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NORTH CAROLINA
Environmental Quality

DAQ-09-001.2 Standard Operating Procedure (SOP)
Markes-Agilent Automated Gas Chromatograph
OPERATOR RESPONSIBILITIES

Revision 0

1.0 Approval Sign Off-Sheet

I certify that I have read and approve of the contents of the Markes-Agilent Automated Gas Chromatograph Standard Operating Procedure with an effective date of April 22nd, 2021.

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Disclaimer: This document, and any revision hereto, is intended solely as a reference guide to assist individuals in the operation of the instrument, related to the North Carolina Division of Air Quality's Ambient Monitoring Program.

SOP Acronym Glossary

ADQ – Audit of data quality

AQS – Air Quality System (EPA's Air database)

ASTM – American Society for Testing Materials

AutoGC – Agilent Automated Gas Chromatograph with Markes Front End

°C – degrees Celsius

cc – cubic centimeter

cc/min – cubic centimeters per minute

CCV – Continuing calibration verification

CDS – Chromatography data system

CFR – Code of Federal Regulations

CGA – Compressed Gas Association

Chief – Ambient Monitoring Section chief

COA – Certificate of analysis

.csv – comma separated values file format

DAQ – North Carolina Division of Air Quality

DAS – Data acquisition system

DEQ – North Carolina Department of Environmental Quality

Director – Division of Air Quality Director

DIT – North Carolina Department of Information Technology

ECB – Electronics and Calibration Branch

e-log – electronic logbook

EPA – United States Environmental Protection Agency

EPC – Electronic Pressure Controller

ERG – Eastern Research Group

EST – Eastern Standard Time

FEM – Federal equivalent method

FID – Flame Ionization Detector

FRM – Federal reference method

GC – Gas Chromatograph

≥ - greater than or equal to

H2 – hydrogen gas

hr – hour

ICAL – Initial Calibration

ID – Inner diameter

in – inch

≤ - less than or equal to

L – Liter

LAB – Laboratory Analysis Branch of DAQ (4403 Reedy Creek Rd. Raleigh, NC 27607)

m – Meter

min – minute

mL – milliliter

mm – millimeter

MDL – Method detection limit

MIC – Markes Instrument Controller

MSA – Metropolitan statistical area

NC – North Carolina

NIST – National Institute of Standards and Technology

NIC – Network interface card

O_3 – Ozone

OD – Outer diameter

pA – picoamps

PAMS – Photochemical Assessment Monitoring Station

PC – Personal Computer

PDF – Portable document format

PDMS – Polydimethylsiloxane

PLOT – Porous layer open tubular

± - plus or minus

PM – Particulate matter

P/N – Part Number

PPB – Projects and Procedures Branch

ppb_c – parts per billion carbon

ppb_v – parts per billion volume

PPE – Personal protective equipment

psi – pounds per square inch

QA – Quality assurance

QA/QC – Quality assurance/quality control

QAPP – Quality assurance project plan

QC – Quality control

R^2 – correlation coefficient

RCO – Raleigh central office

RF – Response Factor

RPD – Relative Percent Difference

RSD – Relative Standard Deviation

RSD% - percent relative standard deviation

RT – Retention Time

RTS – Retention Time Standard

s – seconds

SOP – Standard Operating Procedure

SSCV – Second Source Calibration Verification

TB – Terabyte

TD – Thermal desorber

TSA – Technical systems audit

µm – micrometer

USB – Universal serial bus

VOC – Volatile organic compound

VPN – Virtual private network

.XLSX - Excel Microsoft Office Open XML Format Spreadsheet file

Table of Contents

2.0 SCOPE AND PURPOSE

The scope and purpose of this SOP is to describe the steps required to successfully calibrate, collect, analyze, process data, and validate data associated with the photochemical assessment monitoring station (PAMS) automated gas chromatograph (AutoGC) for hourly continuous operation during the monitoring season. The AutoGC is used to measure ozone (O_3) precursors, which are VOCs, that can react with nitrogen dioxides and sunlight to from ground level ozone at the Millbrook site located at 3801 Spring Forest Road in Raleigh, NC. This PAMS site is used to monitor the metropolitan statistical area (MSA) air-shed of Raleigh.

