: Atmospheric air or synthetic mixture of minimally nitrogen and oxygen from which hydrocarbons have been removed to achieve a total hydrocarbon content of nominally ≤ 0.01 ppmC.

Zero air generator (ZAG): Device employed to scrub ambient air of hydrocarbons, water, and other gases that may interfere with the analysis of hydrocarbon VOCs. ZAG units typically employ sorbent materials, desiccants, and thermal and/or catalytic oxidation to produce air meeting the cleanliness acceptance criterion for zero ai

1. Introduction

1.1. Purpose and Scope

This document describes the operation of the Markes UNITY-xr equipped with the Kori-xr and CIA Advantage-xr sampling inlet systems with Agilent 7890B automated gas chromatography (Auto-GC) system for the analysis of volatile organic compounds (VOCs) identified under the EPA's Photochemical Assessment Monitoring Stations (PAMS) program to be ozone precursors or relevant to atmospheric ozone formation. This SOP describes procedures for installation, setup, calibration, operation, and data handling are described herein. This SOP should be used in conjunction with the equipment manufacturers' model-specific user guides and manuals and Ecology's air monitoring Quality Assurance Plan (QAP). Monitoring requirements, training requirements, data validation and verification, and data reporting to AQS are outside the scope of this SOP.

1.2. Summary of Method

Hourly speciated VOC measurements are required for PAMS, from June 1 through August 31. The Markes-Agilent GC system draws in ambient air from the inlet probe to collect and preconcentrate VOCs from the sampled atmosphere and subsequently separate the VOCs for detection via a dual flame ionization detector (FID). A new sample commences at the top of each hour. Figure 1-1 Figure shows the Markes/Agilent system principle of operation. Ambient atmosphere is drawn into the CIA- Advantage-xr sampling inlet by the vacuum supplied by the system's sampling pump and routed through a two-phase sorbent trap maintained at -27ºC by Peltier cooling. Sample collection occurs for 40 minutes, and flow is controlled to 20 mL/minute by a mass flow controller (MFC) to acquire 800 mL of sample. Sampled atmosphere is routed through a Kori-xr dryer to remove moisture prior to passing the sampled atmosphere to the cold trap in the UNITY-xr. Permanent gases pass through, while VOCs of interest are captured. At the end of the collection period, the trap is flushed for 4 minutes with dry carrier gas to remove any remaining bulk gases and/or residual moisture prior to being desorbed by quickly heating at the rate of 24ºC/second to 300 ˚C.

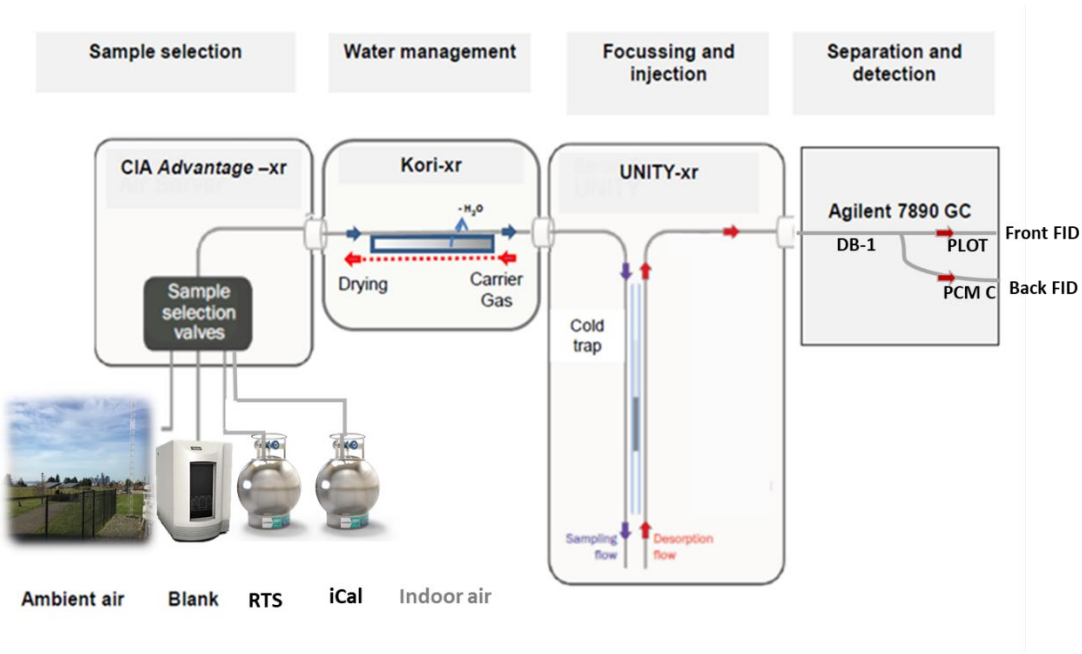


Figure 1-1: Markes/Agilent system principle of operation.

Following desorption, the trap is backflushed with carrier gas to sweep the desorbed VOCs to the Auto-GC. Once in the Auto-GC, the compounds elute from the DB-1 separation column and are routed through a Deans switch, which directs the lighter hydrocarbons (C_2-C_6) through a subsequent alumina PLOT separation column and the heavier compounds (C_6-C_{12}) directs to a back FID. The lighter hydrocarbons (C_2-C_6) are not appropriately separated by the DB-1 column and must be routed through the PLOT column for separation. These light compounds are detected by a front FID as they elute from the PLOT column. The GC program instructs the Deans switch to route the DB-1 column eluate to the back FID following the elution of 1-hexane. Compounds are identified by their retention time as they exit the appropriate separation column and are detected by the FID. The voltage responses of the FIDs are converted to a concentration in parts per billion carbons (ppbC) based on the response factor according to the calibration. The response factor is based on the FID response of propane (C_2-C_6) or benzene (C_6-C_{12}). System functions are controlled by a connected personal computer running OpenLab EZChrom (version A.04.09). Figure 1-1 shows the actual setup of the Auto-GC in the shelter of PAMS site in the downtown Seattle. The Markes UNITY-xr /Kori-xr/CIA-Advantage with Agilent 7890B Auto-GC is supplied by source of helium as a carrier and purge gas, hydrogen as FID fuel from a Hydrogen generator, and zero air as blanks, oxidizer, and purge gas from the TOC 1250 zero air generator (ZAG) with an air compressor, and a method of providing the system with stock standard gases for calibration and ongoing QC checks. Indoor air is used in troubleshooting.

Figure 1-2: Auto-GC instrument system setup at a PAMS site

PAMS target VOCs are listed below in Table 1-1. Priority compounds are those VOCs for which all PAMS sites must report concentrations. Optional compounds are those VOCs that are of interest to the PAMS program, but which are not required to be reported. Table 1-1 includes 1-hexene and n-dodecane, which are not designated as priority or optional compounds by the PAMS program. However, they are included in the 59-component retention time standard VOC mix for reference purposes, specifically for determining Deans switch cut times and defining unknown VOC totals.

Table 1-1: Priority and Optional VOCs for the PAMS Program

Priority/ Optional *	Compound Name	Number of Carbons
o	carbon tetrachloride	1
p	ethane	2
p	ethylene	2
o	tetrachloroethylene	2
o	acetylene	2
o	ethanol	2
p	propane	3
p	propylene	3
o	1,3-butadiene	4
p	1-butene	4
p	cis-2-Butene	4
p	isobutane	4
p	n-butane	4
p	trans-2-butene	4
p	isopentane	5
p	isoprene	5
o	cyclopentane	5
p	n-pentane	5
o	1-pentene	5
o	cis-2-pentene	5
o	trans-2-pentene	5
p	benzene	6
p	n-hexane	6
o	cyclohexane	6

Priority/ Optional *	Compound Name	Number of Carbons
o	2,2-dimethylbutane	6
o	2,3-dimethylbutane	6
x	1-hexene	6
o	2-methylpentane	6
o	3-methylpentane	6
o	methylcyclopentane	6
p	toluene	7
o	2,3-dimethylpentane	7
o	2,4-dimethylpentane	7
o	n-heptane	7
o	methylcyclohexane	7
o	2-methylhexane	7
o	3-methylhexane	7
p	2,2,4-trimethylpentane	8
p	ethylbenzene	8
p	m-/p-xylene	8
p	o-xylene	8
p	styrene	8
o	2-methylheptane	8
o	3-methylheptane	8

Priority/ Optional *	Compound Name	Number of Carbons
o	n-octane	8
o	2,3,4-trimethylpentane	8
p	1,2,3-trimethylbenzene	9
p	1,2,4-trimethylbenzene	9
p	m-ethyltoluene	9
p	o-ethyltoluene	9
p	p-ethyltoluene	9
o	isopropylbenzene	9
o	n-nonane	9
o	n-propylbenzene	9
o	1,3,5-trimethylbenzene	9
o	n-decane	10
o	m-diethylbenzene	10
o	p-diethylbenzene	10
o	a-pinene	10
o	b-pinene	10
o	n-undecane	11
x	n-dodecane	12

* o = optional; p = priority; x = VOC contained in RTS but neither priority nor optional compounds (concentrations not reported to AQS)

1.3. Interferences and Considerations

Planning: The PAMS season is defined as the period from June 1 through August 31. A PAMS field campaign consists of three phases: preventive maintenance and method establishment in the pre-season, operation and data acquisition during the season, and method and data verification in the postseason. Proficiency tests (PT) conducted by a third party are scheduled at the beginning and end of the season.

To operate with minimal disruption during the season, it is critical to have the Auto-GC instrument and its support equipment in good condition by performing preventive maintenance (PM) at least eight weeks before the season begins (see Table 2).

Preventive maintenance includes not only the replacement of consumable parts and software updates but also the processes of stabilizing and cleaning. Following this, a series of steps such as retention time establishment, calibration, and Method Detection

Limits (MDL) testing must be performed sequentially, with each step meeting PAMS criteria. Even if all PM is performed as recommended by the manufacturers, it is wise to have a supply of common consumable parts and gases such as UHP helium, PAMS-Kori trap, PAMS-UNITY trap, columns, FID, and various O-rings on hand to minimize the risk of failure or downtime.

Table 1-2: Pre-season preventive maintenance

Component	Items	P/N	Frequency
Air compressor	Piston Rings kit	C0746-1	annual or as needed
	Motor	C0401	3 years or as needed
ZAG (TOC-1250)	Filters	100-12-DX 100-12-BX GS050-05-95	annual
	Catalyst module	76810	3 years
H_2 generator	Filters, cartridges	MKH2PEM-6M	6 months
	Filters, cartridge, desiccant cartridge, Water pump	MKH2PEM-24M	2 years
Consumable	Desiccant cartridge	MKH2PEM-D	as needed
	HC filter	CP17972	annual or as needed
	Carrier gas filter	CP17973	annual or as needed
	Helium	≥ UHP grade	Swap on pressure of 200 psi
Humidification tool	Add DI water		annual
Inlet line	Clean		annual

To minimize interference with the Auto-GC operation during the season, data storing, processing, and verifying are conducted on a separate PC from the onsite operational GC PC. This operational GC PC is dedicated to activities such as daily system check, QC check, and data acquisition.

Upon the completion of a weekly sequence of runs, all GC data files and MIC historical sampling data, along with the appropriate methods, are manually transferred to the GC data PC placed in the NWRO office. These files are then organized into separate folders: one for storing, another for processing, and a third for verifying.

Equipment Conditioning and Storage: Before data collection, it is strongly recommended that the system be operated for a minimum of two months to ensure contaminants have been purged, all equipment operates properly, stable operation is

achieved, the instrument has been properly calibrated, and that operators are familiar with the instrument. Insufficient conditioning may result in interfering chromatographic artifacts, inability to successfully calibrate the instrument, and/or poor target analyte recovery. PAMS starts June 1 and ends August 31 but still operates all year long.

Co-elution: GC-FID identifies compounds solely by RT and can be subject to compound misidentification or incomplete chromatographic separation when chromatograms exhibit unknown substances co-eluting with target analyte peaks. Insufficient separation of target analytes between each other and/or unknown compounds can confound automated integration routines and will require substantial resources to address in acquired data.

RT Shifting and Peak Misidentification: In general, the C6-C12 channel chromatography is stable for RTs when the system is functioning properly, as changes in relative humidity of the sampled gas/atmosphere do not typically result in RT shifts. However, for the C2-C6 channel, the PLOT column is hygroscopic and readily absorbs water, which occupies active sites on the column and results in decreasing target analyte RTs. The Kori-xr water abstraction device, when operating properly, dries gas streams consistently regardless of starting humidity levels, and therefore maintains a constant humidity level on the PLOT column to accomplish stable target analyte RTs. If the Kori-xr dehydrator is not functioning properly (e.g., insufficient purge flow or purge time when purging moisture from the Kori-xr dehydration trap, resulting in retention of residual water), excess water may be transferred to the PLOT column and result in decreased RTs for target analytes – which may make it difficult or impossible for the CDS or analyst to identify compounds appropriately. Additionally, water may result in the Markes system stop sampling.

Compound Loss and Quantitative Transfer: Higher molecular weight (lower volatility) VOCs are susceptible to losses to wetted surfaces of the flow path, whether for sample introduction or connections to standard gases. Where possible, materials comprising the flow path for sample atmospheres and standard gases should consist of chromatographic-grade stainless steel. It is recommended that the chromatographic-grade stainless steel tubing be deactivated by silicon ceramic lining. Heating sampling lines and gas transfer lines aid in the quantitative transfer of low volatility VOCs.

Quantity of Data: Operators should be aware of the large amount of data produced by the Auto-GC system and the need for frequent contact with the instrument to ensure proper operation. QC sample failure and system failure due to malfunction or power outage, etc., can jeopardize the validity of large amounts of data, which could lead to the inability to meet the completeness MQO. Operators/analysts are encouraged to check in on the system daily, if possible, whether on site or via remote login. Operators

should verify that the system is online and collecting data properly, that QC samples have been analyzed and meet acceptance criteria, and that future sample collections are scheduled and queued properly. Additionally, analysts are strongly encouraged to optimize the automated CDS identification and integration routines on a regular basis, as poorly configured data processing methods require substantial analyst resources to reprocess analyte misidentifications and to correct improper peak integrations. Properly configured instruments and automated data processing routines will reduce the frequency with which data qualifiers must be appended to reported data or for which data invalidation is necessary.

1.4. Health and Safety

Refer to the instrument operator manuals for specific safety information for the Markes UNITY-xr TD, Kori-xr, CIA Advantage-xr, Agilent 7890B GC, and ancillary support equipment.

The ZAG system includes an air compressor, which stores air at high pressure in a ballast tank. Ruptures to the tank or connection lines can result in injury to persons near the instrument. Operators should depressurize air prior to performing any regular maintenance.

Helium carrier gas is contained within a high-pressure cylinder. Staff working with high pressure cylinders must be trained on their proper handling. Steel-toed shoes and leather gloves are recommended personal protection equipment (PPE) when moving and changing support gases.

The FIDs utilize hydrogen gas as fuel. Leaks in the hydrogen delivery system may result in hydrogen buildup, which can cause fire or explosion. Instruments should not be operated near open flame and sources of sparks should be eliminated. The shelter in which the instrument is installed has a hydrogen gas sensor (SBS-H2 Hydrogen Gas Detector) in place.

Operators should exercise caution when working on interior components of the instruments as internal components operate at both high temperatures (GC oven, FID, trap during desorption) and low temperature (Peltier cooled trap) which can damage unprotected skin. Operators should allow internal parts to return to room temperature and pressure before handling.

System components are heavy so individuals should exercise caution when moving components. Many of the components (e.g., the GC) require two people to move.

2. Equipment and Materials

The Markes system includes the UNITY-xr TD, Kori-xr water abstraction device and the CIA Advantage-xr gas sampling inlet. The Markes components and Agilent 7890B GC with dual FID comprise the Auto-GC instrument system, along with several other pieces of support equipment. The instrument footprint is approximately 38 inches wide by 24 inches deep; however additional space is required behind and beside the unit for gas and electrical connections, ventilation, and communications connections to the computer controlling the CDS.

Agilent 7890B GC

a. Transfer line – Deactivated Fused Silica: 5 m, 0.10 mm, 0 µm film thickness, P/N 160-2635-5
b. Microfluidics Deans switch
c. Two Capillary FIDs with EPC (211)
d. DB-1 Column: 50-m x 0.32 mm with 1.05-µm film thickness, P/N 123-105F
e. HP-PLOT Column: 50 m length, 0.32 mm inner diameter, 8 µm film thickness, P/N 19091P-S15

Agilent OpenLab EZChrom software, Revision A04.07 SR2 or higher

Markes UNITY-xr TD system

f. Preconcentrator trap – PAMS (VOC Ozone-precursors) TD trap, P/N AGMKI-U-T20PAM
g. GC interface harness P/N SERUTE-5142
h. Sample pump – KNF model N86KN.18

Markes Kori-xr water abstraction system

i. Single empty glass trap P/N MKI-U-T1KORI, 3-mm ID
j. Heated transfer line
k. O-rings P/N G8125-67019

Markes CIA Advantage-xr gas sampling inlet or UNITY-Air Server-xr Inlet System

l. Sample input ports and sample switching valves
m. Heated interface

Markes Instrument Control software, Version 2.0.14

ZAG - Park Balston Total Organic Carbon (TOC) 1250 Gas Generator can provide air containing hydrocarbon levels of less than 0.1 ppm (measured as methane), CO_2 level of less than 1 ppm, and a dewpoint of -100°F(-73°C) at a flow rate of up to 1250 cc/min., from compressed air. This ZAG has sufficient capacity to supply air at the flow of 350 cc/min as oxidizer for the dual FID; be employed for pneumatics operation and purging of the Peltier cooling boxes under pressure of 50 to 60 psig; and be humidified to feed as a blank.

n. Prefilters, PN: 100-12-DX and 100-12-BX

o. Membrane filter PN: GS050-05-95

p. Catalyst module, PN: 76810

Werther air compressor (Model: PC 1/24/379D) can maintain output pressures of 90-94 psig and sustained flow of minimally 1.5 L/minute to feed air into the ZAG.

q. A motor P/N: C0401

Piston Ring kit PN:C0790

Parker H2PEM-100 hydrogen generator: capable of providing UHP hydrogen with sustained flow to meet system demands, minimally 100 cc/minute (higher capacity recommended to provide sufficient reserve capacity). Alternatively, hydrogen gas may be sourced from high pressure cylinders.

Maintenance kit P/N: MKH2PEM-6M, MKH2PEM-24M, MKH2PEM-D

r. In-line carrier gas filters (P/N CP17973) between generator and instruments

Helium gas: cylinder gas – UHP grade, 99.999%, for carrier gas and make-up gas. CGA 580 regulator.

s. Use inline hydrocarbon filters (P/N CP17972) and carrier gas filters (P/N CP17973) between cylinder and instruments

RTS and ICAL standard gases

t. Humidified RTS and iCAL standard gases are provided by EGR. Each standard canister will require a pressure regulator (Airgas® Single Stage Brass 0-100 psi Analytical Line Regulator P/N: Y11241D-AG) to set at 5 psi for steady recovery.

Windows PC: Minimum hardware configuration: 3 GHz dual core processor speed (CPU), 4 GB physical memory (RAM), 160 GB hard drive space, compatible monitor (1280x1024 SXGA), Microsoft® Windows compatible mouse, USB 2.0 port, 100/1000 LAN.

Gas Clean Carrier Gas filter kit: for additional cleanup and drying of the helium carrier gas, FID zero air, and FID make-up gas – includes four moisture filters (P/N CP17971) and two hydrocarbon filters (P/N CP17972).

Gas regulators

u. Single Stage Brass 0-100 psi Analytical inline Regulator (P/N: Y11241D-AG)) to connect standard gas canister(s)

v. CGA580 regulator for connection to helium cylinder(s)

Various lengths of 1/4 inch, 1/8 inch, and 1/16 inch outer diameter (OD) chromatographic-grade stainless steel tubing and associated appropriate compression (Swagelok™) fittings, adapters, crosses, filters, a stainless-steel funnel. It is recommended that all such stainless-steel tubing be silicon ceramic lined. Additionally, connections to standard cylinders or canisters should consist of 1/16 inch OD tubing to minimize dead volume (and internal surface area) and potential losses of higher molecular weight (lower volatility) VOCs.

3.Reagents and Chemicals

1. Zero air – Zero air, or hydrocarbon-free (HCF) air, containing nominally ≤ 0.01 ppmC total hydrocarbons (THC), is provided by the ZAG to supply air for FIDs and may also be employed for purge gas for Peltier cooler boxes on the Kori-xr and UNITY-xr TD and for pneumatics gas for operated valves on CIA-Advantage-xr. HCF employed for purging Peltier cooler boxes must be dried to contain below 1 ppmv (dewpoint ≤ -76°C) of water to ensure proper TD operation.
2. Calibration stock standard gas – National Institute of Standards and Technology (NIST)-certified or NIST-traceable certified multi-component blend standard gas minimally containing propane and benzene. Practically, this standard gas at a concentration of approximately 25 ppbC for each target compound in a balance of UHP nitrogen is supplied by ERG lab under the national contract.
3. Second source stock standard gas – NIST-certified or NIST-traceable certified multi-component blend standard gas containing minimally the two calibration compounds, and preferably containing 15 or more of the target compounds of interest (to represent the molecular weight and volatility range of the target compounds) listed in Table 1-1. Typically, this standard gas is purchased at a concentration of approximately 25 ppbC for each target compound in a balance of UHP nitrogen.
4. Retention time standard (RTS) – Gas mixture containing the target compounds of interest listed in Table . Concentrations of the target compounds range from approximately 20 ppbC to 60 ppbC in a balance of UHP nitrogen. While not required, concentrations of propane and benzene and other compounds may be NIST-traceably certified so this standard can be employed for calibration or calibration verification.
5. Deionized (DI) water – For use in the hydrogen generator and for humidifying standard gases. Typical laboratory-grade water polishing units provide ASTM Type I water with resistivity ≥ 15 MΩ·cm, which meets specifications for most hydrogen generators.
6. Hydrogen (H_2) gas: Hydrogen generator, minimally UHP grade, ≥ 99.999% purity is recommended for FID fuel.
7. Helium (He) gas: Cylinder gas – UHP grade – as carrier gas, purge gas, and also FID make-up gas.

4.Installation Procedure

4.1. Siting Criteria

The PAMS monitoring site is located at the existing urban-scale NCore site in Seattle. Siting requirements for PAMS Auto-GC monitoring probes are summarized in Table 4-1. Operators should refer to 40 CFR Part 58 Appendix E for extensive siting criteria on PAMS Auto-GC monitoring.