The AutoGC system is composed of a gas chromatograph coupled with a Markes front-end: including autosampler, water management device and thermal desorber. The Markes front-end cools down to negative 30°C to trap analytes and remove water from the sample collected over a 40-minute period at the top of each hour. The sample is then thermally desorbed from a sorbent trap and the compounds are transferred onto the gas chromatograph (GC) analytical column. The analytes are separated by their affinity to the column and produce unique retention times that allow for identification on dual flame ionization detectors.

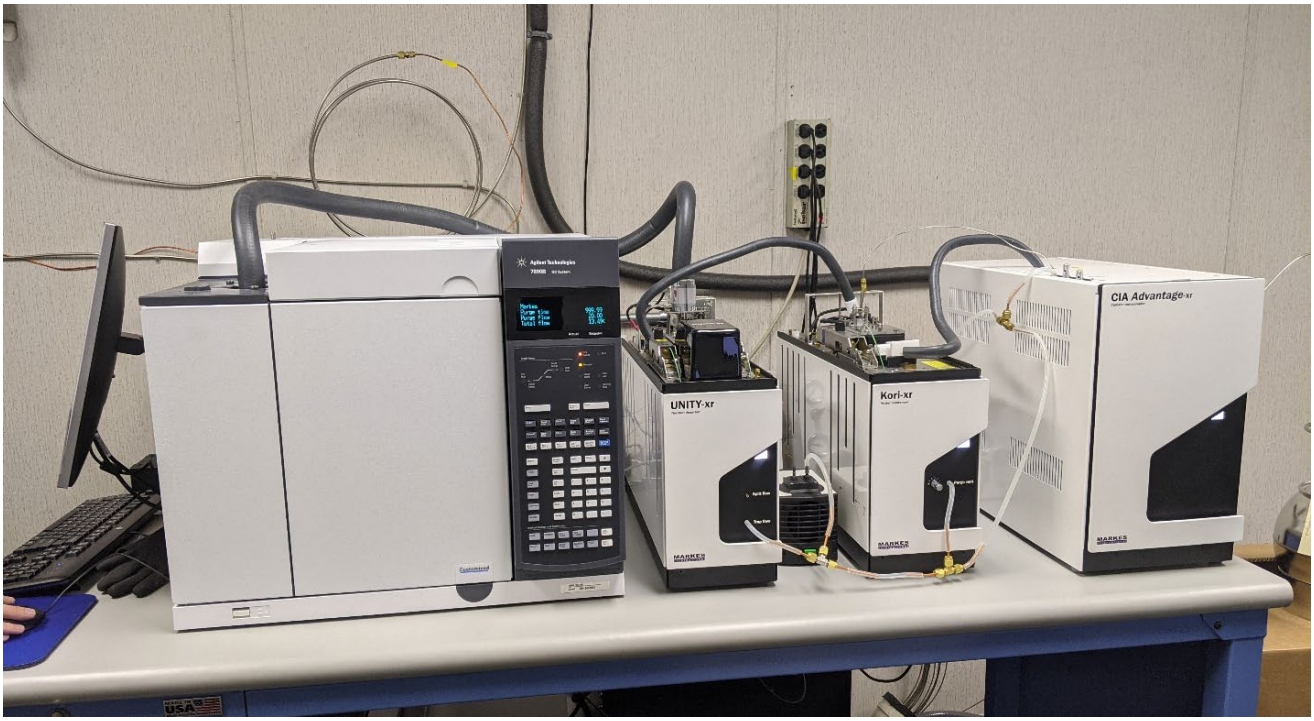

Figure 1: DAQ PAMS AutoGC System

3.0 EQUIPMENT CHECKS AND MATERIALS

This section describes the equipment materials that are required to complete the steps described in this document. Additional subsection(s) or SOPs will also describe the equipment and materials as needed.

3.1 Equipment and Material List

- Agilent 7890B custom GC equipped with:
  - Microfluidic Deans switch
  - Front and Rear flame ionization detectors (FIDs)

  - Agilent 50 m PLOT Al_2O_3-Na_2SO_4 0.32 mm ID column with an 8 µm film thickness or equivalent
  - Agilent 50 m PDMS-coated durabond-1 0.32 mm ID capillary column with a 1.05 µm film thickness or equivalent
  - 0.6 m, 0.100 mm ID transfer line
- Markes Front End System directly interfaced with GC:
  - Markes CIA Advantage-XR with 16-port heated sampling interface
    - Heated transfer line to Kori-XR
  - Markes Kori-XR water management device
    - Empty cold trap (P/N MKI-U-T1KORI or equivalent)
    - Heated transfer line to Unity-XR
  - Markes Unity-XR TD system
    - PAMS (VOC O_3 precursors) trap (P/N MKI-U-T20PAM or equivalent)
    - Heated transfer line to GC
    - Sampling Pump – KNF model N86KN.18 or equivalent
- Desktop computer with Windows 10 operating system and monitor equipped with:
  - USB mouse and keyboard
  - Cradle-Point cellular modem on VPN for secure access into the State of North Carolina network
  - Ethernet Cable
  - 2 TB USB external backup hard drive
  - Agilent Openlab CDS ChemStation software revision C.01.10[201] or higher
  - Markes MIC 2.0 software version 2.0.5 or higher
  - Microsoft office 365 software suite
  - Adobe PDF reader
- Compressed Gasses:
  - Hydrogen gas cylinder (Arc3 Gases Grade 6.0 or equivalent)
    - 1x1 Concoa auto-switchover CGA 350 manifold or equivalent
    - Agilent in-line gas clean moisture filter (P/N CP17971) and hydrocarbon filter (P/N CP17972) or equivalent
    - 1/8-in chromatograph grade tubing stainless steel or copper and corresponding compression fittings and ferrules
    - Equipped with Pulsa telemetry system
  - Helium gas cylinder (Arc3 Gases Grade 6.0 or equivalent)
    - 1x1 Airgas auto-switchover CGA 580 manifold or equivalent
    - Agilent in-line gas clean moisture filter (P/N CP17971) and hydrocarbon filter (P/N CP17972) or equivalent
    - ¼-in and 1/8-in chromatograph grade tubing stainless steel or copper and corresponding compression fittings and ferrules
    - Equipped with Pulsa telemetry system
  - Compressed Air (Arc3 Gases grade 0.1 ultra-zero or equivalent)
    - 3x3 Airgas auto-switchover CGA 590 manifold or equivalent
    - Agilent in-line gas clean hydrocarbon filter (P/N CP17972) or equivalent