Table 4-1: Summary of PAMS Auto-GC siting criteria

Parameter	Category	Siting Requirement
Inlet height	General	2 - 15 m above ground level
Inlet radius clearance	General	1 m vertically and horizontally away from supporting structure
	Near obstructions (building, walls, etc.)	≥ 2x height of the obstruction extended above the probe
	Near overhanging trees	≥ 10 m from the drip line
	Arc of air flow	Unrestricted 270° arc that includes prevailing direction of high concentrations
Distance from roadways	≤ 1,000 vehicles per day	≥ 10 m from nearest traffic lane
	1,000-10,000 vehicles per day	≥ 20 m from nearest traffic lane
	> 10,000 vehicles per day	Refer to 40 CFR Part 58 Appendix E, Table E-1
Distance from minor sources (e.g., incineration flues)	General	As far away as possible

4.2. Shelter Conditions

The shelter must be clean, temperature-controlled, and have ample and reliable 110-120 VAC power. To sustain an optimal operational environment, the shelter must be equipped with adequate HVAC systems to maintain room temperatures between 20 and 30°C year-round. The temperature should be controlled by a thermostat, ensuring that the standard deviation of daily room temperature over 24 hours is no more than 2.1°C. During a heatwave, a portable room air conditioner may be needed to expand the cooling capacity. This is necessary because temperature fluctuations or extended excursions beyond temperature limits can lead to retention time shifts, extended GC

oven cooling times, or failure to begin a sample sequence at the assigned time. Additionally, coolers in Kori and UNITY may struggle to reach -30°C in such conditions.

During the installation of the Auto-GC, the GC exhaust should be vented outside the shelter using 4-inch OD steel ducting suitable for woodburning stoves, gas water heaters, or similar materials exposed to temperatures of approximately 200°C. The Auto-GC exhaust conduit must be kept away from HVAC thermostats to avoid artificially influencing HVAC operation. More detailed guidance can be found in Section 4.4.3 of the PAMS TAD 3 revision.

The required power supply for the Markes UNITY-xr TD/Kori-xr/CIA Advantage-xr and Agilent 7890B GC instrument is a 20A 110V alternating current (AC) circuit. Additional circuits are necessary to supply power to the ZAG, air compressor, hydrogen generator, computer, hydrogen sensor, and inlet heater so on. Components may be connected to an uninterruptible power supply (UPS) unit to ensure power is conditioned to 110V and is continually available (note that Agilent GC isn't recommend using a UPS). Power conditioning is recommended for hydrogen generators as voltage fluctuations can damage components and switch the hydrogen generator to standby mode. The UPS allows instrument components to run uninterrupted during short power outages, with the duration dependent on the UPS unit capacity.

4.3. Inlet Probe

4.3.1. Sampling Train Materials Construction

All portions of the inlet pathway to the instrument inlet (inlet port on the CIA Advantage-xr), the back of the analyzer (BOA), etc. must consist of chromatographic-grade stainless steel, glass, or equivalent. Use of fluorinated ethylene propylene (FEP) Teflon®, rubber, Tygon®, or similar materials are prohibited as these materials may behave as sorbents or sources for VOCs. The use of copper, brass, or non-chromatographic-grade stainless steel is also prohibited, as such materials act as catalysts for destructive reactions of target analytes. Use of polytetrafluoroethylene (PTFE) and perfluoroalkoxy (PFA) Teflon® is discouraged, as these materials similarly adsorb VOCs. Sample inlet lines should be cleaned or replaced on a prescribed frequency as particulate matter buildup on the wetted surfaces may also behave as a sink or source of VOCs.

The inlet probe should be configured such that entrainment of precipitation is minimized by inverting the inlet and installing an inverted glass or stainless-steel funnel. Protection from insects is also recommended such as by installing stainless steel mesh screen into or around the inlet.

Within the instrument, the UNITY-xr TD employs polyetheretherketone (PEEK) tubing for gas transfer and incorporates a PTFE Teflon® valve for selecting gas streams during sample collection and desorption.

The auto-GC permits near real-time analysis of ambient air. Ambient atmosphere is routed through the inlet dedicated to the auto-GC. In our case, the manifold inlet configuration consists of a stainless-steel inlet probe outside the shelter extending inside the shelter and connecting to a stainless-steel manifold plenum. A vacuum pump is connected to the manifold to pull ambient air into the manifold at a known rate exceeding two-fold the combined flow demand of all connected instruments.

4.3.2. Sampling Residence Time

The length and internal diameter of the stainless-steel tubing is selected to ensure a residence time ≤ 20 seconds from the inlet probe to the inlet of the CIA Advantage-xr. The Markes UNITY-xr TD samples at 20 mL/minute. To maintain a residence time of 20 seconds or less at this sampling rate, the lengths of 1/18 inch or 1/16-inch OD tubing (internal diameters of 1.4 and 1.02 mm, respectively) must be no more than 4.3 m or 8.1 m respectively, to an inlet probe or laminar flow manifold. Documentation demonstrating this residence time must be kept within site records.

Note that for instruments connected to a manifold inlet, if the blower motor power is interrupted during an electrical outage, the auto-GC will be sampling stale air from the manifold, and not fresh ambient air. In such cases, the associated data must be invalidated with a NULL code when reported to AQS.

4.3.3. Sampling Inlet Probe Siting

Sampling inlet probe siting must comply with the siting criteria listed in the governing PAMS QAPP. Briefly, the inlet probe must be 2 to 15 m above ground level (AGL) and minimally 1 m horizontally or vertically from any supporting structure. Further details on spacing from trees, obstructions, and roadways are listed in the PAMS QAPP.

4.3.4. Sample Timing and Schedule

Ambient air samples are to be collected continuously hourly for the duration of the PAMS season, except when the instrument is sampling and analyzing QC samples. Ideally, sample collection begins at the beginning of the hour. Sample collection must commence no earlier than 10 minutes before and no later than 30 minutes after the top of the hour. For example, during the 10:00 hour, sample collection must commence between 9:50 and 10:30 for the sample to be valid. This ensures that at least 30 of the 40 minutes, or 75%, of sample collection occurs during the hour. Samples collected outside this timing window or for less than 40 total minutes are invalid.

5.Auto-GC Procedure

A flow chart detailing the Auto-GC operation procedure is presented in Figure 5-1. It consists of four major steps: maintenance and conditioning (section 5.1), Retention time establishment (section 5.2), Calibration (5.4), and definition of Method Detection Limits (MDLs) (section 5.5).

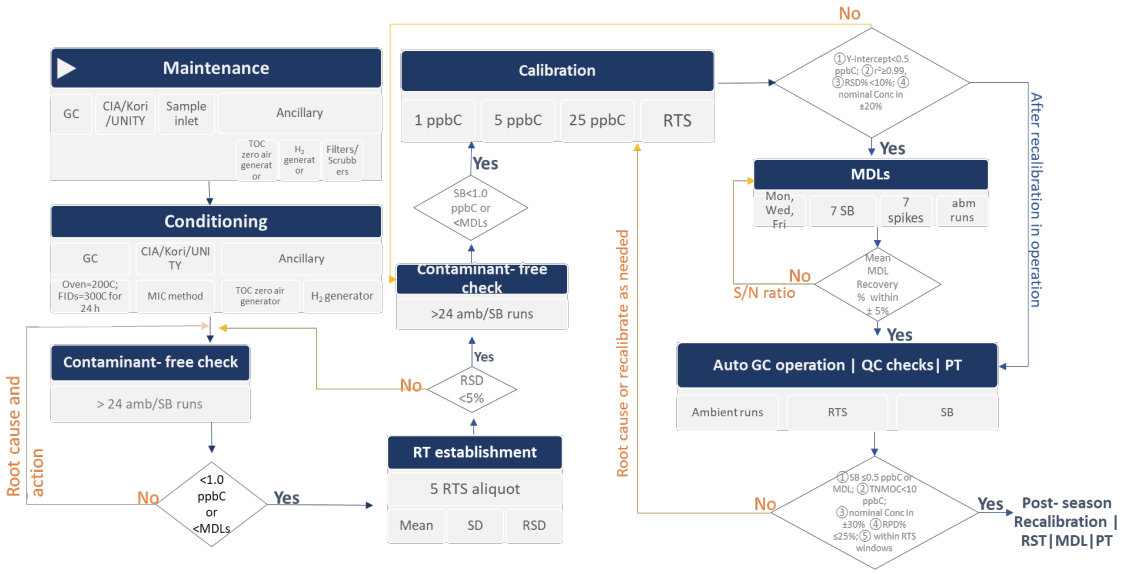


Figure 5-1: Auto-GC operation procedure

5.1. System Startup, Shutdown and Conditioning

In the PAMS required site, an Agilent qualified representative installed the instrument and performed setup when newly purchased. The initial startup steps are described in detail in the instruments' user manuals. Refer to the instrument manuals for further information, diagrams, and instructions for connections and operations.

Support Gases: It is important to ensure that ZAG and H_2 generators are powered on and running for an approximately 24-hour conditioning period and performing according to manufacturer specifications prior to connection to and the power up of the TD components and GC. Direct connection of equipment prior to completing a conditioning period risk introducing contaminants into the instrument that may be difficult and time-consuming to eliminate. Compressed gas cylinders are useful in tracing potential contamination in ZAG systems and H_2 generators as well as ensuring dry gases (HCF zero air and UHP helium) employed for purging Peltier cooler boxes are sufficiently dry.

Preconcentrator Trap Installation: When installing a new preconcentrator trap (whether initially or as a replacement) in the UNITY-xr TD, the system should be set to

perform the following trap conditioning method shown in Table (“Trap Heat” method in Markes Instrument Control [MIC] software) involving staged intervals of incremental heating, while flowing carrier gas to eliminate contaminants and moisture without damaging trap sorbents:

Table 5-1: Thermal Desorber Trap Conditioning Method

Stage	Temperature (°C)	Duration (minutes)
Trap desorb 1	100	10
Trap desorb 2	200	10
Trap desorb 3	320	30

The MIC settings configuration for the “Trap Heat” method for conditioning new traps is shown below in Figure.

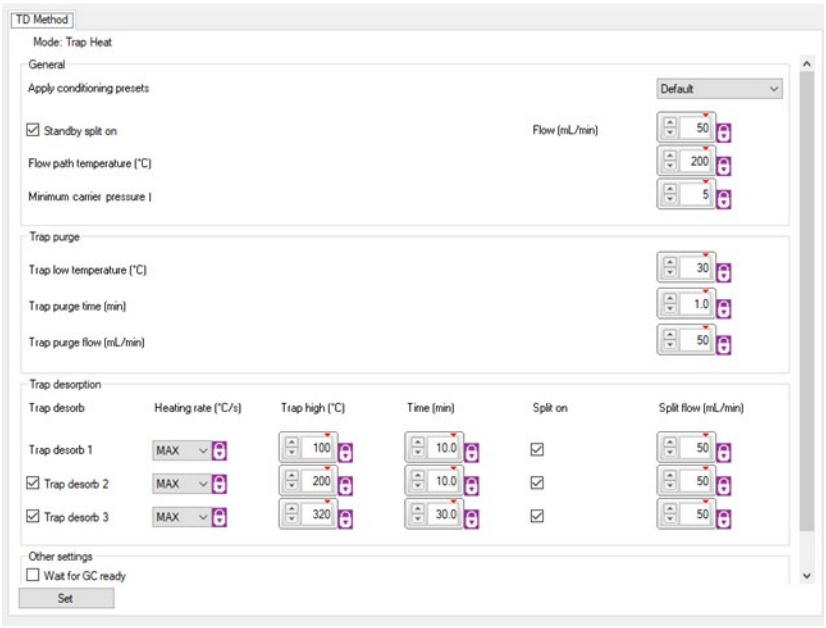


Figure 5-2: Screen capture of MIC “Trap Heat” method settings

In the operation of the auto-GC there are many cases where the system needs to startup and shutdown.

The general startup procedure is as follows:

1. Power on air compressor, making sure the tank is free of water and rust buildup.
2. Power on the TOC 1250 generator and warm up at least 45 minutes for the hydrocarbon scrubbers reach operating temperature.
3. Turn on the H_2 generator and allow the flow rate to reach the setting point.
4. Open a main valve of the helium tank and adjust the regulator output pressure to 80 psi.

5. Power on the GC 7890B, UNITY-xr, Kori-xr, CIA-Advantage-xr, and sample pump.
6. Open EZChorm and MIC.

The shutdown procedure is like the startup process in reverse. Its steps are:

1. Power off the 7890B GC after the last run completes.
2. Power off the UNITY-xr, Kori-xr, CIA-Advantage-xr, and sample pump.
3. Power off the TOC-1250 ZAG and the air compressor.
4. Close a shutoff valve controlling the H_2 generator, then select a standby mode.
5. For a long shutdown, press STOP-> Menu -> Shutdown. Wait for the system to completely shut down before powering off the equipment.
6. Close the main valve of the helium cylinder its regulator.
7. Exit EZChrom and MIC.
8. Ensure that all valves on standard gas canisters, helium, and humidified zero air are closed, and that the ambient air pump is switched off.

5.2. Retention Time Establishment

Once the instrument is set up and the trap conditioning program is completed, the analyst should perform subsequent test runs of SB (humidified HCF zero air) analyses to evaluate whether artifacts have been successfully purged from the new preconcentrator trap. Review acquired chromatograms for contaminants and artifacts, which should decrease with repeated SB analyses. Once the SB chromatograms appear to be stabilizing in contaminant levels, set the Deans switch timing according to Section 5.3 and analyze an RTS (recommended concentration range is to dilute the RTS to < 25 ppbC to ensure instrument is not contaminated with high concentration standard) and establish rough retention windows for the target analytes per the elution order shown in Table . Prepare overlay chromatograms of the RTS with recent SBs to determine whether any remaining residual contaminants in the SBs are target analytes. At this point, a period of several days of analyzing ambient air is helpful to further condition the instrument, establish repeatable RTs, and make fine adjustments to split and purge flows, and GC oven program to optimize peak separation.

After it is determined that the system is clean, a humidified RTS should be run a minimum of five times to establish a retention time window for the analytes. The mean, standard deviation, and percent relative standard deviation (RSD) of the RTs for each compound should be calculated for the five aliquots. If the percent RSD of the mean RT

exceeds 5% for any compound, the RT may not be stable for that compound and/or the peak identification may not be correct. If peak identifications are correct, the instrument operator should analyze additional RTS aliquots until the RTs stabilize (RT RSDs < 5%).

Once the RT window is established, a series of humidified zero air blanks should be analyzed to verify the instrument is clean and free of carryover.

Table 5-2: Elution order of target analytes in the 59-component RTS

Compound	# Carbon	Elution Order	FID Channel
ethane	2	1	PLOT
ethylene	2	2	PLOT
propane	3	3	PLOT
propylene	3	4	PLOT
isobutane	4	5	PLOT
n-butane	4	6	PLOT
acetylene	2	7	PLOT
trans-2-butene	4	8	PLOT
1-butene	4	9	PLOT
cis-2-butene	4	10	PLOT
cyclopentane	5	11	PLOT
isopentane	5	12	PLOT
n-pentane	5	13	PLOT
1,3-butadiene	4	14	PLOT
trans-2-pentene	5	15	PLOT
1-pentene	5	16	PLOT
cis-2-pentene	5	17	PLOT
2,2-dimethylbutane	6	18	PLOT
2,3-dimethylbutane	6	19	PLOT
2-methylpentane	6	20	PLOT
3-methylpentane	6	21	PLOT
isoprene	5	22	PLOT
1-hexene	6	23	PLOT
n-hexane	6	24	DB-1
methylcyclopentane	6	25	DB-1
2,4-dimethylpentane	7	26	DB-1
benzene	6	27	DB-1
cyclohexane	6	28	DB-1
2-methylhexane	7	29	DB-1
2,3-dimethylpentane	7	30	DB-1
3-methylhexane	7	31	DB-1
2,2,4-trimethylpentane	8	32	DB-1
n-heptane	7	33	DB-1
methylcyclohexane	7	34	DB-1
2,3,4-trimethylpentane	8	35	DB-1
toluene	7	36	DB-1
2-methylheptane	8	37	DB-1
3-methylheptane	8	38	DB-1
n-octane	8	39	DB-1
ethylbenzene	8	40	DB-1
m-/p-xylene	8	41	DB-1
styrene	8	42	DB-1
o-xylene	8	43	DB-1
n-nonane	9	44	DB-1
isopropylbenzene	9	45	DB-1
a-pinene	10	46	DB-1
n-propylbenzene	9	47	DB-1
m-ethyltoluene	9	48	DB-1
p-ethyltoluene	9	49	DB-1
1,3,5-trimethylbenzene	9	50	DB-1
o-ethyltoluene	9	51	DB-1
b-pinene	10	52	DB-1
1,2,4-trimethylbenzene	9	53	DB-1
n-decane	10	54	DB-1
1,2,3-trimethylbenzene	9	55	DB-1
m-diethylbenzene	10	56	DB-1
p-diethylbenzene	10	57	DB-1
n-undecane	11	58	DB-1
n-dodecane	12	59	DB-1

5.3. System Settings for Normal Operation

a) The CIA Advantage-xr is set to sample the desired inlet port.

b) The Kori-xr trap setting is -27°C during the sampling phase and <300°C for the post-sampling purging phase.

c) System settings for the Agilent 7890B GC are provided in Appendix A: Agilent GC Method Parameters.

d) System settings for the Markes UNITY-xr are shown in Appendix B: Markes Method Parameters.

e) Setting Deans Switch Timing: Once the instrument conditioning period is complete, the analyst will need to ensure the Deans switch timing is properly set. Initially, the Deans switch should be set to “on” for approximately 12 to 13 minutes which routes the BP-1 column eluent to the PLOT column for subsequent further separation of the light hydrocarbons. The time at which the Deans switch is to be turned “off” should be adjusted so that n-hexane shows up as the first peak on the rear detector from the DB-1 column (identify the target analytes according to the elution order listed in Table 5-2). Setting the deans switch timing in EZChrom is shown in Figure 5-3. Incorrect timing will result in incomplete separation of C2-C6 compounds on the BP-1 channel or the routing of higher molecular weight compounds to the PLOT column, which can contaminate the PLOT column and result in ghost peaks in subsequent chromatograms (high molecular weight compounds have a high affinity for the PLOT stationary phase). Analyze several replicates of the RTS and observe stable RTs to ensure the Deans switch timing is correct.

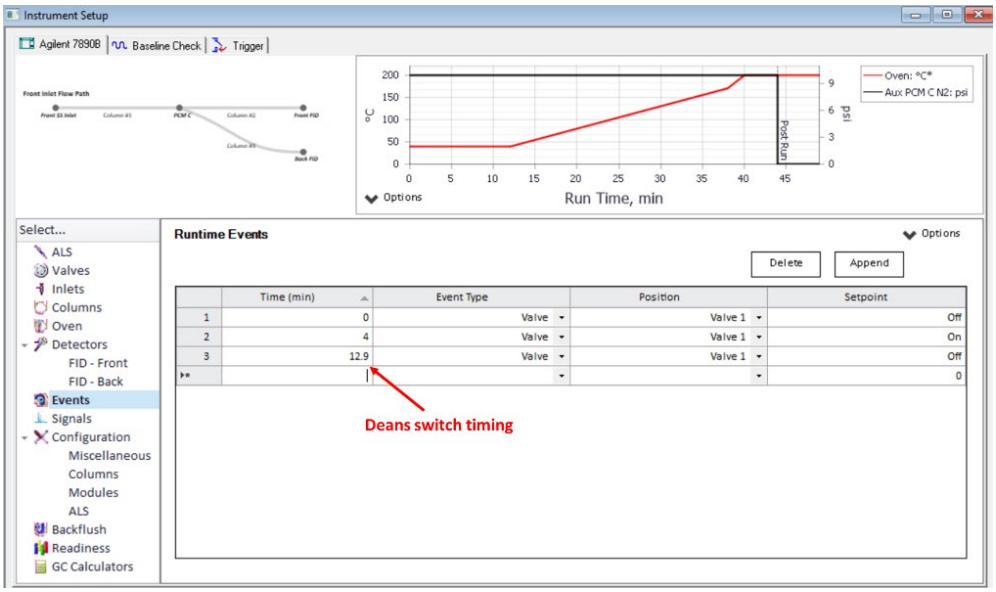


Figure 5-3: Deans switch timing setup in EZChrom.

5.4. Initial Calibration (ICAL) and Calibration Verification

5.4.1. ICAL Timing

The ICAL is established prior to performing sample analysis for data reporting, following instrument maintenance that would reasonably impact the instrument response (preconcentrator trap change, detector change, changes in sampling flows or outlet split flows, etc.), and when CCVs fail acceptance criteria and indicate recalibration is necessary (e.g., CCV failures that cannot accurately be explained by a bad injection or other justifiable rationale). At the end of the monitoring season the analyst is strongly encouraged to conduct an ICAL. This concluding ICAL demonstrates the calibration response remained appropriate over the monitoring season.

5.4.2. ICAL Standard Levels

The Markes UNITY-xr TD and Agilent 7890B GC system is calibrated by analyzing three separate concentration levels of a NIST-traceable certified standard gas. Instrument calibration is established using a carbon-based response where concentrations of light hydrocarbons (C_2-C_6) are determined according to the response of propane and concentrations of heavier hydrocarbons (C_6-C_{12}) are determined according to the response of benzene. Calibration curves will include a minimum of three concentration levels covering approximately 1 ppbC to 25 ppbC (e.g., 1, 5, and 25 ppbC). Calibration curves are established separately on each FID channel and are modeled by least-squares linear regression.

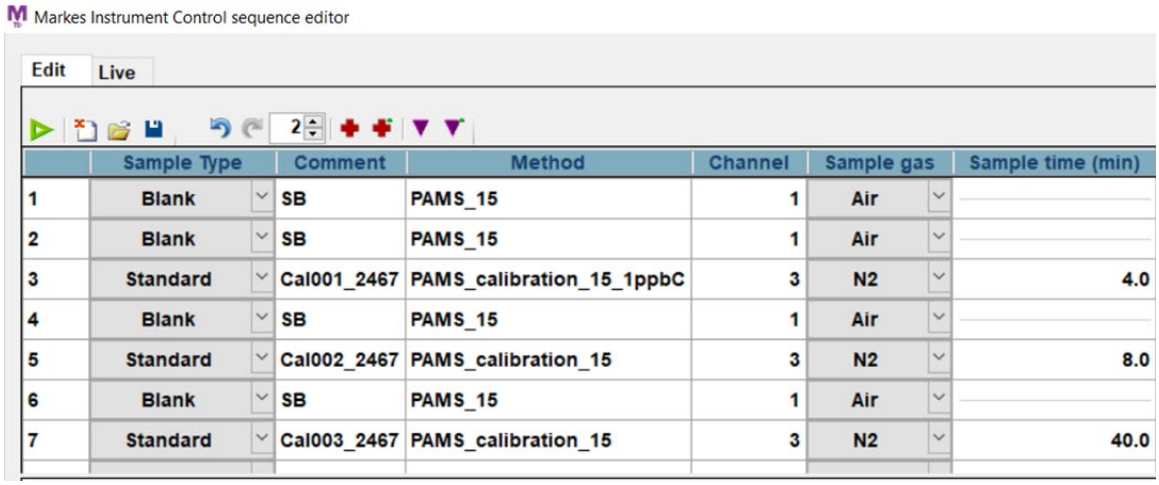
5.4.3. Establishing the ICAL

The iCAL can be established by one of two conventions: direct introduction of diluted standard gases prepared at the desired concentration or effective dilution of standard gases. We use a hybrid of both methods to establish the ICAL.

1. Direct introduction of standard gases for an upper calibration point. The Auto-GC is operated in its normal sampling program and the preconcentrator samples the stock standard gases with humidified UHP N_2under the typical sampling duration and flow settings (20 mL/minute for 40 minutes).
2. Effective dilution of standard gases for middle and low calibration points: For this convention, the Auto-GC preconcentrator is not operated at the typical flow and duration settings but rather these parameters are altered to mimic the relative amount of target analyte mass that would be trapped based on the typical sampling duration and flow settings. Users can adjust the sampling flow settings and duration of sampling in the MIC software for effective standard dilution. For example, if the stock standard gas is 25ppbC and the analyst intends to prepare an effective 5 ppbC standard, then at the setting flow of 20 mL/minute for 8 minutes of sampling

duration could reach the intended point. For the low point of 1 ppbC, the flow rate sets to 10 mL/min with the sample duration of 4 minutes considering Markes limitation of 2- minute sample duration.

To reduce peak shift without impairment of peak height and instrument sensitivity, the UNITY desorb split flow set to 15 mL/min. The Markes and EZChrom sequences for the ICAL are shown in Figure 6 and Figure 7.



	Sample Type	Comment	Method	Channel	Sample gas	Sample time (min)
1	Blank	SB	PAMS_15	1	Air	
2	Blank	SB	PAMS_15	1	Air	
3	Standard	Cal001_2467	PAMS_calibration_15_1ppbC	3	N2	4.0
4	Blank	SB	PAMS_15	1	Air	
5	Standard	Cal002_2467	PAMS_calibration_15	3	N2	8.0
6	Blank	SB	PAMS_15	1	Air	
7	Standard	Cal003_2467	PAMS_calibration_15	3	N2	40.0

Figure 5-4: Markes TD calibration sequence.

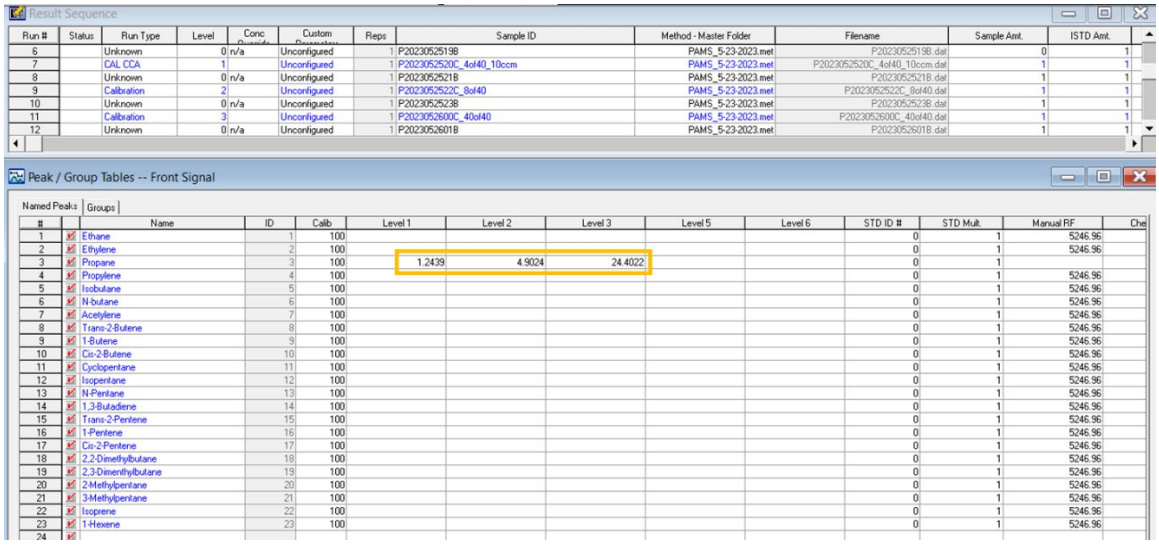


Figure 5-5: EZChrom calibration sequence and method.

5.4.4. ICAL Acceptance Criteria

The linear least-squares regression calibration curve generated within the OpenLab software for each FID channel is evaluated separately and must demonstrate linearity with a correlation coefficient (r^2) ≥ 0.995 and have an x-intercept (equivalent to the absolute value of the y-intercept/slope) ≤ 0.5 ppbC. Calibration curve regressions must not be forced through the origin, as this eliminates the intercept term and does not

permit evaluation of the curve behavior at zero concentration. The determined concentration (the resulting concentration when inputting the area response into the generated calibration curve) at each ICAL level must be within ±20% difference from the theoretical nominal concentration and the RSD of determined RFs must be ≤10%. If these three criteria (correlation coefficient, intercept, and back calculated concentration) are met, the average RFs are employed for quantitation of target analytes.

Immediately following establishment of the ICAL, a SSCV standard must be analyzed within the calibration curve range to verify the calibration. Quantitation of the SSCV against the established calibration curve or average RF must show the calibration compounds are within ±30% of the expected theoretical nominal concentration.

5.4.5. Using the average RF to calculate amounts for the rest of the compounds.

The instrument calibration is based on a carbon response, where concentrations of light hydrocarbons (C_2-C_6) are determined using the response of propane, and concentrations of heavier hydrocarbons (C_6-C_{12}) are determined using the response of benzene. To apply the propane/benzene calibration to the rest of the compounds within EZChrome, follow the steps below:

First, generate a full peak table like normal or save a method with a full calibration table as a new name. Usually, the date when the calibration is performed is used as the new method name. Right click on the “Peaks” table and be sure the “Manual RF” box is checked (see Figure 5 6). Usually, the date when the calibration is performed is used as the new name of method. Right click on the “Peaks” table and be sure the “Manual RF” box is checked (see Figure 5-6).

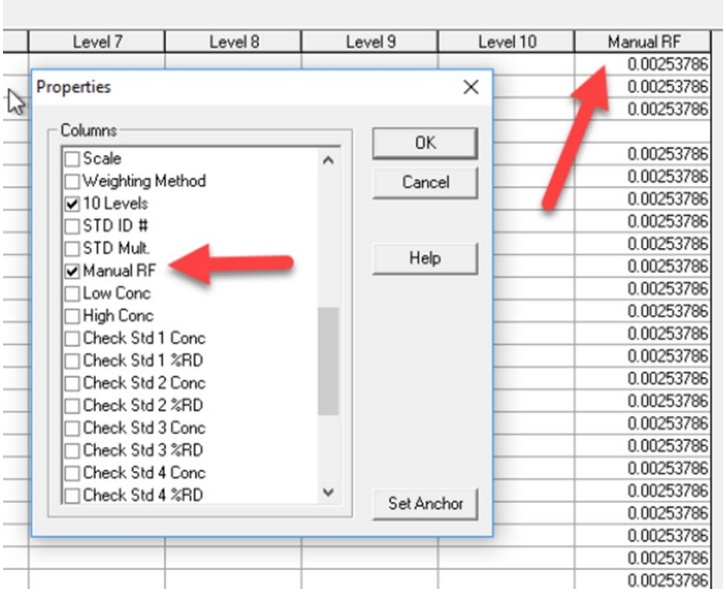


Figure 5-6: EZChrom calibration establishment using RF part 1

One Peak (Propane for the front column, Benzene for the rear column) in the "Review Calibration" table must have a standard calibration curve. Use this peak to get the Average RF (see Figure 5-7).

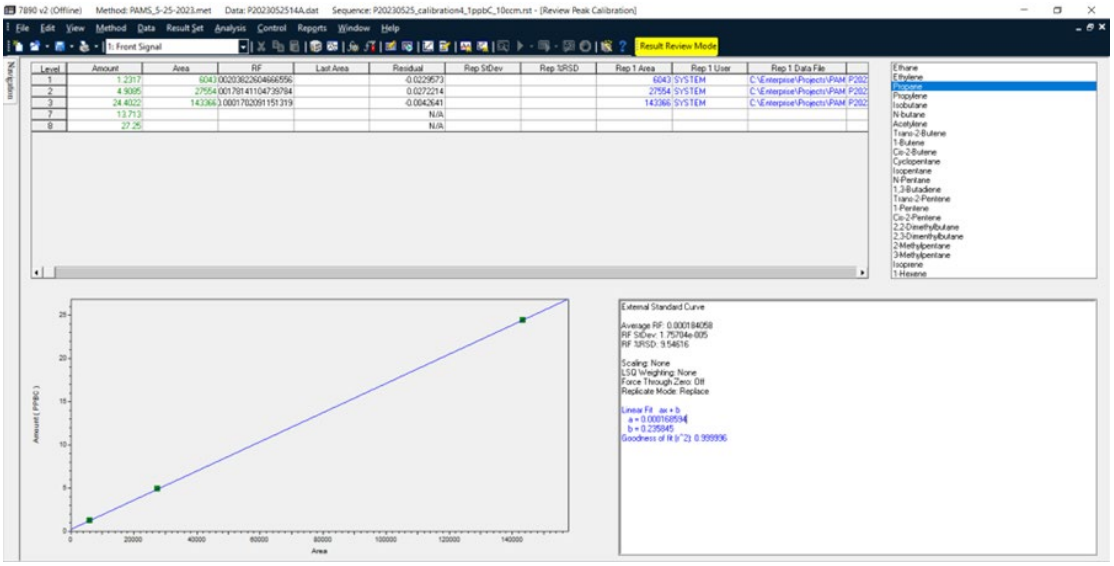


Figure 5-7: EZChrom calibration establishment using RF part 2.

Prior to filling down the "Average RF", be sure that the response factor definition is amount/response or Response/Amount. Enter the "Average RF" into the Manual RF for the first peak and then fill down for the rest. The peak that has a calibration curve must have no value in the Manual RF column. The software will ignore the calibration level info for the peaks that have a "Manual RF" value (see Figure 5-8).

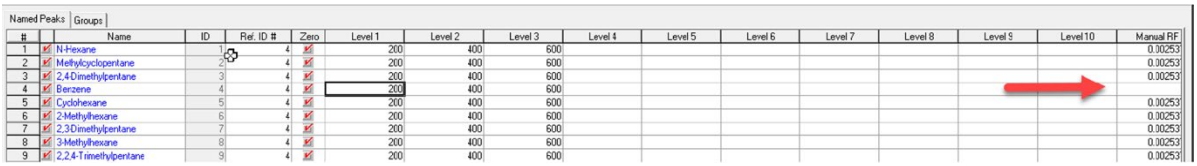


Figure 5-8: EZChrom calibration establishment using RF part 3.

5.5. Method Detection Limits (MDL)

MDL is essential in data verification and validation. The principle of MDL is well described in section 3.3.5.1 of PAMS TAD Revision 3. The MDL procedure is elaborated in 40 CFR Part 136 Appendix B, the Method Update Rule (MUR). As the PAMS required site, we perform the MDL procedure by analyzing at least seven spike samples and seven matrix blanks over three or more different non-consecutive days after the Auto-GC and support equipment have been replaced, conditioned and stabilized. The calculation of MDLs is presented in Figure 5-9 below.

It is notable that the method for spike MDL is different from that of the matrix blanks. For the MDLsp, its value should meet the requirement of MDLsp < Nominal Conc. < 10 * MDLsp. If the left term is not met, the spiking concentration should be adjusted higher by approximately 2- or 3-fold. If the right term isn't met, the spiking concentration should be adjusted lower by approximately 2- or 3-fold. The MDLsp should be repeated until the requirements are met. The MDLsp method we use is to deliver RTS for 2.3 minutes at the 10 mL/min of the sample flow rate.

For matrix blanks, it is simple when the analyte concentration in blanks is zero; MDL is determined by MDLsp. If not, MDLb for these analytes less than 0.5 ppbC is calculated as the sum of the mean concentration and their standard deviation multiplied by *t*. The MDL is the maximum value between MDLsp and MDLb. For these analytes greater than 0.5 ppbC, causes must be investigated and actions taken to ensure the instrument is contaminant-free, then the MDL procedure starts over.

Note that MDL is not a mean concentration, but rather reflects the precision and accuracy of measurement with the instruments.

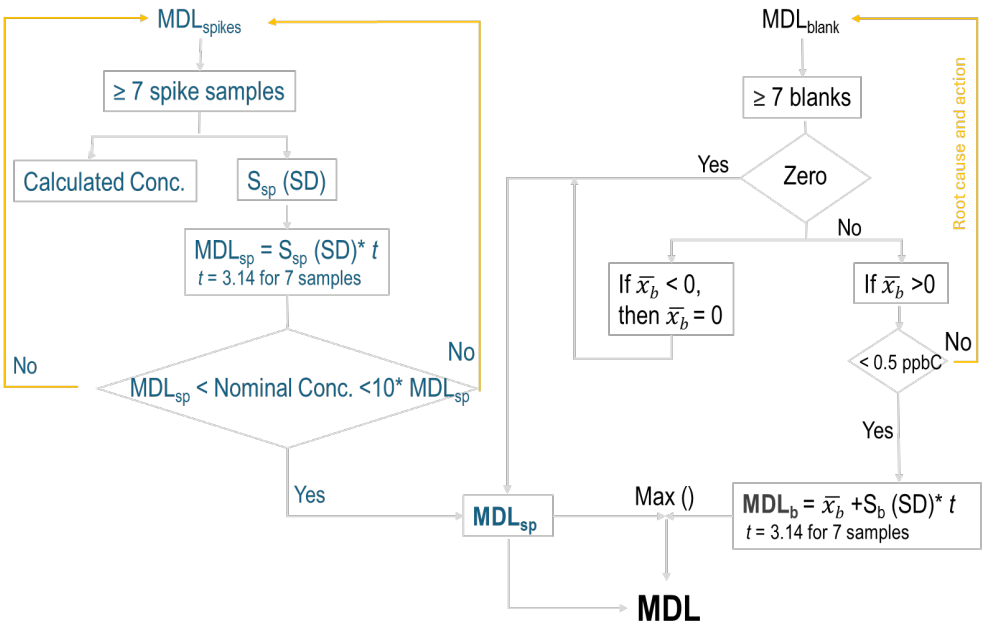


Figure 5-9: Flow chart of MDL calculation

Where MDLsp (in blue) is the MDL of the spike samples; MDLb (in gray) is the MDL of the method matrix blanks; ssp is the standard deviation of the calculated concentrations for the spiked samples; sb is the standard deviation of the method blank concentrations; (xb̄) is the average concentration of the method blanks; and t is the one-sided 99th percentile student's value.

5.6. Methods and Sequences

Please refer to the Markes UNITY-xr and Agilent OpenLab user manuals for generating methods and sequences. The Markes, including UNITY-xr, Kori-xr, and CIA Advantage-xr, is controlled within the MIC software interface, and the GC within the Agilent OpenLab software package (EZChrom). Because different methods are defined to enable sampling from different sources (ports on the CIA Advantage-xr) for the purpose of introduction of QC samples, it is important that both the MIC and EZChrom sample introduction and data processing method parameters remain identical for all sampling methods whether the method is for ambient air or QC sample analysis.

5.6.1. Creating Analysis Sequences

Sequences created within the Markes MIC software to control the introduction of different sample types are not linked to the EZChrom Sequence Wizard, therefore a separate sampling sequence must be created for both the preconcentrator (in MIC) and the GC (EZChrom). Each hourly sample within the MIC is a discrete line in the sequence table and defines the CIA Advantage-xr sampling port to be sampled. If analysis

sequences are generated in the MIC software for sampling, the analyst must define a convention for identifying QC samples in the sequence generated in the EZChrom software either by utilization of date-time stamp (DTS) in a repeating single line EZChrom sequence or by generation of a matching sequence in EZChrom with sequence lines containing descriptive information about sample type corresponding to the MIC sequence table. Within the EZChrom sequence, the analyst prescribes the folder location for where the datafiles will be saved.

Note that the UNITY-xr TD and the EZChrom CDS do not communicate with one another apart from providing basic start and stop commands. If sample introduction is determined through the MIC (and not within EZChrom) the EZChrom filenames will be agnostic as to whether the analyzed sample was a QC sample or ambient air sample. When EZChrom data filenames do not readily permit distinguishing QC samples from ambient air samples, analysts must define which data files correspond to which samples – which can be accomplished through a separate table listing the MIC sampling table sequence and the associated EZChrom data filename.

5.6.2. Defining Sample Collection Methods Within Markes MIC Software

The Markes system runs continuously using the instrument operation parameters defined in the generated sequence. These parameters include the sample collection parameters defining the sample port on the CIA Advantage-xr, sampling flow rate, collection duration, Kori-xr trapping and UNITY-xr trapping and desorbing temperatures, purge gas flows, and carrier gas flows for the Markes sample introduction and TD components. These parameters may require the analyst to update for their application to maximize response of the high volatility VOCs (e.g., C_2 compounds) and minimize carryover of the low volatility VOCs (e.g., C_9 and C_{10} compounds). These settings should be revisited and revised if changed.

In general, the instrument conditions for the TD method designations entered in the MIC sequence table will be identical in most respects apart from the CIA Advantage-xr sample port assigned to the various gas streams (whether ambient air, standard gas, SB, RTS, etc.).

More information on setting up Markes sequences in MIC and GC sequences in EZChrom for PAMS ambient sampling are provided in Appendix C: Agilent Sequence Setup and Appendix D: Markes Sequence Setup.

The 6-week rotation schedule (Figure 5-10) recommended in PAMS TAD revision 3 is adapted to maximize ambient air sample collection at night. Here the starting times of the QC samples are staggered to be analyzed nightly starting between 20:00 and 02:00

hours (and are highlighted in blue). Ambient samples are noted as “amb” in the figure. This schedule can be repeated.

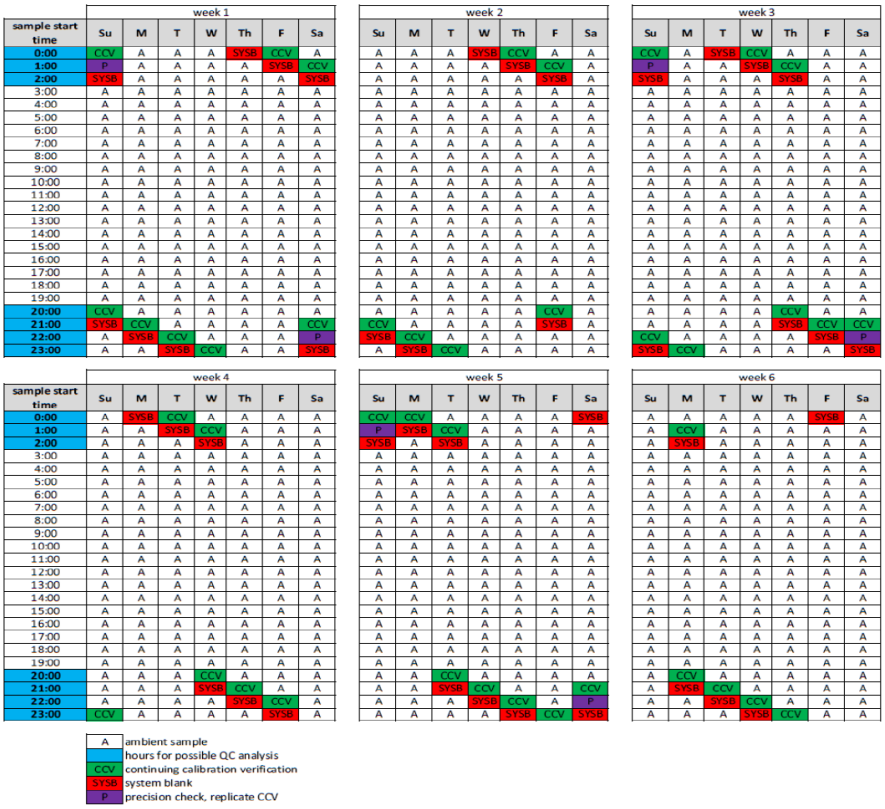


Figure 5-10: Sampling schedule for a 6-week period including QC samples

EZChrom requires creation of an overall chromatographic method which outlines both the GC instrument parameters and the chromatographic processing parameters to define how a sample, blank, or standard is collected, analyzed, and quantitated. The GC analysis instrument method parameters and data processing method parameters will be identical across methods employed for ambient air samples and QC samples.

Instrument parameters define the sample collection parameters and the GC program parameters including carrier gas flows, timing for Deans switch actuation, and oven program, among others.

Processing parameters define the settings for EZChrom to identify and quantitate the target compounds within the chromatograms. These settings prescribe the integration parameters, RT windows, target compound list, and maintain the RFs based on the established calibration, among other aspects of data processing.

The EZChrom instrument method employed for this analysis is detailed in Appendix A. For more details. Please refer to the Markes UNITY-xr, Kori-xr, CIA Advantage-xr and Agilent OpenLab user manuals for technical details.

5.7. Analysis of Ambient Air

Ambient air samples are to be collected continuously for the duration of the PAMS season as defined in the governing QAPP, except when the instrument is sampling and analyzing QC samples. Sample collection begins at the start of each hour. However, it may commence as early as 10 minutes before or as late as 30 minutes after the hour. For example, for 10:00 sample collection, the sampling must commence between 9:50 and 10:30 for the sample to be valid for that hour. This ensures that at least 30 of the 40 minutes, or 75%, of sample collection occurs during the hour. Samples collected outside this timing window or for less than 40 total minutes are invalid.