        - ¼-in and 1/8-in chromatograph grade tubing stainless steel or copper and corresponding compression fittings and ferrules
        - Equipped with Pulsa telemetry system
    - Nitrogen gas cylinder (Arc3 Gases Grade 5.0 or equivalent)
        - 1x1 Concoa auto-switchover CGA 580 manifold or equivalent
        - 1/8-in chromatograph grade tubing stainless steel or copper and corresponding compression fittings and ferrules interfaced with a Restek humidification chamber, or equivalent, and connected to the CIA-Advantage™ "Humid Gas Purge" port. Fill the humidification chamber about two-thirds of way with Type 1 ASTM Deionized Water.
        - Equipped with Pulsa telemetry system
    - Wall mounted cylinder straps, one per cylinder
    - Gas grade purity information is detailed in appendix A
- Agilent Electronic handheld gas leak detector model G3388B or equivalent
- Snoop leak detection fluid
- AutoGC Inlet: composed of an inverted stainless steel conical rain guard connected to 17 in of ¼-in OD (0.21 in ID) chromatographic grade stainless steel tubing coupled to a 15 µm particulate filter and 207 in of 1/8-in OD (0.085 in ID) chromatographic stainless-steel tubing that is directly interfaced with the CIA-Advantage-XR on the AutoGC system.
- PPE:
    - Steel-toe nonslip shoes or boots
    - Gloves
        - Textured grip, heat resistant work gloves
        - Nitrile gloves
    - Safety glasses: prescription or impact resistant are acceptable
- Certified clean 6-L Silco-treated summa canisters
    - Certification and cleaning process detailed in **SOP DAQ-03-005.2 Entech 3100A Canister Cleaner Operation**
- NIST-traceable analytical compressed gas standards stored at the DAQ LAB:
    - Airgas Specialty Gases – 56 VOC compound blend at 100ppb$_v$, balance nitrogen. A COA detailing all compounds contained in the standard is included in Appendix B.
    - Linde SPECTRA Environmental Gases – 61 VOC compound blend at 100 ppb$_v$, balance nitrogen. A COA detailing all compounds contained in the standard is included in Appendix C.
- Various lengths of 1/16-in (0.02 in ID), 1/8-in, ¼-in stainless steel chromatographic grade tubing and corresponding compression fittings and ferrules
- Required hand tools:
    - Adjustable tubing cutter
    - 9/16-in wrench
    - ½-in wrench
    - 7/16-in wrench
    - ¼-in wrench
    - 6 or 8-in Adjustable wrench
    - 12-in Adjustable wrench or larger (for cylinders)
    - Philips head screwdriver

  - Flat head screwdriver
  - T20 Torx screwdriver
  - Ceramic column scorer
  - Markes trap alignment and removal tools
  - Markes o-ring insertion and removal tools
- Agilent ADM flow meter model G6691-90000 with valid flow cartridge and certificate. Flow certificate example shown in Appendix D.
- NIST-Traceable Clock: Fisherbrand Traceable Big-Digit Radio Atomic Wall Clock or equivalent – see certificate of calibration in Appendix E
- KimTech lint free wipe or equivalent
- Agilent CrossLab Silver Support Contract or equivalent:
  - Covers entire AutoGC system for parts, labor, and travel for repairs and service.
  - Unlimited telephone technical support at 1-800-227-9770.
  - Yearly preventative maintenance.

3.2 Chemical and Material Checks

Chemicals and materials used in this SOP are inspected prior to use and upon receipt at the LAB. No damaged, uncalibrated, or expired equipment is to be employed in the discharge of procedures detailed in this document. Standards are prepared by **DAQ SOP-03-006.2 Entech 4700 Precision Diluter Operations** in certified clean 6-L canisters run through **DAQ SOP-03-005.2 Entech 3100A Canister Cleaner Operations.**

3.3 AutoGC Instrument Module Checks

3.3.1 FID Baseline Check

Examine the FID output in Agilent Openlab CDS ChemStation prior to any execution of an analytical sequence. If the baseline output is about 10 pA, then refer to section 9.2 for corrective action.

3.3.2 Kori Trap Purge Flow Check

Turn on the Agilent ADM flow meter and allow it to warm up for 60 seconds. Connect the flow meter tubing to the Kori purge vent by removing the already connected polymer tubing circled in red in the figure below:

Figure 2: Kori water condenser with purge vent circled in red

Engage a Markes sequence as detailed in section 5.4 and 5.6. Measure the purge flowrate as the Kori operates the purge step, it should read 100cc/min on the flow meter. If it is not, see section 9.13 for corrective action. Reconnect the polymer tubing to the purge vent when measurement is complete.