Once the sequence tables have been created and saved for both the TD (within MIC) and the GC (within EZChrom), the TD sequence can be programmed to start at a desired date and time. The GC sequence can be initiated, which will place the GC sequence on hold until the TD triggers to start the associated GC run.

5.8. Data File Structure and Naming

An Auto-GC sampling hourly for 59 compounds will generate 1400 individual concentration data points in 24 raw data results files. The CDS will also generate files containing chromatograms for each sample hour for each FID, totaling approximately 100 data files each day. Due to this volume, it is important to include the date, sample hour, sample type, and whether the data file is original or has been reprocessed in the file name.

Once the sequences begin to run, data files are written to the specified folders under *C:\Enterprise\Projects\PAMS\Result*. Chromatographic data files (.dat) are named and stored with a date and time of sample collection according to the convention described in Table 5-3.

Filename Format = P12345678&.dat

Table 5-3: Auto-GC file naming convention

Position	Detail	Character or Character Combination
P	PAMS season	
1-2	4-digit year (YYYY)	4-digit numeric
3-4	2-digit month (MM) 00 through 12	00 through 12
5-6	2-digit day (DD) 00 through 31	00 through 31
7-8	2-digit hour from 24-hour clock	00 through 23
&	Sample type	A = ambient sample B = blank sample C = continuing calibration verification (CCV) I = initial calibration standard P = precision check standard S = second source calibration verification (SSCV) X = exploratory or experimental (troubleshooting, conditioning, etc.)

For an ambient sample collected for the 6:00 p.m. hour on July 31, 2024, on the light hydrocarbon channel that had not been processed, the file name would be: *P2024073106A.dat.*

Upon processing, transfer the raw data files to the GC data logger. Raw data files may be temporarily moved to *D:\GC Data\Data processing* for analysis to avoid disrupting instrument operation.

5.9. Collection of Data

The Auto-GC instrument will run unattended to execute the prescribed sequences. To safeguard data, the operator/analyst performs the daily checks on instrument status, the latest QC reports, and recent ambient sample chromatograms. Confirm that instrument method parameters in range, blank and CCV results are acceptable, and no unusual spikes are present in ambient chromatograms. During each site visit, check flow rates and pressures of the inlet, support equipment, cylinders and canisters. Once the 1 or 2-week sampling sequences are complete, it is best to transfer the raw data files to the GC data logger or the D: drive as early as possible to identify errors quickly.

5.10. Exporting Concentration Data from EZChrom

To export concentration data files from EZChrom follow the steps in Figure 5-11 below.

The Advanced section of the method allows you to setup an export for each detector channel. Each channel will be a separate export. Once this is setup, the software keeps

appending data file results to the same file. If the file is moved to a new location, the software will make a new one for the next set of data files processed. If the same data file is processed twice, it will append the results twice.

Once exported there will be two files, one for the front column and one for the rear column. The files are named after the method name used, not sequence, so should be manually changed to the following *PAMS_yyyymmdd_ yyyymmdd_v1-Front Signal*, where the yyyymmdd's are the start and end dates of the sequence, v1 would be the version number, and Front or Back signal would be indicated.

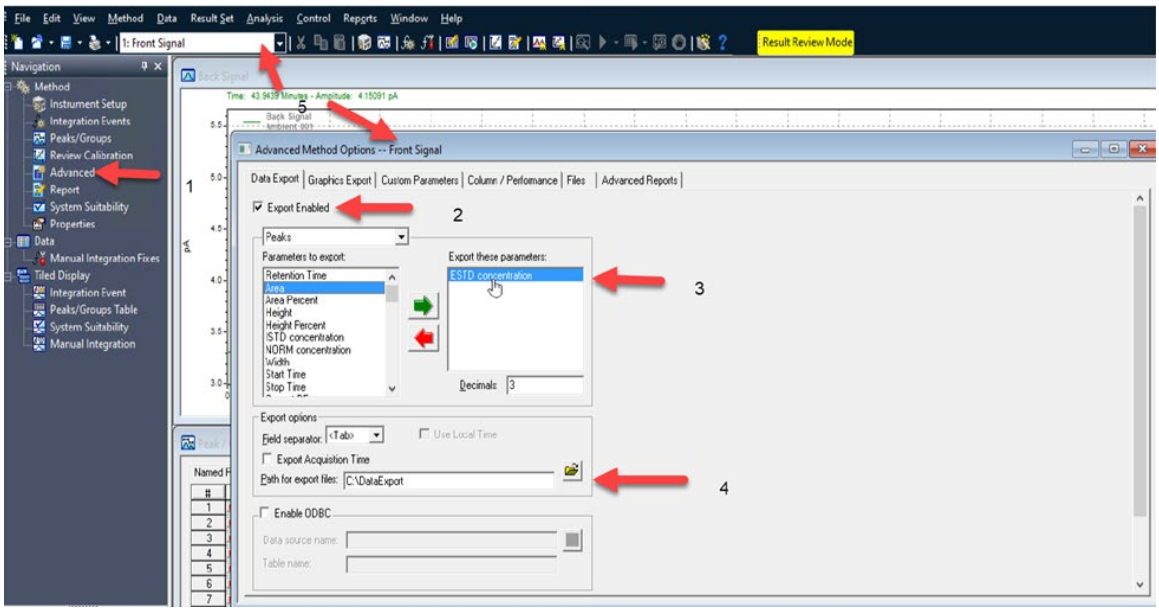


Figure 5-11: Exporting ESTD concentration file from EZChrom GC sequence.

5.11. Processing and Evaluating Collected Data

Refer to the Agilent OpenLab EZChrom user manual for specific instructions for viewing and manipulating collected data. The CDS will identify target analyte peaks, integrate the associated area per the defined data processing method, and quantitate the concentration of each target analyte within each sample on both FID channels per the established calibration regressions. The analyst will review the processed data per the data verification processes in Section 1 to ensure the data files were properly acquired, the target analytes were properly identified, chromatographic peaks were properly integrated, and QC samples met the acceptance criteria. The analyst will document adjustments needed to the processed data.

Viewing Chromatograms: Acquired chromatograms for collected samples may be viewed within the OpenLab EZChrom CDS or OpenLab CDS software. This software enables users to create overlays of chromatograms in several different viewing

configurations. Ambient air sample chromatograms can be overlaid with standard (e.g., CCV, RTS, and/or SSCV) or SB chromatograms to investigate RT shifts, baseline behavior, or carryover of target compounds or interferences. An overlay of example chromatograms for ambient air (blue), SB (light blue), and RTS (green) is shown in Figure 5-12.

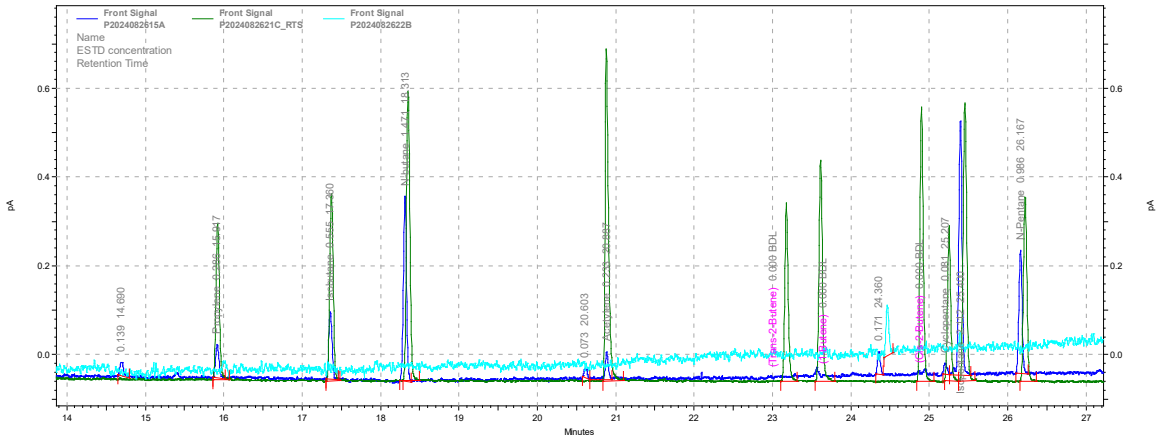


Figure 5-12: Example overlay of chromatograms for ambient air, retention time standard, and a system blank.

Processing Collected Data: prior to processing data, be sure that these raw data are back up. Analysts perform post-processing of collected chromatographic data within the EZChrom software. To adjust RT windows, the operator can adjust these within the processing method by clicking and dragging the RT window (refer to Figure 5-13 for an example of an RT window for 2,3-Dimethylpentane) or within the parameters table. Similarly, the integration parameters can also be adjusted within the method to optimize the automated CDS integration. Once the RT window and/or integration parameters is/are satisfactorily updated, the data processing method is then saved and data files for affected samples are reprocessed to properly identify and/or integrate target compounds. The analyst will then review the reprocessed chromatograms to ensure proper identification and integration for the target analytes. If specific target analyte peaks do not lend themselves to adjusting the RT window and/or integration parameters, the analyst can manually adjust these. A guide to proper integration techniques is included in the CDS. Refer to the CDS user manual for more information on adjusting in the CDS. Specific data reviewing procedures are described in the data verification section (Section 1).

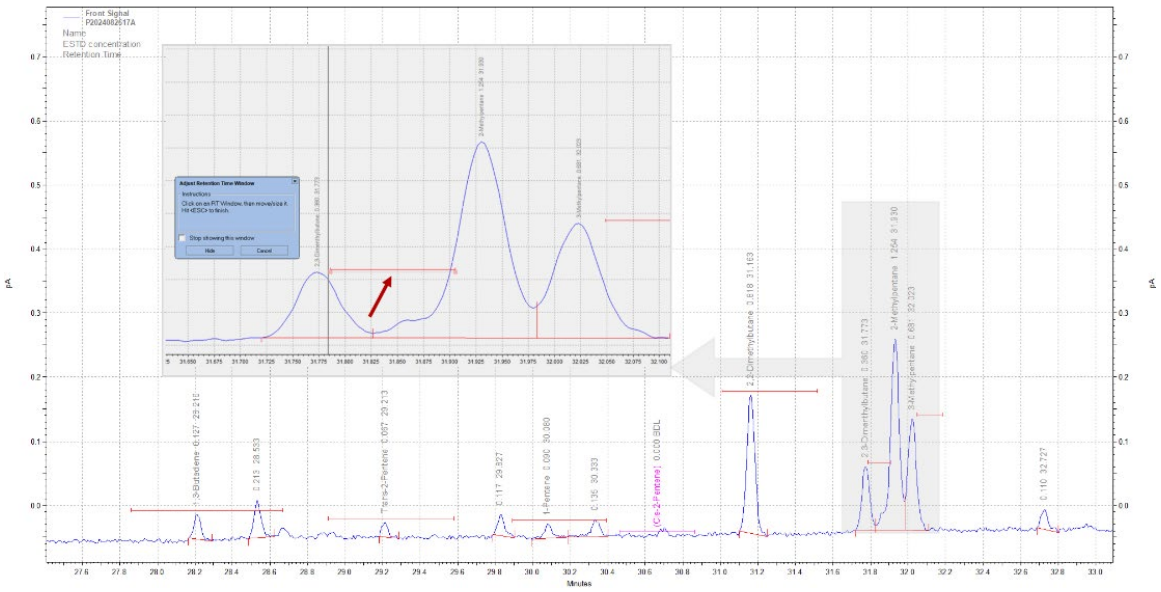


Figure 5-13: Example retention time (RT) window for 2,3-Dimethylpentane

6.Calculations

Measured concentrations must be reported in units of ppbC. This unit is specified in settings for system calibration, which ensures the instrument provides results in ppbC. Consult the PAMS TAD and the AQS reporting guide for specific reporting parameters and conventions.

Conversion of ppbV to ppbC:

$$C_{ppbC} = C_{ppbV} \cdot N_C$$

Where: C_{ppbC} = concentration (ppbC)
C_{ppbV} = concentration (ppbV)
N_C = number of carbon atoms in the molecule

Standard dilution concentration via dynamic dilution:

$$C_d = \frac{(F_s \cdot C_s)}{(F_s + F_d)}$$

Where: C_d = diluted concentration (ppbC)
C_s = stock standard concentration (ppbC)
F_s = flow of stock standard gas (standard mL/minute)
F_d = flow of diluent gas (standard mL/minute)

Standard dilution concentration via static dilution:

$$C_d = \frac{(P_s \cdot C_s)}{P_f}$$

Where: C_d = diluted concentration (ppbC)
C_s = stock standard concentration (ppbC)
P_s = partial pressure of stock standard gas (mm Hg)
P_f = final pressure of vessel (mm Hg)

Standard dilution concentration by effective dilution:

$$C_d = C_s \cdot \frac{T_d}{T_s} \cdot \frac{F_d}{F_s}$$

Where: C_d = effective diluted concentration (ppbC)
C_s = stock standard concentration (ppbC)
T_d = sampled time of effective dilution (minutes)
T_s = standard sample time (minutes)
F_d = sampled flow of effective dilution (mL/minute)
F_s = standard sample flow (mL/minute)

Quantitation of Sample Using Calibration Response Factors:

$$C = \frac{A_c}{R_{fc}}$$

Where: C = concentration of compound measured in ppbC

A_c = integrated peak area of the compound being measured in the sample

Rf_c = response factor of the target compound based on the calibration (area/ppbC)

Quantitation of Sample Using Linear Regression:

$$C = \frac{(A_c - b)}{m}$$

Where: C = concentration of compound measured in ppbC

A_c = integrated peak area of the compound being measured in the sample

m = slope of the linear regression (area/ppbC)

b = y-intercept of linear regression (area)

Relative Standard Deviation (RSD):

$$RSD = \frac{Standard\ Deviation}{Mean} * 100$$

Absolute Relative Percent Difference (RPD):

$$RPD = \frac{|result\ A - result\ B|}{mean\ of\ results\ A\ \&\ B} * 100$$

Absolute Percent Difference (APD):

$$APD = \frac{|result\ measured\ -\ result\ expected|}{result\ expected} * 100$$

Percent Recovery:

$$\%\ recovery = \frac{concentration\ measured}{concentration\ expected} * 100$$

Total collected sample volume:

$$V_s = F_s * Ds * 106$$

Where: V_s = collected sample volume (m^3)

F_s = sample flow rate (standard mL/minute)

D_s = duration of sampling (minutes)

7. Quality Control

To ensure proper operation of the Auto-GC, QC checks and maintenance must be conducted at regular intervals. QC requirements and acceptance criteria are summarized in Table 7-1 and described in section 4.6 of the PAMS TAD Revision 3.

7.1. Initial Calibration (ICAL)

After instrument conditioning and the Deans switch timing are established, the instrument can be calibrated by establishing the carbon-based response of both FID channels with a certified standard (typically this is accomplished with propane for the light HC (HP-PLOT column) channel and benzene for the heavy HC (DB-1 column) channel. Instructions for completing the ICAL are detailed in Section 5.4.

7.2. Method Detection Limits (MDLs)

When initially placed into service and prior to reporting data from the Auto-GC system, the MDL must be determined for each PAMS priority compound and should be determined for optional compounds. The MDL is determined following the procedure described in the PAMS TAD, which is an adaptation of the method update rule (MUR) to the 40 CFR Part 136 Appendix B procedure3 whereby the analyst performs a series of measurements of a low concentration standard and measurements of blanks over minimally three different dates. The MDL is an estimate of the concentration at which a given analyte can be detected above background 99% of the time. The MDL must be determined when the instrument is placed into service initially and following maintenance or changes to the instrument or method that can reasonably be expected to significantly change the sensitivity of the instrument or method, such as: replacement of the FID, replacement of the preconcentrator trap(s), or change of carrier gas (i.e., from He to H_2). Determined MDLs are to meet the measurement quality objective (MQO) criteria (MDL ≤ 0.5 ppbC) specified in the governing PAMS QAPP. To ensure MDLs are representative of the typical measurement conditions, MDLs should be determined once the instrument has been conditioned, calibrated, and readied for ambient air analysis (i.e., the MDLs should not be determined when the instrument conditions are changing, and contaminants are being purged from the measurement system). Refer to section 5.5 for further instruction on determining MDLs.

7.3. Routine QC Checks and Acceptable Criteria

Once the ICAL is established, QC samples are to be analyzed routinely to demonstrate continued suitability of the instrument calibration, acceptable levels of target analyte

contamination, acceptable reproducibility of measurements, and proper identification of analytes. We refer to Figure 5-10 for a 6-week period. Additional information on the required QC checks is detailed in Table 7-1. The frequency for QC sample measurements will be either approximately daily or weekly, depending on the check.

Daily QC Checks: The most frequent QC checks consist of a system blank (SB) and continuing calibration verification (CCV), which are to be analyzed approximately daily (every 24 ± 4 hours of operation). These QC checks should be scheduled in the analytical sequence to occur successively (CCV followed by SB) to begin nightly between the hours of 20:00 and 02:00.

- **System blank (SB):** This blank sample consists of humidified zero air and is analyzed to demonstrate contamination levels of target analytes are sufficiently low. All target analytes must analyze less than the determined MDL or 0.5 ppbC, whichever is lower.
- **Continuing calibration verification (CCV):** The CCV is analyzed to demonstrate the instrument calibration remains within specification. Calibration compound (e.g., propane and benzene) response must be within ±30% difference from the expected theoretical nominal concentration to ensure proper carbon-based instrument calibration response. Additional target compounds in the CCV analysis must also be within ±30% of the theoretical nominal concentration. TNMOC should be less than 10 ppbC.
- **Latest ambient air samples:** If the TNMOC exceeds the total PAMSHC by more than 20%, identify the unknown hydrocarbon species. Such an investigation may identify hydrocarbons that are of importance to ozone formation at the site and monitoring agencies may consider measuring these compounds at the site on an ongoing basis.

Weekly QC Checks: In addition to the daily QC checks, a precision check, second source calibration verification (SSCV), and RTS check are required minimally weekly. Note that if the RTS contains the appropriate target compounds at certified concentrations, this can be analyzed as the SSCV or the CCV.

- **Retention time standard (RTS):** The RTS is analyzed at least weekly to verify the RT windows assigned to each target analyte are appropriate. If there are shifts in RTs that result in the CDS misidentifying or missing peaks, the RT window(s) must be adjusted and saved as a new method.
- **Second Source Calibration Verification (SSCV):** The SSCV is analyzed immediately following the ICAL and weekly thereafter to independently verify the quality of the calibration. Calibration compound (e.g., propane and benzene) response must be within ±30% difference from the expected theoretical nominal

concentration to ensure proper carbon-based instrument calibration response. Additional target compounds in the CCV analysis must also be within ±30% of the theoretical nominal concentration.

- **Precision check:** A replicate (back-to-back analysis) of the CCV is analyzed weekly to assess the precision of replicate measurements. Replicate measurements must show precision of ≤ 25% relative percent difference (RPD).

Table 7-1: Quality control checks

QC Parameter	Description	Section	Required Frequency	Acceptance Criteria	Suggested Corrective Action
Initial calibration (ICAL)	Multi-point calibration with at least one representative hydrocarbon for each GC column-FID combination (e.g., propane and benzene). Minimum of three concentrations between 10 to 25 ppbC. May use other high level concentrations (e.g., 50 or 80 ppbC).	5.4.2, 5.4.3, 5.4.4	• Start of PAMS season • After instrument maintenance • Following multiple failed calibration checks • End of PAMS season • May analyze primary calibration standard weekly (optional)	• $r^2 \geq 0.99$ • Intercept ≤ 0.5 ppbC or ≤ MDL, whichever is lower • RSD of determined RFs ≤ 10%. • Each concentration evaluated must be within ±20% If the above are met, average RF can be used (although linear regression is preferred). Data exceeding calibration range is flagged "EH".	• Recalibrate if calibration criteria are not met • Investigate: • Contamination or interferences • Leaks and trap degradation • Carryover from high-concentration samples or standards • Check if the traps were not properly conditioned Do not report PAMS data unless calibration meets all criteria.
System blank (SB)	Analysis of humidified zero air to confirm the system is sufficiently clean for continued analysis.	5.4.5	• Prior to ICAL • Every 24 ± 4 hours of operation • Preceding/following CCV (following preferred)	• All target VOCs ≤ MDL or 0.5 ppbC, whichever is lower. • TNMOC < 10 ppbC.	• Analyze another blank • Investigate system for contamination • Qualify samples as “LB” in AQS (unless technical explanation is provided)

QC Parameter	Description	Section	Required Frequency	Acceptance Criteria	Suggested Corrective Action
Continuing Calibration Verification (CCV)	Analysis of a known standard representing the molecular weight range and prepared within the calibration curve to check that the instrument calibration remains within tolerance. Concentration should be 2 to 5 ppbC for target analytes.	5.4.5	Every 24 ± 4 hours of operation	All target VOCs must recover within ±30% of the expected theoretical nominal concentration.	• Check chromatogram for retention time shifts causing misidentification • Investigate instrument contamination • Check for system leaks or trap malfunction • Qualify samples as "QX" in AQS for affected compounds since last passing CCV • Invalidate as "AS" if recovery is exceptionally high or low (at analyst's discretion)
Second Source Quality Control Standard (SSQC)	Analysis of a known standard gas from a different supplier than that used for the ICAL. This check independently verifies the quality of the ICAL for compounds across the molecular weight range.	5.4.5	• Immediately following ICAL • Weekly • May serve as the CCV	±30% for all target VOCs	• Do not commence analysis if propane or benzene fail SSCV immediately after ICAL. • Investigate discrepancy between ICAL and SSCV • Review chromatogram for RT shifts causing peak misidentification • Investigate for contamination or leaks • Qualify samples as "QX" and potentially invalidate ("AS") for affected compounds back to last acceptable SSCV

QC Parameter	Description	Section	Required Frequency	Acceptance Criteria	Suggested Corrective Action
Retention Time Standard (RTS)	Analysis of a ~59-component blend of VOCs in the ~2- 60 ppbC range to verify established retention time RT windows	5.4.5	Weekly	All target VOCs within established RT windows	• Evaluate previous week's ambient and QC check samples for RT shifts • Reassign or adjust RT windows • Reprocess data collected since most recent RTF • May invalidate ambient samples with "BH" (null) code
Precision check	Replicate CCV to determine the reproducibility of the analysis. Replicates are analyzed sequentially	5.4.5	Weekly	Absolute relative percent difference ≤ 25% for each target VOC	• Investigate for contamination, leaks, or suppression as indicated by trends in compound behavior • Qualify samples since the last passing precision check with "QX"
Method Detection Limit (MDL)	Estimate the concentration at which the analyte is detected above the background level 99% of the time. The MDL must be determined following the method update rule (MUR) of 40 CFR Part 136 Appendix B as described in Section 4.3 of Revision 2 of the PAMS TAD.	5.5	• Annually • Following a significant change to the instrument, such as detector replacement, trap replacement, or change in carrier gas	MDLs must be determined per the prescribed procedure and should be (are not required to be) ≤ 0.5 ppbC for each target VOC	• Investigate instrument for carryover or contamination. • Verify spiking level for the MDL procedure is appropriate. • Adjust spiking level and repeat procedure. • Targets not meeting this specification should be reported with QA qualifier "QX" in AQS.

8. Data Verification

During ambient concentration data review, operators and data reviewers will invariably encounter situations where compounds exhibit interferences. QC checks may fail acceptance criteria, and target compound and interference responses may be questionable as to the presence or absence of the compound. Below are general procedures for performing data verification. Data are ready for validation upon completion of verification.

Data verification processes are intended to ensure that the generated data are representative measurements produced by instruments that are calibrated, operating properly and within defined tolerances, and are accurately recorded. Verification activities involve routine Auto-GC checks by the operator as well as subsequent review of collected data by the instrument operator and an independent individual intimately familiar with instrument operation and data collection.

8.1. Site Operator Routine Checks

It is critical that the operator routinely ensures the Auto-GC is operating properly, and that instrument errors and QC sample failures, humidified standard gas canister pressure, DI water in a H_2 generator, whether operational (e.g., instrument malfunction or performance degradation) or QC-related (contamination in an SB), are addressed in a timely manner. Operators are encouraged to check on instrument operation daily and ensure that QC sample (e.g., CCV and SB) checks met acceptance criteria. This allows corrective action to be taken immediately. The complexity of the Auto-GC makes it susceptible to more frequent failures than other instruments.

Even if there are problems with the collected data such as RT shifts, blank contamination, or chromatography issues resulting in poor automated integration or missed peak identifications, the data can most often be corrected in post-acquisition processing, provided the instrument is operating correctly. If the instrument has entered a fault mode due to a power outage or other instrument failure and ceases to run each hour, those data cannot be salvaged, and those sampling hours are lost. Therefore, it is of utmost importance to check the instrument status routinely to ensure the instrument is online and operating as expected.

Instrument operators will perform the data verification steps listed below and summarized in the flowchart shown in Figure 8-1.

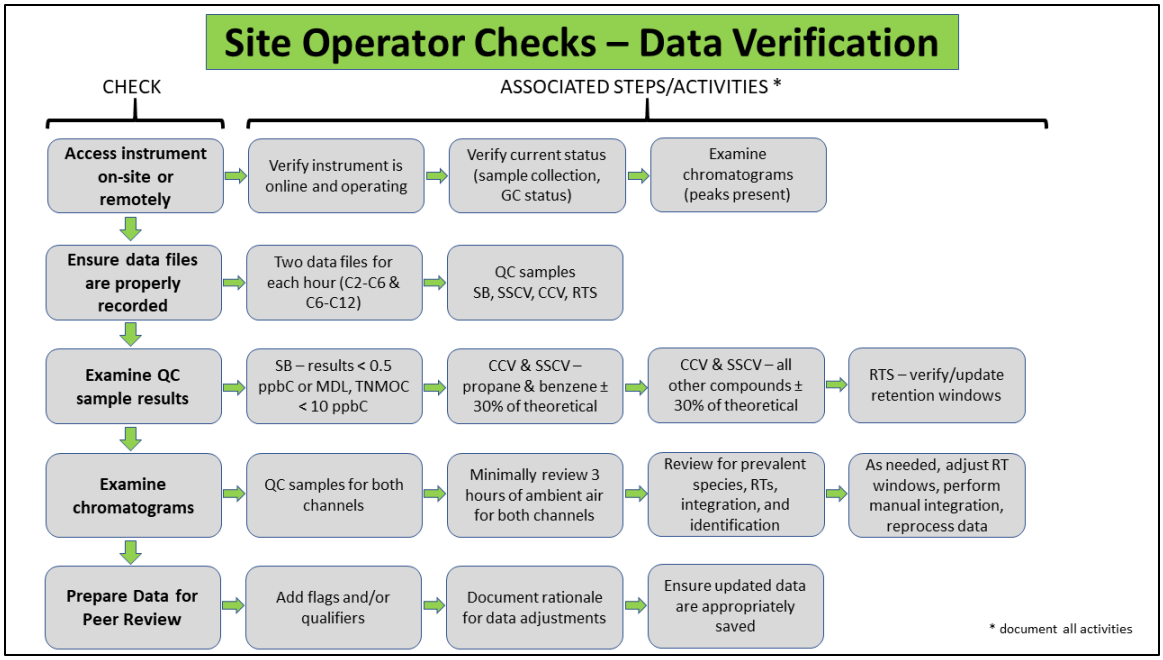


Figure 8-1: Flowchart of Site Operator Data Verification Checks.

8.1.1. Verify Current Instrument Status

Verify the instrument is operating properly (that there are no error messages or faults indicated by the CDS) and that the statuses in the sample collection and analysis cycles are as expected (e.g., that the instrument is collecting samples during the first 40 minutes of the hour). If not, take immediate corrective action. Errors/faults should be evident from the instrument software systems (Markes MIC software or Agilent OpenLab); however, operator understanding of the correct operation status should generally correspond to the following steps in Figure 8-2:

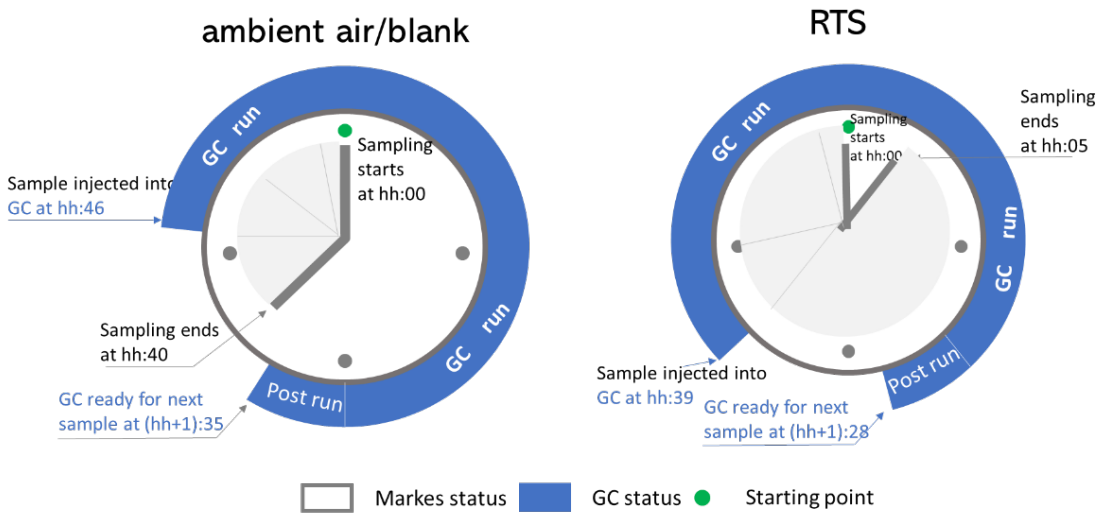


Figure 8-2: A cycle of an Auto-GC run

1. If a QC sample is scheduled to run (typically scheduled for 22:00 to 02:00), ensure the instrument is sampling from the correct inlet stream/port and a valve controlling a standard gas canister is open.
2. Between the top of the hour (e.g., 8:00 a.m.) and 40 minutes past the hour (e.g., 8:40), the pre-concentrator should be actively sampling.
3. At 40 minutes past the hour the GC injection should occur after which the GC should continue to run and collect data until the end of the GC run.
    a. The signal on the C_2-C_6 (PLOT) FID should continue until the Deans switch occurs (occurs once 1-hexene elutes from the PLOT column)
    b. Following the Deans switching, target compounds should be actively eluting on the C_6-C_{12} (DB-1) channel.
4. After injection to the GC, the pre-concentrator suite of components should perform purges (Kori-xr should switch to purge mode to remove captured water) and should cool the sample dryer and preconcentration traps to be ready for collection of the next sample at the top of the hour.
5. At the end of the GC program, the GC should cease data acquisition and begin cooling the oven to be ready for the next injection approximately 40 minutes after the top of the hour.

8.1.2. Verify Data Files

Review the data since the last operator check-in to ensure data files are saved and complete for each ambient air sampling hour and expected QC sample hour. Missing files may be indicative of an instrument failure (such as a stalled collection or GC run).

1. For missing data files, examine data from nearby hours (at least one hour before and two hours after) for impact on the collected data. If missing files indicate an instrument failure, the sample immediately preceding a missing data hour will be invalidated.
2. Failed sample collection events may result in contaminants remaining on the preconcentrator trap (due to incomplete desorption or purging of the preconcentrator trap) or within one or both separation columns which contaminate the following sample.
3. Incomplete sample collection or leaks may permit the instrument to still collect a sample even though there is an error. These data should be reviewed closely to investigate for chromatographic changes that may relate to the error. Examples of conditions which may cause error messages but not interrupt the sample collection include small leaks in the inlet path or elsewhere in the system and flow or pressure criteria out of specification.

8.1.3. Review QC Data

Examine the concentration data in the results summary files for the most recent SB, CCV, SSCV, and RTS and evaluate against the following acceptance criteria:

1. SBs must show that all target VOCs are < MDL or 1.0 ppbC, whichever is lower, and total non-methane organic carbon (TNMOC) is < 10 ppbC.
2. CCVs and SSCVs must show that the calibration compounds (e.g., propane and benzene) are within ±30% of the theoretical nominal concentration and should demonstrate that any other compounds in the CCV are also within ±30% of the theoretical nominal concentration.
3. RTSs do not have discrete acceptance criteria unless also serving as the CCV and/or SSCV. Analysts will evaluate the established RT windows against RTS analyses to ensure the Deans switch timing remains appropriate and will adjust RT windows as needed to ensure proper target analyte peak identification.

8.1.4. Review/Examine Chromatograms and Prepare Data for Peer Review

Site operators will examine chromatograms for each QC check as well as minimally three ambient air sample hours. Particular attention should be paid to examine chromatograms for failing QC checks to ensure that failing QC results are not due to improper peak identification, peak integration, and/or interference. SBs and/or CCVs following an ambient sample with relatively high concentrations may exhibit carryover from the high concentration sample which may lead to SB levels exceeding criteria or CCVs showing excessive recovery.

When reviewing chromatograms, examine the chromatogram baseline, accuracy of peak identification, and quality of peak integration. If corrections or changes are warranted, maintain the original automated output and record (e.g., annotate the chromatogram electronically or document in a separate log) the rationale for the change(s).

1. **Examine Baseline:** Examine the baseline in the chosen chromatograms for excessive noise, uncharacteristic rises, dips, spikes, a hump and/or other uncharacteristic behavior. When zooming in on the baseline, some noise will be evident; however, excessive/atypical noise may indicate degradation of that channel's FID or system electronics. Rises and dips in the baseline may indicate pressure fluctuations resulting from cycling of the ZAG compressor, leaks or partial clogs in the support gas delivery, and/or excessive moisture or contamination in carrier gas streams. Practically, these perturbations in the baseline may, depending on their magnitude, complicate proper peak integration, requiring additional instrument operator efforts to properly identify and integrate adversely affected chromatograms.

Note: Analysts should carefully consider the assignment of the peak area reject threshold setting. This parameter is useful to ensure that the EZChrom does not mistakenly identify detector noise as a chromatographic peak (whether target analyte or unknown peak). Setting this value too low will result in the EZChrom identifying noise responses as peaks and requiring the analyst to manually eliminate these noise responses as detections. The level of effort required to manually eliminate these responses may be considerable. However, setting this value too high will result in the EZChrom overlooking true chromatographic peaks and will require the analyst to review all chromatograms to manually identify target and non-target analytes.

2. **Review Peak Identification:** Examine the identification of target analyte peaks on both channels to ensure proper identification. Ambient air sample chromatograms should be examined to ensure that abundant species are present as expected and properly identified. RT shifts, particularly on the C_2-C_6 channel due to the PLOT column's sensitivity to humidity changes, may occur and confound automated identification. A best practice is to prepare the reviewed chromatograms with the most recent RTS, or other multi-component standard, to confirm proper identification (Refer to Figure 5-13). Misidentifications by the *EZChrom* must be over-ridden and the correct peak identified, if possible. A useful tool is to plot the RTs of the target analytes (on the y-axis) against the chronological sample order to more easily identify peaks RTs that are out of the norm and may indicate there are chromatograms for which an RT shift has occurred, or the peak(s) has been misidentified. Refer to the example in Figure 5-13 which shows the RT of major target analytes acquired on 6/10/2024 and 6/12/2024.

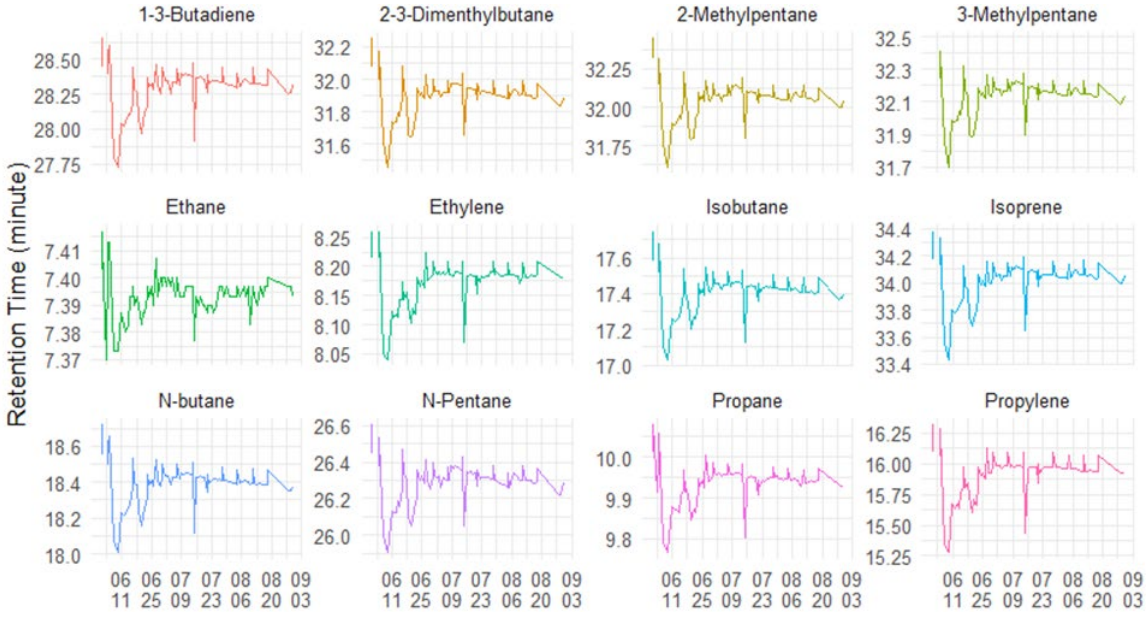


Figure 8-3: Example plot of compound retention times

Commonly misidentified target compounds are detailed in Table 8-1.

Table 8-1: Commonly misidentified target compounds.

FID Channel	Compound(s)	Interference
C_2-C_6	acetylene	Acetylene requires a wide RT window - when not present automated routines may incorrectly identify a non-target peak as acetylene.
C_2-C_6	cyclopentane and isopentane	These two compounds co-elute/elute closely together and may be misidentified when RTs shift.
C_2-C_6	2,3-dimethylbutane, 2-methylpentane, and 3-methylpentane	These "three sisters" partially co-elute and may be misidentified when concentrations are low and/or RTs shift.
C_6-C_{12}	methylcyclopentane and 2,4-dimethylpentane	These two compounds co-elute/elute closely together and automated routines may incorrectly identify these compounds when one is absent in the chromatogram, or an additional unknown compound co-elutes.
C_6-C_{12}	2-methylhexane and 2,3-dimethylpentane	These two compounds co-elute/elute closely together and automated routines may incorrectly identify these compounds when one is absent in the chromatogram, or an additional unknown compound co-elutes.
C_6-C_{12}	styrene	Styrene may exhibit poor peak shape and automated integration parameters may result in this compound being missed.
C_6-C_{12}	m-ethyltoluene and p-ethyltoluene	An unknown compound elutes/co-elutes just prior to m-ethyltoluene and p-ethyltoluene co-elutes on the backside of m-ethyltoluene which can confound automated identification routines.
C_6-C_{12}	region of the chromatogram between alpha-pinene and 1,2,4-trimethylbenzene	This portion of the chromatogram is congested with target compounds and may show additional unknown peaks attributed to biogenic compounds (e.g., limonene, camphene, and other terpenes/terpenoids). These peaks may be large in relative magnitude and may co-elute or elute closely with target compounds, confounding identification.

3. **Review Peak Integration:** Examine target analyte peaks in the chosen chromatograms to ensure the integration is appropriate and consistent. Where possible, automated integration routines should be configured to properly integrate analyte peaks without analyst intervention. However, even when configured optimally for ambient air, the integration may require manual adjustment when unknown (non-target) compounds co-elute with target analytes, when RTs shift, or when standard or blank gases are analyzed. Conversely, when automated

integration routines are optimized for standard or blank gases, integration for ambient air samples may require manual adjustment, particularly for peaks with co-elution interferences absent in the standard chromatogram. Therefore, peak integration should be examined closely in the CCV, RTS, and SB as well as in ambient air sample chromatograms.

A discussion of chromatographic peak integration practices is detailed in Appendix E: Basics of Chromatography. Agilent *EZChrom* OpenLab software packages permit analysts to drag and drop an integration baseline and perpendicular or employ more sophisticated peak integration regimes. When manually adjusting integration parameters, the *EZChrom* will flag the modified data (e.g., with an asterisk "*") to indicate the peak(s) was manually integrated/modified.

Common rationales for modifying automated integration and recommended associated abbreviations are shown in Table 8-2.

When reviewing target analyte peak integration, analysts should review the integration of all peaks in the chromatograms undergoing review. When target analyte peaks show improper integration, analysts should review those peaks in adjacent sample hours and adjust integration as required in the subsequent sample hours.

Table 8-2: Common rationales for manual peak integration.

Rationale for Modification	Details and Examples	Suggested Abbreviation
Not a peak	Peak or integrated portion of chromatogram is not a valid peak – e.g., integrated area has signal to noise ratio (S:N) < 3	NP
Misidentification	Incorrect target analyte assignment	MI
Poor integration	Automated integration poorly reflects peak area – e.g., integration includes baseline noise or excludes appropriate peak area	PI
Co-elution	Integration adjusted to eliminate a co-eluting substance	CO

8.1.5. Integration Adjustment Priority

Measured concentrations of many of the target analytes will likely be ≤ 1 ppbC. As analyte concentrations decrease and approach the MDL (note: the MDL MQO is ≤ 0.5 ppbC), peak S:N concomitantly decreases, increasing the difficulty for automated integration regimens to properly integrate these low concentration peaks. Manually adjusting those peaks which were improperly integrated may require substantial analyst time, therefore analysts should prioritize performing manual integrations in the following order of decreasing priority:

1. Priority compounds > 0.5 ppbC
2. Priority compounds ≤ 0.5 ppbC
3. Optional compounds > 0.5 ppbC
4. Optional compounds ≤ 0.5 ppbC
5. Unknown (non-target) compounds (sum for TNMOC)

For optional or priority compounds at low concentrations (i.e., < 0.5 ppbC or MDL) for which integrations are not reviewed, the associated concentration data will be flagged with QA qualifier LJ when reported to AQS.

8.1.6. Reprocess Data, Add Qualifiers and Flags, and Confirm Changes are Saved

Once the acquired data have been reviewed and any needed adjustments made, the operator/analyst will ensure any data requiring adjustment have been properly reprocessed per the appropriate method, flags and qualifiers have been added as warranted, and documentation of changes and their rationale are recorded. The operator/analyst will also verify the updated data have been properly saved.

When preparing data for peer review, the analyst will flag data according to the scheme in Table 8-3. Listed flags are relevant QA qualifier codes or NULL codes. Data with QA qualifier codes are reported to AQS with the concentration value intact; however, data with NULL codes are invalid and the concentration value is not input into AQS.

Table 8-3: Description and assignment of data qualifiers.

Category	Description	Data to Flag	Flag to Append	Qualifier Type
Missing data	Intended data collection hour missing	Target analytes for missing ambient hours	AF	NULL qualifier
Missing data	Intended data collection hour missing	Target analytes for one hour following missing hours	AQ	NULL qualifier
Instrument malfunction or collection error	Collected data exhibit instrument malfunction or collection error	Target analytes for affected hours	AN (for malfunction) AQ (for collection error)	NULL qualifiers
Data outside required time	Collected data do not comply with start time 10 minutes before or 30 minutes after the hour and/or do not comprise 40 minutes of sample collection	Target analytes for ambient hours not meeting timing requirements	AI	NULL qualifier
Chromatography Problems or Interferences	Collected sample shows severe chromatographic issue(s) (RT shift, artifacts, interferences) impacting the FID channel	Target analytes for the associated FID channel for the affected ambient hours	DA	NULL qualifier
Chromatography Problems or Interferences	Collected sample shows severe chromatographic problem (co-elution, RT shift) isolated to specific region in chromatogram	Target analytes with concentrations appearing to be biased by more than ± 50% (based on analyst judgement) in affected ambient hours	BH	NULL qualifier
Chromatography Problems or Interferences	Target analyte identified with co-elution or interference	Target analytes with concentrations appearing to be biased high (bias not to exceed +50%) in affected ambient hours	LK	QA qualifier

Category	Description	Data to Flag	Flag to Append	Qualifier Type
Chromatography Problems or Interferences	Target analyte identified with co-elution or interference	Target analytes with concentrations appearing to be biased low (bias not to exceed -50%) in affected ambient hours	LL	QA qualifier
Chromatography Problems or Interferences	Target analyte identified with co-elution or interference	Affected target analytes for which the analyte concentration is an estimate (bias not to exceed ±50%)	LJ	QA qualifier
Analyte not detected	Target analyte not detected (not within RT window or S:N ≤ 3:1)	Target analytes not detected in affected ambient hours (0 ppbC)	ND	QA qualifier
Concentration below MDL	Target analyte detected but ≤ MDL	Target analytes detected in ambient hours at ≤ MDL	MD	QA qualifier
Concentration between MDL and sample quantitation limit	Target analyte detected between MDL and ≤ 3.18·MDL	Target analytes detected in ambient hours at > MDL but ≤ 3.18·MDL	SQ	QA qualifier
Exceeds calibration range	Target analyte in ambient hour exceeds upper range of calibration	Affected target analyte in affected ambient hours	EH	QA qualifier
QC Sample Failure – SB	Target analyte measured in SB at > 0.5 ppbC or MDL, whichever is lower	Ambient hours for that target analyte back to the most recent acceptable SB and forward to the next acceptable SB	LB, FB and QX	QA qualifiers
QC Sample Failure – CCV or SSCV	Target analyte measured in CCV or SSCV < 70% recovery of nominal	Ambient hours for that target analyte (and associated target analytes*) back to the most recent acceptable CCV/SSCV and forward to the next acceptable CCV/SSCV	LL and QX	QA qualifiers

Category	Description	Data to Flag	Flag to Append	Qualifier Type
QC Sample Failure – CCV or SSCV	Target analyte measured in CCV or SSCV > 130% recovery of nominal	Ambient hours for that target analyte (and associated target analytes*) back to the most recent acceptable CCV/SSCV and forward to the next acceptable CCV/SSCV	LK and QX	QA qualifiers
QC Sample Failure – CCV or SSCV	Target analyte measured in CCV or SSCV < 50% or > 150% recovery of theoretical nominal	Ambient hours for that target analyte (and associated target analytes*) back to the most recent acceptable CCV/SSCV and forward to the next acceptable CCV/SSCV	AS	NULL qualifier

* Associated target analytes refer to those analytes that are not included in the CCV and/or SSCV but are associated with the failing target analyte. For example, if the CCV does not include all target analytes (e.g., consists of 15 of 59 target compounds), the target analytes with similar molecular weights will be assigned to the closest target analyte in the CCV and/or SSCV – e.g., if 1,3,5-trimethylbenzene fails in the CCV and/or SSCV (which does not include other C_9 target analytes), target analytes with nine carbon atoms will require flagging

8.2. Peer Review

Once the operator has completed the routine self-checks and data review listed above in Section 8.1, and resources and staffing are available, the measurement data are to be reviewed by a separate individual who is knowledgeable with the Auto-GC measurements and the instrument's operation principles, the typical behavior of the target analytes, and common issues or problems that occur with VOC measurements. This independent review of the Auto-GC data should be performed biweekly and is intended to verify the site operator has properly completed the first level of data verification steps and to examine the data more completely. The peer reviewer will follow up with the site operator/instrument analyst for clarifications, missing information, or data that require correction. It is not intended for the peer reviewer to make changes to the data.

Peer reviewers will perform the following data verification steps listed below weekly and summarized in the flowchart shown in Figure 8-4.

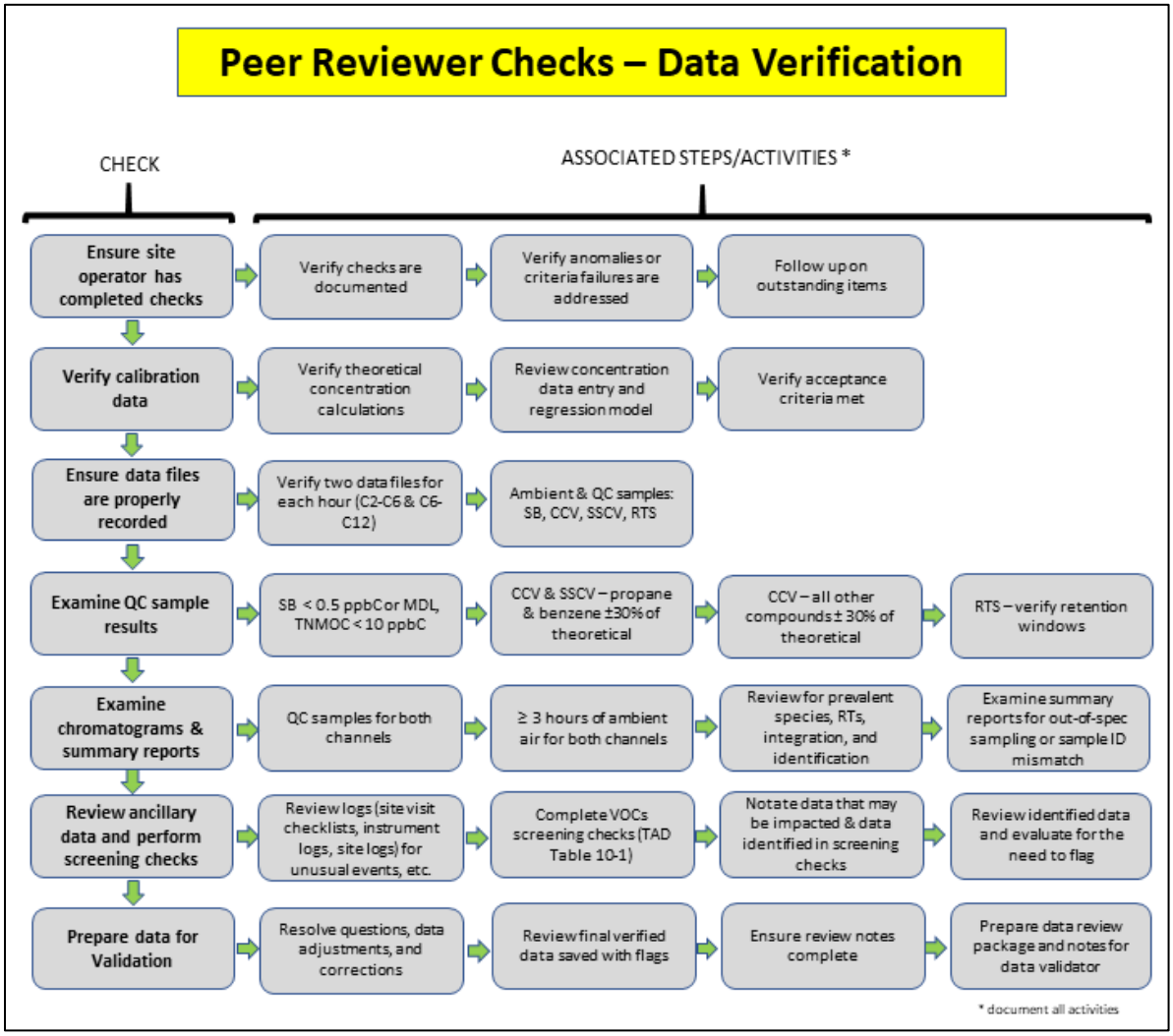


Figure 8-4: Flowchart of Peer Review Verification Steps.

1. **Verify Site Operator/Analyst Checks**: Ensure the operator/analyst has completed the required review checks and documented data anomalies, acceptance criteria failures, manual changes to data, and the aspects of analysis reviewed (e.g., date ranges, filename ranges, etc.). Note where these items are incomplete and require follow up by the operator prior to performing peer review.
2. **Verify Calibration Data**: Review the calibration records for the Auto-GC to ensure that the calibration was properly established. This includes reviewing calculations for dilutions and ensuring that certified values for the target analytes have been entered properly for the theoretical concentrations into the calibration regression. Peer reviewers should then ensure that the correct regression models and options have been employed and that acceptance criteria have been met (refer to Table). Once reviewed, the calibration records need only be reviewed again if the calibration (or RFs) are updated.
3. **Ensure Data Files are Properly Recorded**: Examine data storage folders for missing data files and ensure that the expected files are present, including all anticipated QC check files (e.g., CCV, SB, and RTS) and ambient air sample hours for both FID channels (C_2-C_6 and C_6-C_{12}) for 24 sampling hours of each day. Review the sample starting time for each to verify the sampling started within the proper time window. Verify that the sample type matches for the designated hour for both channels (i.e., both channels indicate that the same sample type was analyzed). Verify that the site operator/analyst has addressed any missing files and invalidated them and the preceding hour if the missing file is due to an instrument malfunction.
4. **Examine QC Sample Results**: Examine the CCV and SB data for each day and the weekly SSCV and RTS to ensure acceptance criteria are met and note where failures occur (or verify that the operator has noted these failures) as the associated ambient data will need to be qualified or invalidated (i.e., flagged with a NULL qualifier) when reported. Review chromatography to ensure that target analyte peaks were identified properly that RT windows remain valid, and that peak integration is consistent and appropriate. Review QC charts for trends indicating the instrument performance is approaching out of control status.

5. **Examine Chromatograms and Data Summary Reports**: Chromatograms should be examined for misidentified compounds, suitable and consistent peak integration (whether with automated integration routines or through manual adjustment), interferences that impact data quality, abundant species expected in ambient air samples but that are missing, and target analytes with unexpected high concentrations exceeding the calibration range, particularly those that exceed the FID response range (this results in flat-topped peaks). Examine sample hours preceding and following high concentration samples to evaluate potential carryover. Prepare overlays with standard chromatograms, such as the RTS, to verify compound RT windows. If problems with compound identification are observed, additional ambient sampling hours should be reviewed to characterize the extent of the specific issue. Review data summary reports for insufficient collection durations (e.g., < 40 minutes), out-of-specification sample collection flows or volumes, and unexpected analyte concentrations indicative of a sample identifier mismatch (e.g., an ambient daytime sample that appears to be a blank).
6. **Review Ancillary Data and Perform Screening Checks**: Review site logbooks, site visit checklists, instrument maintenance logbooks, and instrument audit trails for information that may indicate collected sample and/or QC data are impacted. Such aspects include unusual events (e.g., wildfires), unscheduled maintenance, and large volumes of reprocessed sample data. Complete speciated VOC screening checks which assess whether ambient sample data exhibit characteristics such as presence/absence of target analytes, compare target species for expected relationships, and assess trends in target analyte concentration such as analytes exhibiting a diurnal pattern. These screening checks are detailed in Table 10-1 of the PAMS TAD[2]; however, some of the checks may not specifically apply to all PAMS sites based on the mix of sources at a given site. Modifications to these checks should be carefully considered and justified based on historical measurements or other documented factors. Failures of the screening checks will result in further review of additional chromatograms or datafiles and confirmed failure of the screening checks will prompt qualification of the data when reported to AQS (as described in Table 10-1 of the PAMS TAD).
7. **Prepare Data for Validation**: Resolve outstanding questions, data adjustments, or corrections, and review the final verified data to ensure the data are saved with the appropriate qualifiers or flags. The dataset at this point should be as complete and correct as possible and should be ready for subsequent data validation.

9. Data Validation

Once data have gone through the data verification processes with the site operator and peer reviewer, the data will have been appropriately flagged or invalidated based on their suitability and compliance with the PAMS QAPP. Data validation *should not commence* until the data verification steps have been completed and the dataset to undergo validation is appropriately complete and correct (that the dataset includes all collected data, and these data represent the collected sample measurements, and measurements that are compromised are appropriately flagged or invalidated). At the validation stage, the data are examined for their internal consistency within the dataset, consistency with historical data, and consistency with other datasets acquired from other nearby sources.

It is important that data be validated in a timely manner after the data have been collected and verified. Data verification, in theory, when performed comprehensively and in a timely manner, should identify the most serious of nonconformances, allowing prompt corrective action. However, systematic errors and problems that are not evident during data verification steps can still be identified during data validation when a larger portion of the dataset is examined at a higher level. To be meaningful, data validation should be performed on a temporal range of sample data encompassing approximately three or more weeks, so trends and a sufficient amount of the dataset can be examined in totality. The delay in acquiring such a quantity of sample measurements and verifying the data typically means that data will be one month or more from collection when data validation can begin.

Several software platforms are available for monitoring agencies to validate data. These software tools may employ range finding checks, graphing capabilities and tools for data visualization, statistical tools, interparameter comparisons, and data flagging. Software tools used in data validation include, but are not limited to DART, R, and excel.

A general discussion of recommended data validation procedures follows and refers heavily to the comprehensive data verification and validation section (Section 10) in the PAMS TAD Revision 3.

9.1. Validation Tools

Individual data points or ranges of data identified as anomalous or spurious in the following procedures will be further examined to ensure data are correct. It is anticipated that many such values will have been already examined during data verification and any issue(s) already sufficiently explained in the data verification notes. Issues identified during these examinations that are not already satisfactorily explained will result in determining whether additional data should be examined.

9.1.1. Statistical Tests and Reports

Perform the following statistical tests on each parameter within the dataset:

- Determine the central tendency of the dataset (calculate the arithmetic mean, geometric mean, median, and/or mode).
- Calculate the variability of the dataset by determining the standard deviation.
- Determine the minimum and maximum concentrations.
- Examine the statistical data for extremely high values (e.g., statistical or apparent outliers), large standard deviations (e.g., exceeding 30% of the mean), large differences between average and median values (e.g., exceeding 30% of the mean), and other unexpected outcomes. Note that for analytes exhibiting diurnal behavior (i.e., isoprene), large standard deviations of concentration (e.g., > 30% of the mean) may be normal.

Review the following audit reports for identified issues and their impact on data undergoing validation:

- Proficiency Test (PT) results – unacceptable results
- Technical Systems Audit (TSA) reports – audit findings or auditor recommendations
- Audit of Data Quality (ADQ) reports – identification of data input errors, data calculation errors, and/or documentation gaps

Review Corrective Action Reports for:

- Issues or problems that have impacted data
- Open or unresolved issues that may continue to impact data

9.1.2. Visualization Tools

Prepare the following graphical outputs of the ambient concentration data undergoing validation. Suggested aspects to examine/inspect are listed below; however, monitoring agencies should tailor these and list specific chemical species and criteria for evaluation. Data points that do not fit expectations should be investigated for proper instrument collection and data processing (e.g., proper peak identification and data handling).

Time Series Plots: Ambient concentration sample data are plotted chronologically (date and hour of sampling is plotted on the x-axis and the concentration on the y-axis) and plots are investigated for expected concentration changes due to automobile traffic patterns, diurnal behavior, maximum/minimum concentrations, periods of missing data (due to instrument malfunction or invalidation), periods of identical concentrations (sticking), step changes in concentrations (possibly due to changes in instrument status), and general trends over time indicating potential instrument calibration drift. Prepare time series overlays of several analyte species expected to have a proportional relationship (e.g., benzene, toluene, and xylenes).

Scatterplots: Concentrations of pairs of parameters are plotted such that each species has a dedicated axis, and the coordinates of each plotted point are contributed by the two species (e.g., benzene on the x-axis and toluene on the y-axis). The resulting points, if there is a correlation, show a relationship indicated by a well-defined region (clumping around a straight line) of datapoints.

Points outside the well-defined region can indicate data that diverge from the expected relationship.

Fingerprint Plots: Compounds are listed along the horizontal axis in a consistent order (e.g., retention order, alphabetical, molecular weight, etc.) and the associated concentration for each is plotted. These hourly plots are reviewed successively for changes in relative concentration pattern, missing compounds, and most abundant species.

Stacked Bar Charts: Like time series plots, ambient sample hours (or other aggregate of sample hours) are chronological along the x-axis and concentration is on the y-axis; however, concentrations of the several different selected compound species are stacked in a consistent manner to create a composite bar chart where the bar is the sum of the species, and the individual segments are from the individual component contributions.

Box and Whisker Plots: Statistics for the given parameter are shown such that the box represents the middle 50th of concentrations (top of the box is the 75th percentile and bottom of the box is the 25th percentile), the median (the 50th percentile) is a horizontal line within the box, and the mean is typically a symbol (e.g., dot) within the box (this is a typical convention for the box and whisker plots). Vertical lines, or whiskers, extend from the top and bottom of the box to indicate the 90th and 10th percentile values, respectively. Values outside the 10th and 90th percentiles are typically shown as individual points. Useful preparations are to show data for a single parameter prepared as side-by-side graphs aggregated by week, month, or other time range.

Diurnal Profiles: Plot one (e.g., isoprene – refer to Figure 9-1) or more parameters expected to exhibit diurnal behavior (increase or decrease during daytime hours) on a plot with the time of day on the x-axis and the concentration on the y-axis. Isoprene is one such target compound that increases during the day due to daytime emissions from plants.

Identify Outliers: Using the data sources and tools above, investigate concentration values that appear very large or small compared to the rest of the population (e.g., values several standard deviations from the mean or identified by statistical outlier tests), appear anomalous graphically in data visualization plots, and/or are associated with procedural deviations that may impact data quality.

Comparison to other pollutants: Relationships with other measured pollutants at the monitoring site can also identify data quality issues. On-site meteorological data can also be used to generate pollution roses and identify deviations from characteristic meteorological conditions.

9.2. Levels of Data Validation

Level 1: Evaluates the *internal consistency* of the dataset to identify values that appear atypical within the dataset. Evaluation includes tests for internal consistency to identify outliers and extreme differences that may indicate anomalous data.

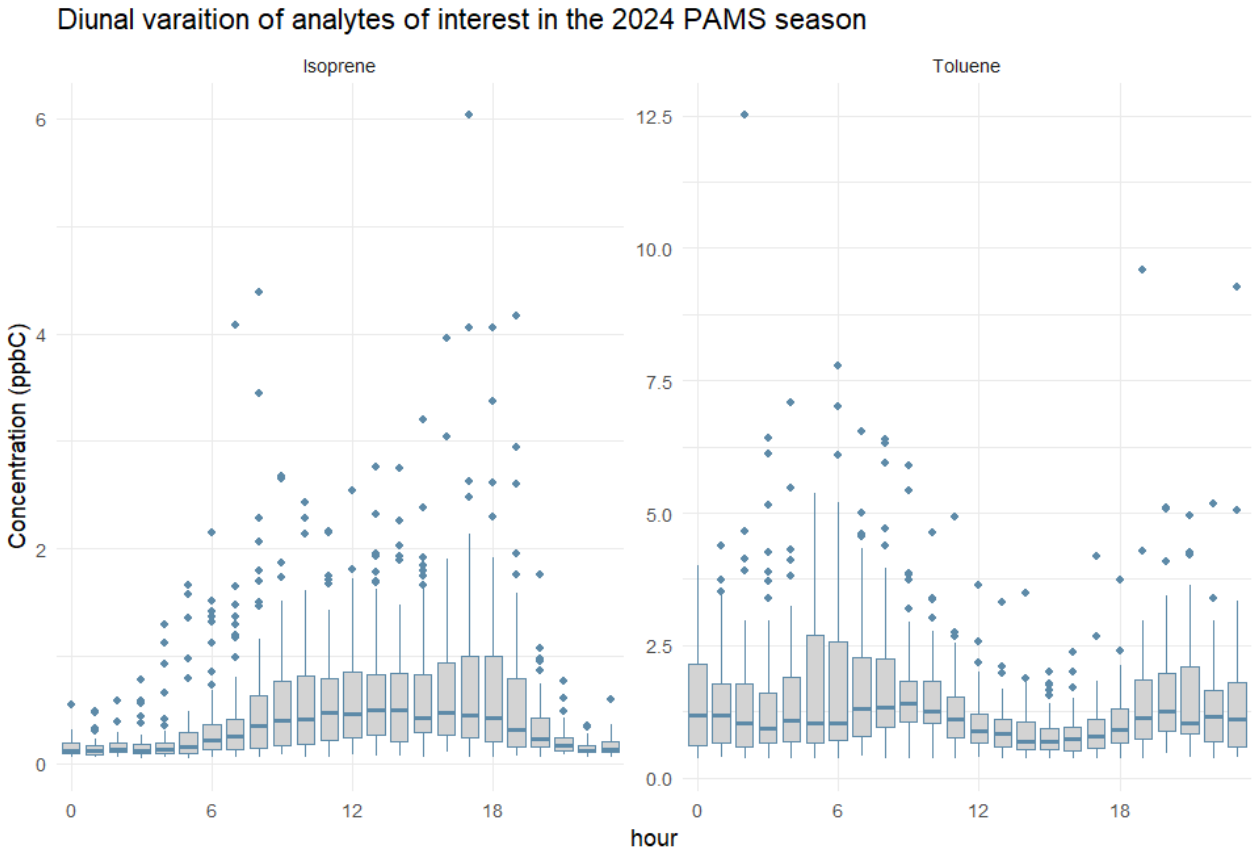


Figure 9-1: Diurnal profile illustrating daytime increase of isoprene and toluene

Level 2: Data that have undergone Level 1 validation are then compared to historical data to evaluate the *temporal consistency* with previous datasets.

Level 3: Data that have undergone Level 2 validation are then compared to data from other sites within the airshed and/or collocated instruments to evaluate differences for systematic bias or to confirm expected differences.

9.3. Data Reporting

Data are to be reported to AQS following data verification and validation processes described in Sections 1 and 9. The reporting of data to AQS is outside the scope of this SOP.

10. Resources

Video for changing the preconcentrator trap in the Markes UNITY-xr:
https://www.markes.com/Resources/How-to-video/How-to-replace-the-focusing-trap-on-the-UNITY-xr.aspx

Video for changing the heated fused-silica transfer line from the Markes UNITY-xr to the GC:
https://www.markes.com/Resources/How-to-video/How-to-replace-the-fused-silica-transfer-line-to-the-GC.aspx

11. References

40 Code of Federal Regulations, Part 136 Appendix B, Clean Water Act Methods Update Rule for the Analysis of Effluent, Revision 2, effective July 1, 2024.

e-CFR 40 CFR Part 136 Appendix B

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Appendices

Appendix A: Agilent GC Method Parameters

GC
Oven
Temperature
Setpoint On
(Initial) 40 °C
Hold Time 12 min
Post Run 200 °C
Program
#1 Rate 5 °C/min
#1 Value 170 °C
#1 Hold Time 0 min
#2 Rate 15 °C/min
#2 Value 200 °C
#2 Hold Time 4 min
Equilibration Time 1 min
Max Temperature 200 °C
Maximum Temperature
Override Enabled
Slow Fan Disabled
Cryo Off
Front SS Inlet He
Mode Splitless
Heater On 150 °C (optionally disable heater as this inlet only supplies carrier gas)
Pressure On 36.349 psi
Total Flow On 23.1 mL/min
Septum Purge Flow On 0.1 mL/min (higher flows of 1-2 mL/min reduces occurrence of split peaks and ghost peaks)
Gas Saver Off
Purge Flow to Split Vent 20 mL/min at 999.99 min (lower flows down to 1 mL/min are recommended to conserve gas)
Column
Column #1
Flow
Setpoint On
(Initial) 3 mL/min
Post Run 3 mL/min
Agilent 123-105F
DB-1
0 °C—325 °C (350 °C): 50 m x 320 µm x 1.05 µm
Column lock Unlocked
In Front SS Inlet He
Out PCM C
(Initial) 40 °C
Pressure 36.349 psi
Flow 3 mL/min
Average Velocity 20.978 cm/sec
Holdup Time 3.9724 min
method: C:\Enterprise\Projects\PAMS\Method\ PAMSOFF_10-25-2024..met
Column #2
Flow
Setpoint On
(Initial) 4.5 mL/min
Post Run 4.5 mL/min
HP-PLOT AL203
0 °C—200 °C (200 °C): 50 m x 320 µm x 5 µm
Column lock Unlocked
In PCM C He
Out Back Detector FID
(Initial) 40 °C
Pressure 26.618 psi
Flow 4.5 mL/min
Average Velocity 50.933 cm/sec
Holdup Time 1.6361 min
Column Outlet Pressure 0 psi
Front Detector FID
Heater On 300 °C
H2 Flow On 35 mL/min
Air Flow On 350 mL/min
Makeup Flow On 10 mL/min
Carrier Gas Flow Correction
Does not affect Makeup or Fuel Flow
Flame On
Electrometer On
Back Detector FID
Heater On 300 °C
H2 Flow On 35 mL/min
Air Flow On 350 mL/min
Makeup Flow On 10 mL/min
Carrier Gas Flow Correction
Does not affect Makeup or Fuel Flow
Flame On
Electrometer On
Valve 1
Other Off

PCM C
PCM C He
PCM C He Supplies Column 2
Aux PCM C He
Pressure
Setpoint Off
(Initial) 10 psi
Post Run 0 psi
Signals
Signal #1: Back Signal
Description Back Signal
Details Back Signal (FID)
Save On
Data Rate 5 Hz
Dual Injection Assignment
Front Sample
Signal #2: Front Signal
Description Front Signal
Details Front Signal (FID)
Save On
Data Rate 5 Hz
Dual Injection Assignment
Front Sample
Signal #3: Test Plot
Description Test Plot
Details
Save Off
Data Rate 5 Hz
Dual Injection Assignment
Back Sample
Signal #4: Test Plot
Description Test Plot
Details
Save Off
Data Rate 5 Hz
Dual Injection Assignment
Back Sample
Run Time Events
Run Time Events
#1 Time 4 min
#1 Event Valve
#1 Position Valve 1
#1 Setpoint On
#2 Time 12 min
#2 Event Valve
#2 Position Valve 1
#2 Setpoint Off

Appendix B: Markes Method Parameters

- Trap: U-T20PAM-2S
- Trap temperature setting during sampling: -30°C
- Trap desorb temperature: 300°C
- Trap hold time: 5 minutes
- Flow path temperature: 120°C
- Trap purge: 2 minutes at 50 mL/minute
- Split flow: 15 mL/minute

Below is a screenshot of the MIC method applied for PAMS sampling.

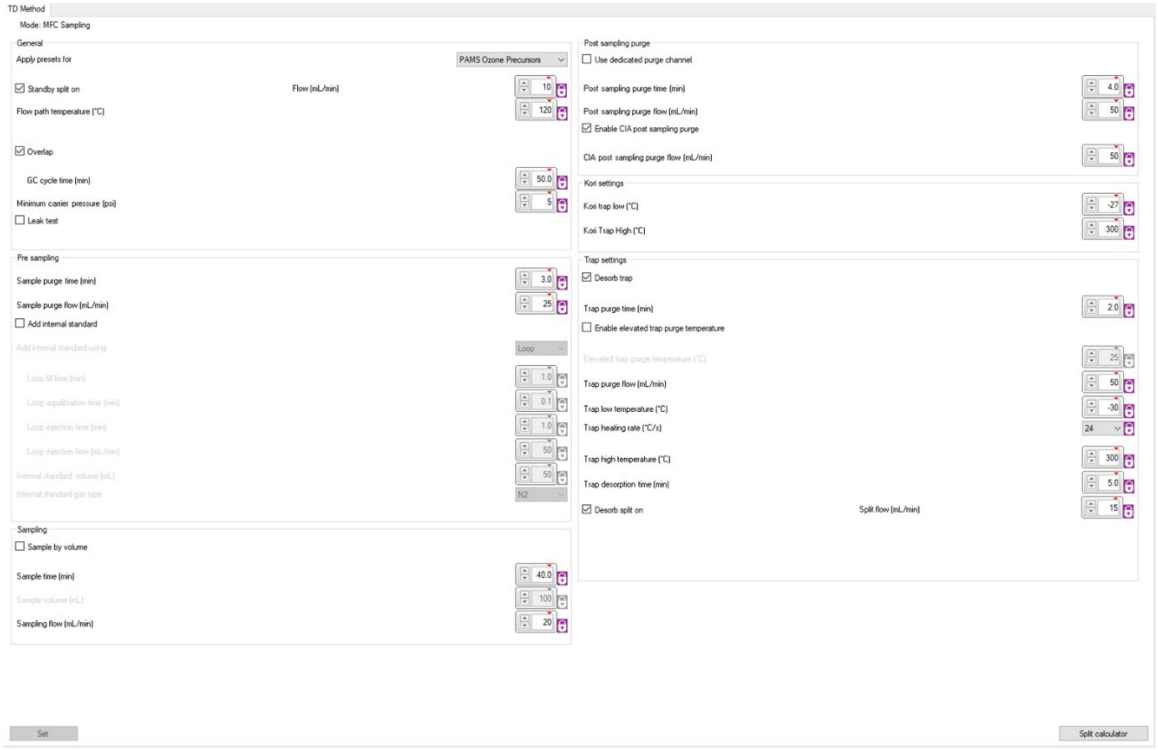


Figure B-1: Markes MIC method

Appendix C: Agilent Sequence Setup

The Agilent GC sequence can be set up in EZChrom. Figure C-1 shows a typical PAMS sequence. The red arrow shows how the fill down option can be used to match the Filename to the Sample ID.

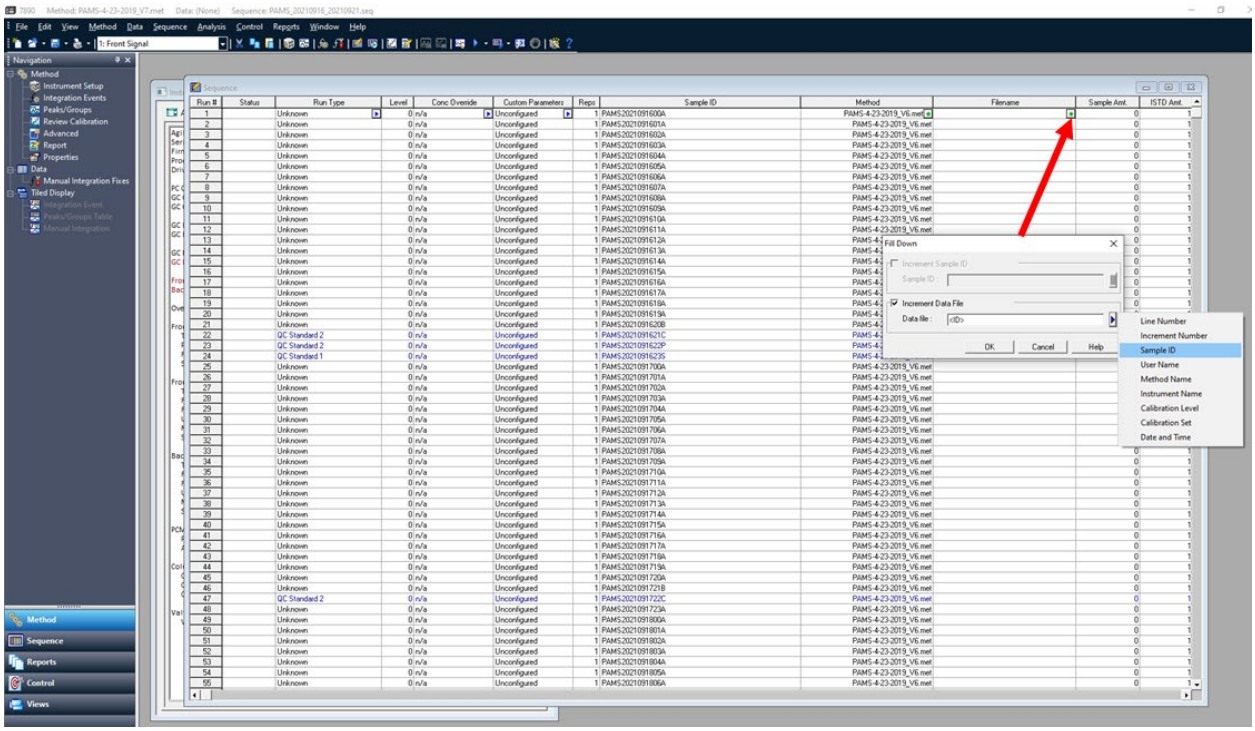


Figure C-1: Agilent EZChrom Auto-GC sequence setup

Appendix D: Markes Sequence Setup

Set up Markes sequences to run for exactly 60 mins by going into Setting -> Sequence Options and using the settings seen below.

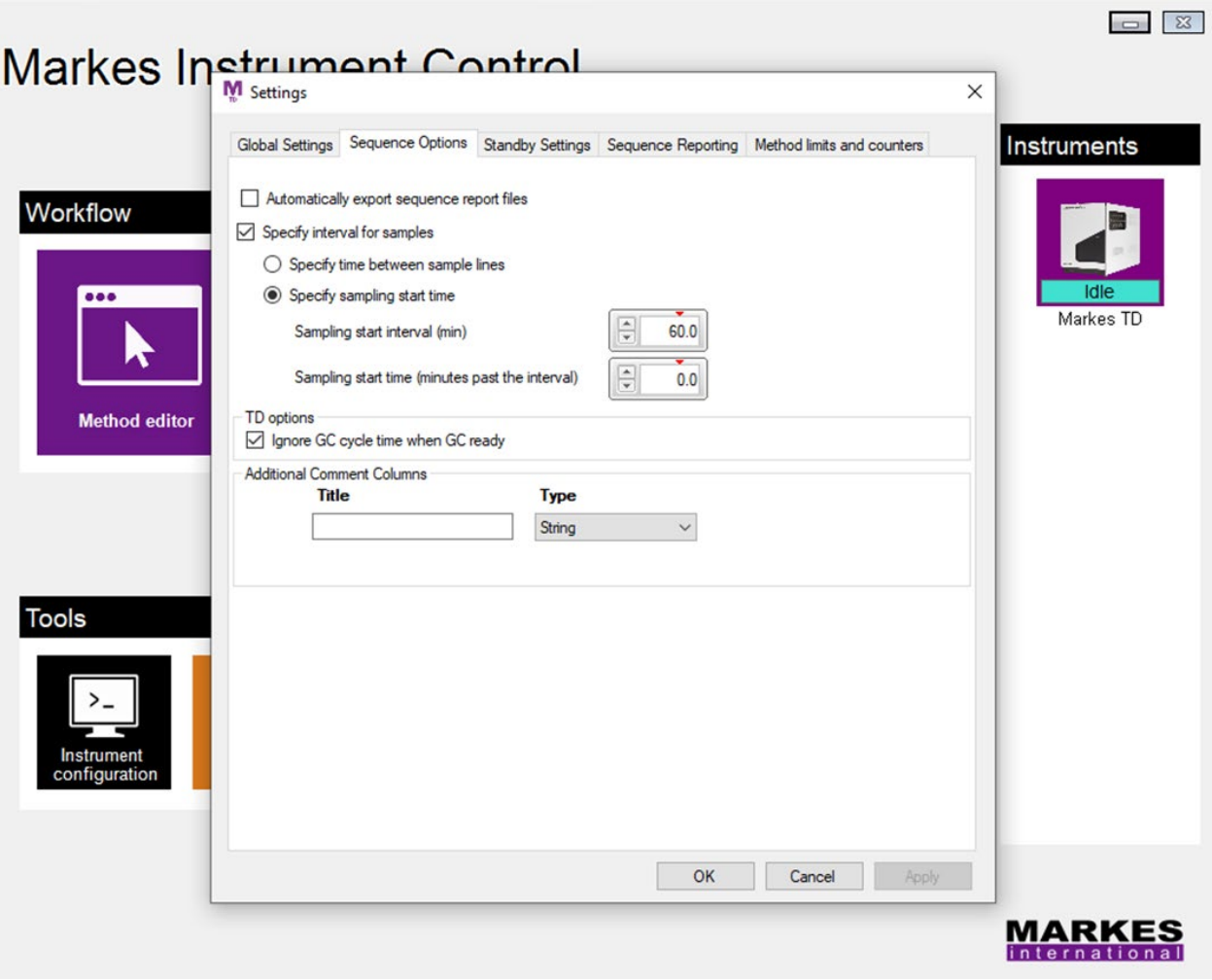
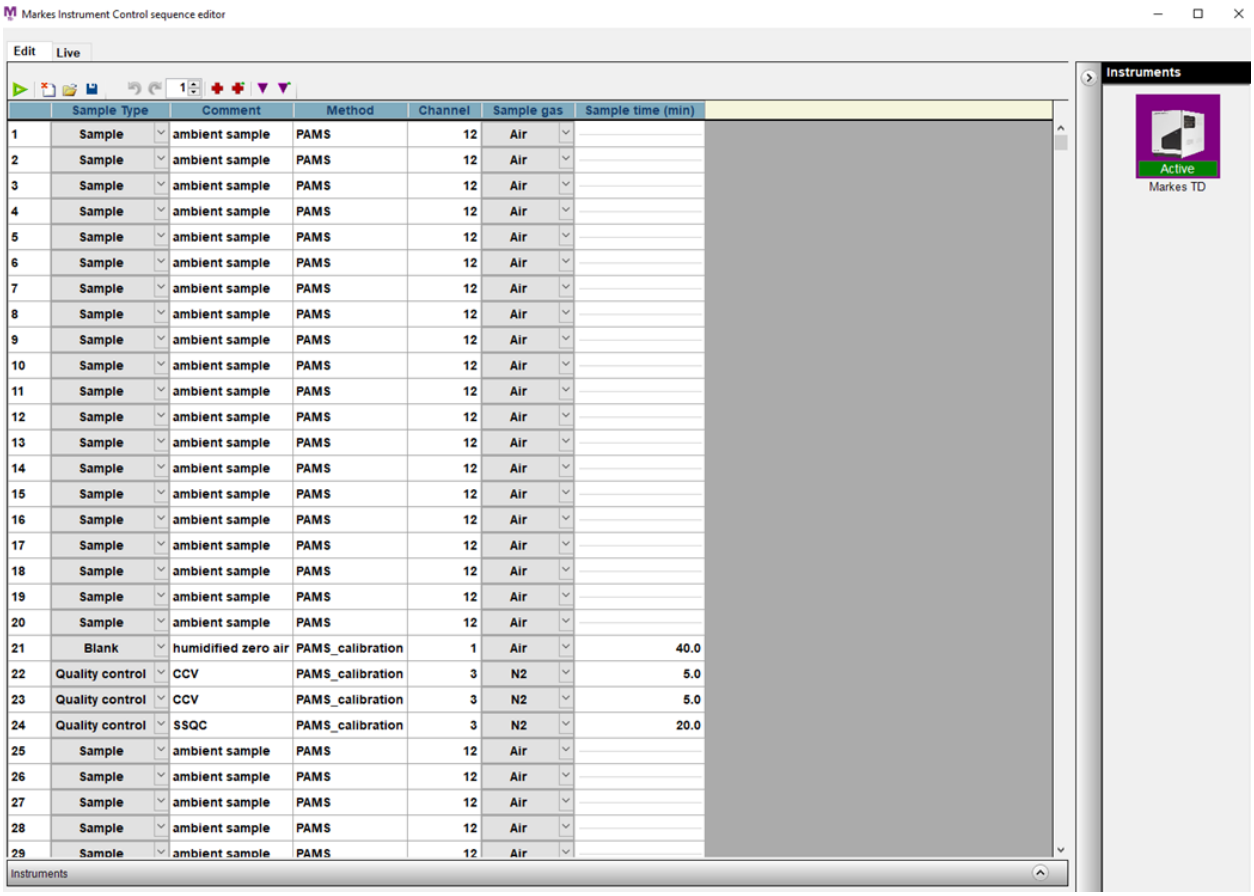


Figure D-1: MIC Software settings for specifying samples to run exactly for 60 mins



	Sample Type	Comment	Method	Channel	Sample gas	Sample time (min)
1	Sample	ambient sample	PAMS	12	Air	
2	Sample	ambient sample	PAMS	12	Air	
3	Sample	ambient sample	PAMS	12	Air	
4	Sample	ambient sample	PAMS	12	Air	
5	Sample	ambient sample	PAMS	12	Air	
6	Sample	ambient sample	PAMS	12	Air	
7	Sample	ambient sample	PAMS	12	Air	
8	Sample	ambient sample	PAMS	12	Air	
9	Sample	ambient sample	PAMS	12	Air	
10	Sample	ambient sample	PAMS	12	Air	
11	Sample	ambient sample	PAMS	12	Air	
12	Sample	ambient sample	PAMS	12	Air	
13	Sample	ambient sample	PAMS	12	Air	
14	Sample	ambient sample	PAMS	12	Air	
15	Sample	ambient sample	PAMS	12	Air	
16	Sample	ambient sample	PAMS	12	Air	
17	Sample	ambient sample	PAMS	12	Air	
18	Sample	ambient sample	PAMS	12	Air	
19	Sample	ambient sample	PAMS	12	Air	
20	Sample	ambient sample	PAMS	12	Air	
21	Blank	humidified zero air	PAMS_calibration	1	Air	40.0
22	Quality control	CCV	PAMS_calibration	3	N2	5.0
23	Quality control	CCV	PAMS_calibration	3	N2	5.0
24	Quality control	SSQC	PAMS_calibration	3	N2	20.0
25	Sample	ambient sample	PAMS	12	Air	
26	Sample	ambient sample	PAMS	12	Air	
27	Sample	ambient sample	PAMS	12	Air	
28	Sample	ambient sample	PAMS	12	Air	
29	Sample	ambient sample	PAMS	12	Air	

Figure D-2: Markes sequence setup

Appendix E: Basics of Chromatography

This appendix is intended to assist the Auto-GC-FID operator in understanding basic terms and concepts of chromatography as well as proper techniques for data interpretation and processing. It is not meant as an in-depth discussion of chromatographic principles and theory, for which there are numerous available resources.

E.1. Basic Chromatography Theory

Briefly, a gas chromatograph (GC) separates the substances in an injected sample within a separation column containing a solid phase which inhibits the substances from being separated as they are carried through the separation column by an inert carrier gas flowing at a constant rate. The introduced substances are separated within the column based on their affinity for the solid phase, and at the end of the column exit, or elute, to a detector – for PAMS Auto-GCs, the detector is a flame ionization detector (FID). Typically, the GC oven containing the column is heated according to a temperature program to decrease the time it takes for later eluting substances and shorten the overall GC run time. The detector responds to the substance in proportion to the amount (i.e., mass) of substance as a function of time and the detector response and associated time since injection are continually recorded by the data system to prepare a chromatogram.

E.2. Anatomy of a Chromatogram

A GC chromatogram is a plot of the detector response as a function of time for a single injection on the GC. The detector response (on the y-axis or ordinate) is typically displayed in units of millivolts (mV), picoamperes (pA), counts per second (cps), or other relevant unit indicative of an electric or electronic change within the detector. Time (on the x-axis or abscissa) is displayed in minutes or seconds which starts at the injection time (the time the sample was injected onto the separation column). There will typically be a time delay for beginning data collection (acquisition) on a chromatogram such that the detector response recording begins just prior to the elution of the first expected target substance. Refer to Figure E-1 for a detailed example chromatogram illustrating basic chromatogram components.

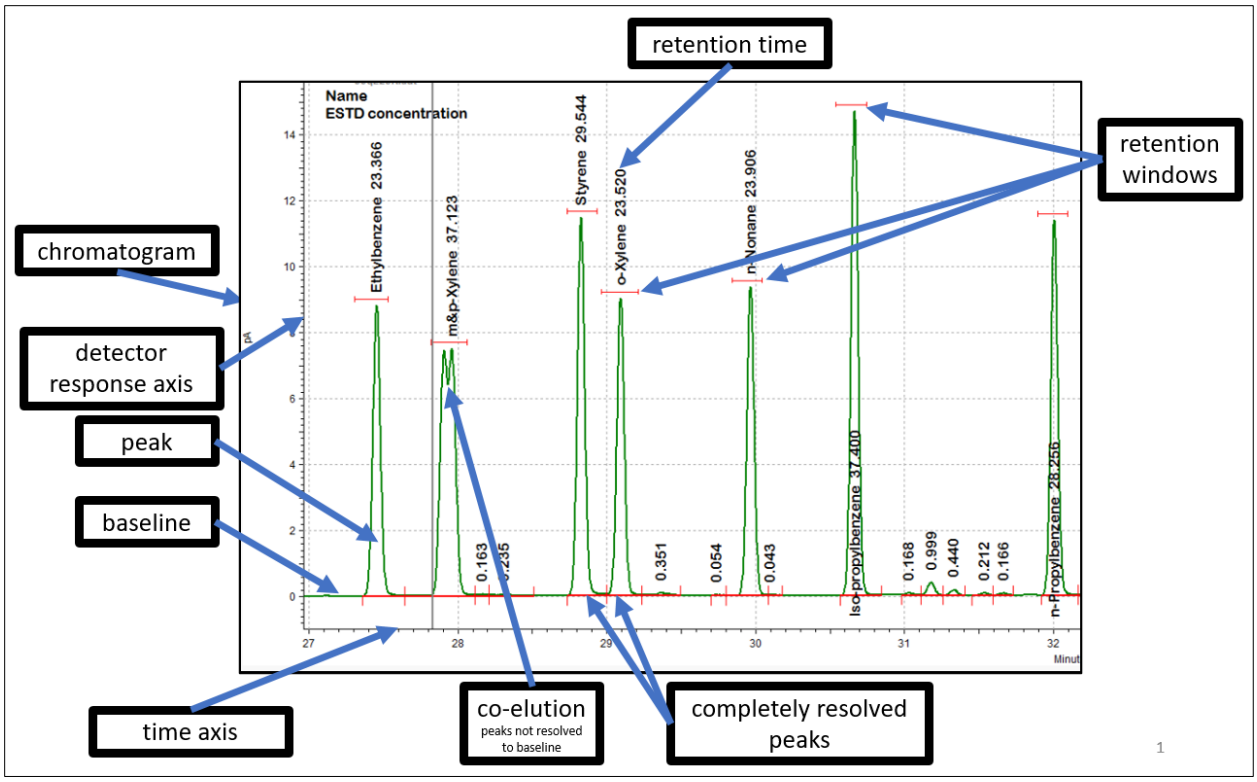


Figure E-1: Basic GC-FID chromatogram detailing components

E.3 Basic Chromatography Terminology

The following basic descriptions correlate to aspects of gas chromatography and/or chromatograms for which instrument operators must be familiar.

Baseline: The detector response to the carrier gas and make-up gas in the absence of a substance (Figure E-1). The baseline should be sufficiently free from noise. Baselines will typically exhibit some level of electronic noise as shown below in Figure E-2. While baseline anomalies, such as dips, rises, or spikes, are common, they may interfere with proper data processing.

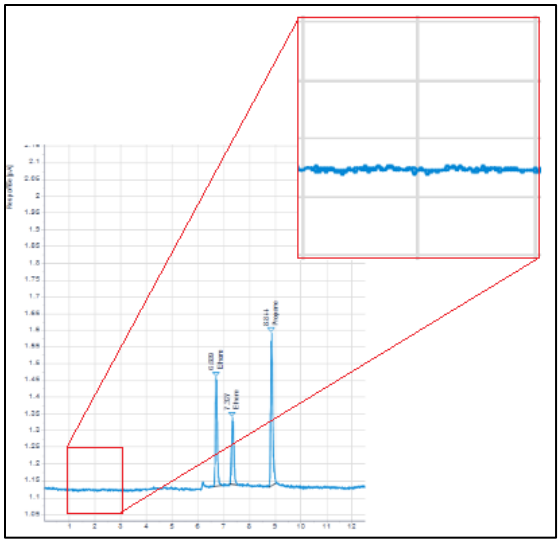


Figure E-2: GC-FID chromatogram detailing baseline noise

Chromatographic Peak: The increase and subsequent decrease of the detector response as a substance elutes from the GC column (Figure E-1). Chromatographic peaks for a single substance are ideally normal Gaussian in profile shape where the peak starts at the baseline, increases to the apex, and decreases to return back to the baseline (Figure E-3). It is common for peaks to be malformed, exhibiting asymmetry.

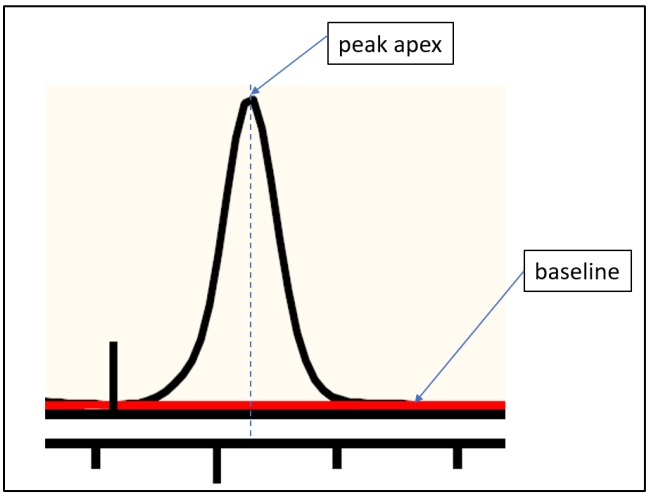


Figure E-3: Example GC chromatogram detailing peak apex and baseline

Co-elution: Simultaneous elution from the GC column of two or more substances resulting in overlapping of their chromatographic peaks where the detector response does not return to baseline between the substances (Figure E-1). Co-elutions for which one of the substances is of much smaller magnitude may show as peak shoulders or “riders” (Figure E-4).

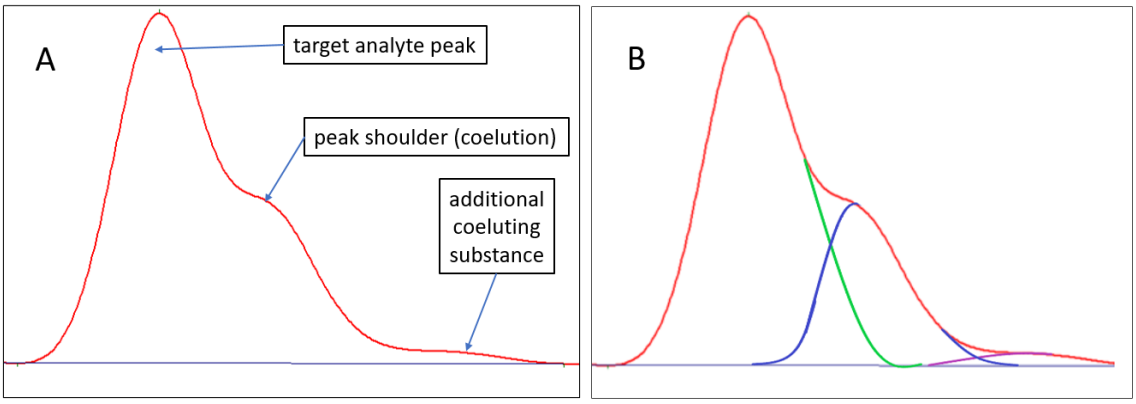


Figure E-4: Chromatogram showing three co-eluting substances (A) and approximate reconstruction of the individual peaks (B).

Retention Time (RT): The time relative to the time of injection that a substance elutes from the column (Figure E-1). The RT is defined at the peak apex (Figure E-3).

Retention Window: The range of time in the GC program during which a target analyte is expected to elute (Figure E-1). The GC operator defines the retention window for a given substance.

Resolution: The extent to which the detector response returns to the baseline between chromatographic peaks (Figure E-1). Peaks are considered to be completely resolved when the detector response returns to the baseline between peaks.

Peak Area: The defining of the bounds of the region under the detector response curve of a chromatographic peak (Figure E-3). This is defined by drawing a line to represent the baseline at the bottom of the peak and the area within these bounds is the total response of the eluted substance. Co-elutions complicate the definition of peak area.

Peak Integration: The defining of the boundaries of area under a chromatographic peak. The parameters for defining integration are user-defined and may be accomplished by chromatography data system (CDS) software (automated integration) or by analyst manual manipulation (manual integration).

Peak Tailing: Asymmetric chromatographic peak shape for which the majority of the peak's area occurs after the peak apex and typically exhibits a slow decay of the detector response back to the baseline (Figure E-5). Tailing peaks typically occur due to the substance having a strong affinity to the column solid phase and/or there is an active site that further inhibits movement of the substance within the column or GC inlet.

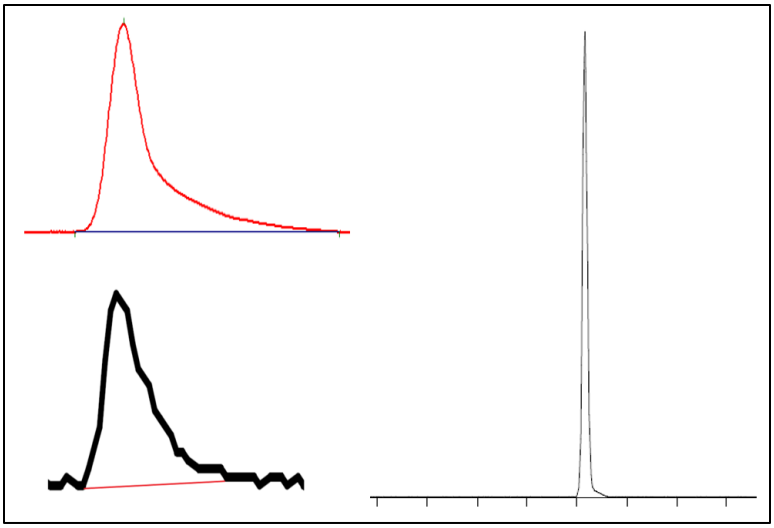


Figure E-5: Examples of tailing chromatographic peaks

E.4. Chromatographic Peak Integration

It is imperative that monitoring agencies define the methods of peak integration to be employed such that integrations are technically justifiable and consistently performed. For example, the chromatogram in Figure E-6 shows a series of four peaks integrated by two different technically justifiable conventions – tangent skim (A) and perpendicular drop (B). The tangent skim convention shown in this example represents the minimum peak area attributable to each peak; however, the perpendicular drop convention attempts to represent the peak areas when taking into account the baseline trend before and after this series of peaks. Given the magnitude of the baseline noise, both conventions are technically justified; however, this is an example for which the monitoring agency SOP must specify the convention preference to avoid ambiguity in justifying the selected convention.

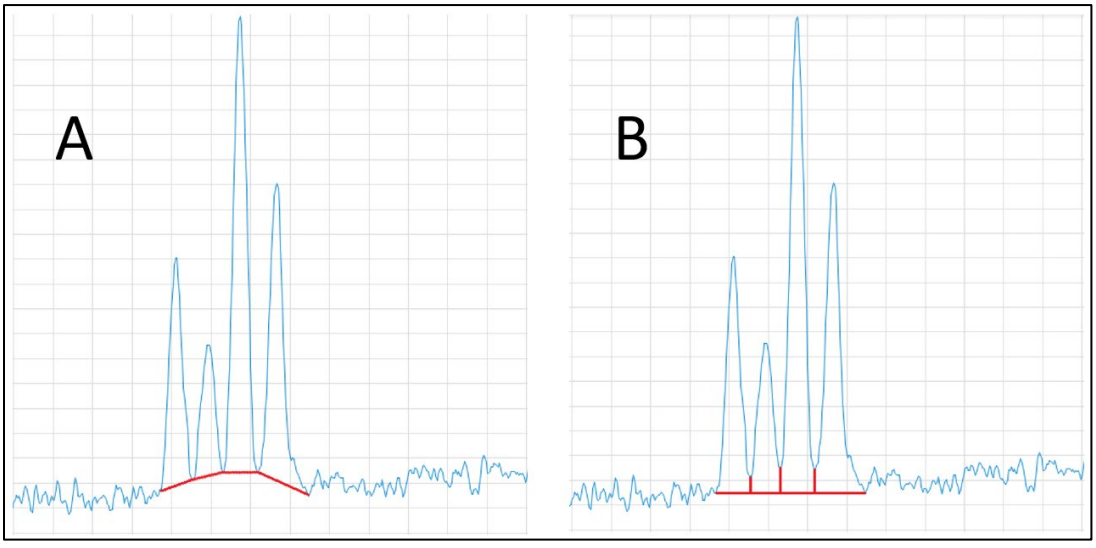


Figure E-6: Example integration of incompletely resolved chromatographic peaks employing tangent skim (A) and perpendicular drop (B).

Under no circumstances may peak integration be improperly adjusted in order to enable calibration standards or QC samples (e.g., blanks or calibration checks) to meet acceptance criteria.

The Agilent CDS software (whether the EZChrom, ChemStation, or OpenLab CDS) includes refined functions and routines for performing automated integration of chromatograms. The default integration parameter settings typically provide proper and suitable peak integration; however, some configuration adjustments may be needed for target analytes that exhibit a low response, are subject to RT shifts, exhibit co-elutions, and/or indicate other interferences.

Proper Integration Techniques

Peak integration is straightforward when chromatographic peaks occur on a stable baseline, have a sufficient (> 20:1) signal-to-noise ratio (S:N), and are completely baseline resolved (start and end at the baseline) without co-elutions. Integration becomes more difficult to perform properly when these conditions are not met and peaks exhibit a low signal-to-noise ratio, co-elutions, and/or the baseline is not stable or is very noisy. In these situations, the CDS automated integration parameters may appropriately integrate the given peak(s); however, may require manual override to integrate properly or according to monitoring agency policy.

A discussion of proper integration techniques follows:

Baseline-to-Baseline: Chromatographic peaks will be normally integrated such that the peak integration baseline start and stop corresponds to the portion of the detector response of the established baseline prior to and after the peak as shown below in Figure E-7.

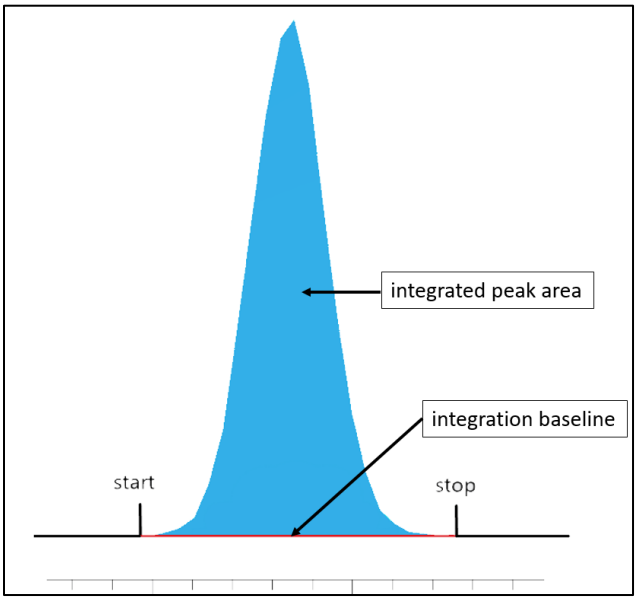


Figure E-7: Example baseline-to-baseline integration of a chromatographic peak.

Co-eluting chromatographic peaks result in an elevated detector response due to the contribution by the co-eluting substances. There are several methods for integrating the overlapping peaks, including the perpendicular drop and tangent skim.

Perpendicular Drop: For situations where the unresolved peaks are relatively similar in magnitude, the peaks can be integrated by dropping a perpendicular from the bottom of the valley between the peaks to the baseline to define the area of the peaks (Figure E-8).

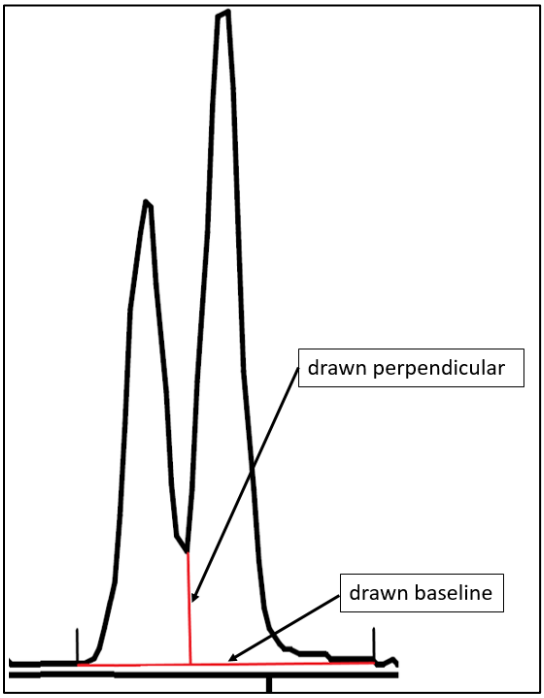


Figure E-8: Perpendicular drop integration for co-eluting peaks

Tangent Skim: For co-eluting peaks where one peak is much larger in magnitude, the peak integration can be accomplished by tangent skim. Tangent skim options within the CDS typically permit use of straight line or exponential tangent skimming, as shown in Figure E-9, peaks (A) and (B), respectively.

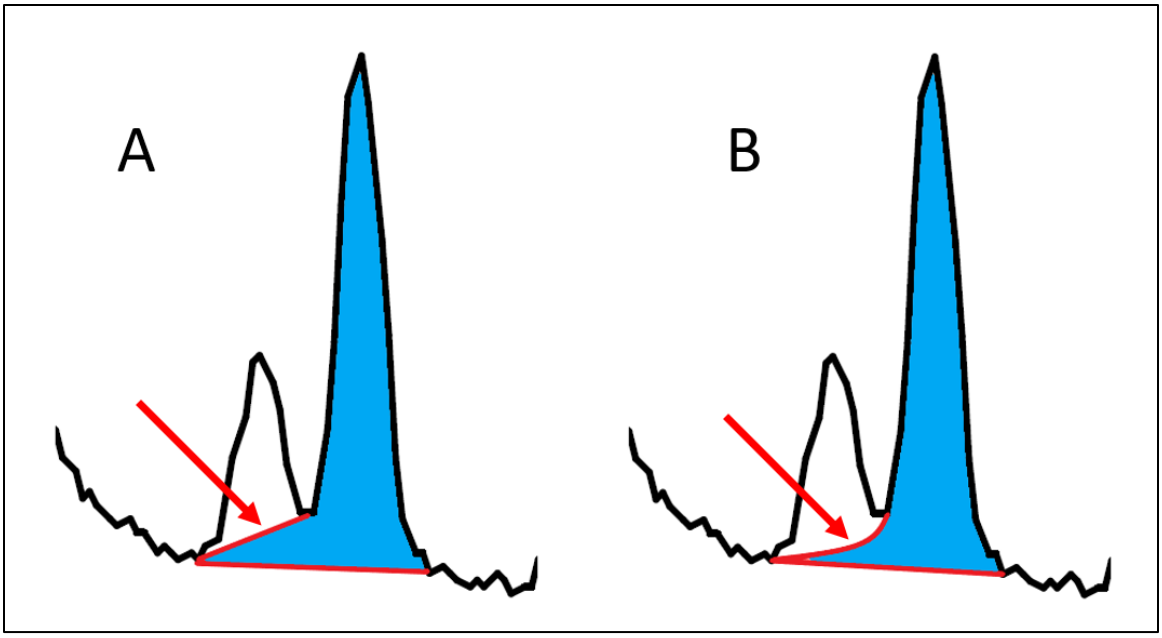


Figure E-9: Examples of straight Line (A) and exponential (B) tangent skim techniques

Improper Peak Integration Practices

Integrating Noise as Target Peak Area: CDS automated integration parameters may improperly identify and integrate baseline noise as target analyte peaks (Figure E-9). This typically occurs when the peak area reject threshold or peak height reject threshold parameter is set too low. Analysts will over-ride such automated identification and integration of noise as target analyte peaks.

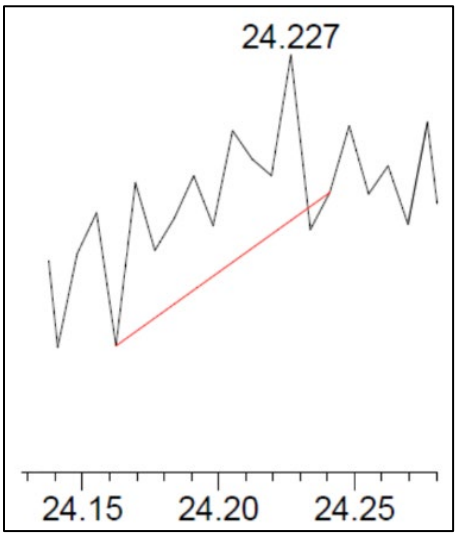


Figure E-10: Baseline noise improperly integrated as a target peak.

Peak Shaving: Peak shaving is the improper reducing of integrated peak area by improperly drawing baselines and/or perpendiculars. Examples of improper peak shaving integrations are detailed in Figure E-10.

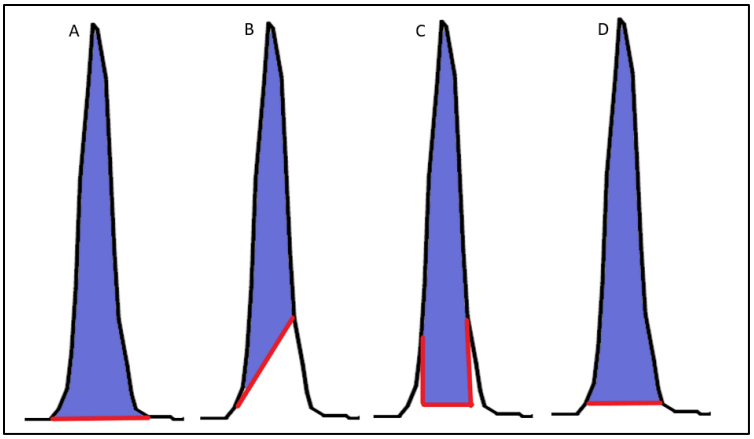


Figure E-11: Proper Peak integration (A), improper tangent skim (B), improper perpendicular drops (C), and improperly drawn baseline (D).

Peak Enhancement: Peak enhancement is the improper inclusion of peak area that does not belong to a chromatographic peak. Practices that improperly enhance peak area are shown in Figure E-12 and include:

1. including baseline noise or additional unrelated peaks before or after the target peak
2. including additional baseline area
3. including co-eluting peaks or shoulders

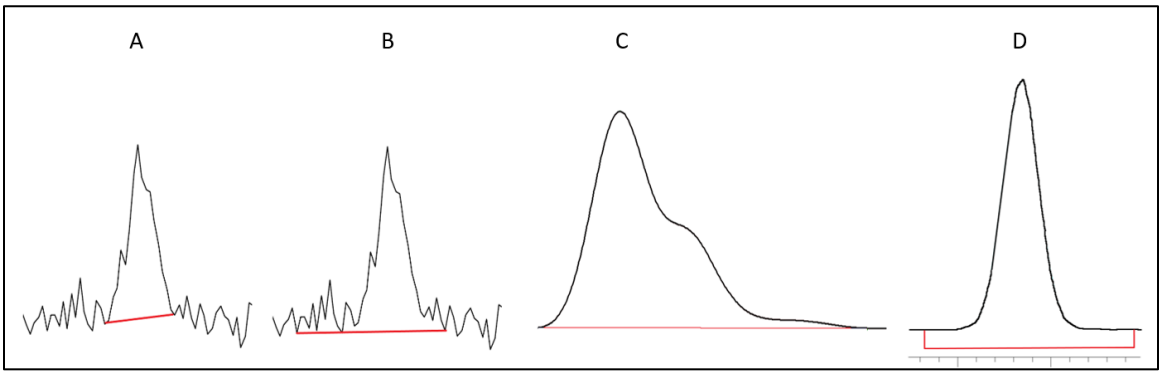


Figure E-12: Proper peak integration (A), improper inclusion of noise (B), improper inclusion of co-elutions (C), and improper inclusion of baseline (D)