3.3.3 Markes Instrument Controller (MIC) System Diagnostics

Open the MIC software to create a sequence as detailed in section 5.4 using the method "TD – Unity: System Diagnostics." This method will leak check the Markes Unit, CIA-Advantage, and Kori to confirm that all valves, solenoids, and heated zones are functional. If a leak or nonfunctional sector has been identified please see sections 9.7, 9.10 or 9.11 for corrective action.

3.4 Support Equipment Checks

3.4.1 Helium and Hydrogen Leak Checks

Power on the Agilent G3388B electronic leak detector and allow it to warm up as shown below:

Figure 3: Agilent G3388B Leak Detector and Probe

The warmup procedure takes 90 seconds. Do not skip this step. The leak detector will beep once the warmup is complete. Gas can be heard audibly flowing through the meter while it is powered on. Place the G3388B probe against all the fittings, valves, and pressure sensors/gauges. Wait about 10-15 seconds per point of interest to allow the gas to reach the leak detector. The detector will read R_LO and bars will fill the screen when a leak is found. The detector will also beep. If a leak is identified in this manner see section 9.10 for corrective action.

3.4.2 Canister Leak Checks

Connect a pressurized, must be greater than ambient conditions, 6-L canister to the CIA-Advantage with supplied 1/16-in chromatographic grade stainless steel tubing fittings. On both fitting ends, dispense snoop leak detection fluid. Open the canister and look for bubbles flowing through the fluid, if any are present a leak has been detected and must be corrected as detailed in section 9.10. Dry fitting connections with a lint free wipe.

4.0 SITE CHECKS

4.1 Daily Operator Check

1 Each workday the operator must remotely connect or physically visit the site to verify the instrument is operational. Any anomalous operation must be recorded and rectified in the electronic logbook.
2 Verify the Pulsa gas system is monitoring gas usage and order replacement cylinders as needed to maintain analytical operations.
3 Data should be processed in a timely manner such that QC checks do not cause large gaps of invalid data. Data is collected in weekly brackets that each begin and end with continuing calibration verification (CCV) and humid blank analyses. Minimally, inspect these chromatograms response daily to ensure the instrument is quantitating appropriately. See section 5.11 for data processing details.

4.2 Site Inventory Check

Each time the site is visited by the operator the inventory of all supplies and consumables should be checked. Any consumed supplies must be reordered and replaced. Minimally the site will contain:

1 One set of back up Agilent columns (one PLOT and one durabond - detailed in section 3.1)
2 One set of back up Agilent gas-clean filters (2 moistures and 3 hydrocarbons - detailed in section 3.1)
3 Six compressed air cylinders as detailed in section 3.1
4 Two helium cylinders as detailed in section 3.1
5 Two hydrogen cylinders as detailed in section 3.1
6 Two nitrogen cylinders as detailed in section 3.1
7 Tools listed in section 3.1
8 One box of KimTech lint-free wipes
9 One bottle of Snoop leak detection fluid
10 One electronic leak detector as detailed in section 3.1
11 One box of Various lengths of 1/16-in (0.02 in ID), 1/8-in, ¼-in stainless steel chromatographic grade tubing and corresponding compression fittings and ferrules
12 One Agilent ADM flow meter with valid flow cartridge as detailed in section 3.1.
13 One set of backup Markes traps: Kori-xr (P/N MKI-U-T1KORI) and Unity-xr (P/N MKI-U-T20PAM).
14 Box of nitrile gloves.
15 Four bottles of Type 1 ASTM Deionized Water

4.3 Site Operator Checks

Each time the operator visits the site the following must occur:

1 Inspect the pressure of the four manifolds: order and replace helium, hydrogen, air, or nitrogen as needed.
2 Inspect the indicators on the Agilent gas clean moisture filters. Replace if the filter has changed to the depleted color as diagrammed on the top of the filter. See section 9.14 for details.
3 Inspect the temperature of the shelter on the digital thermostat. The shelter should maintain a temperature of 20-30°C. The set-point of the thermostat is 27.5°C to prevent water condensation within the insulated sampling inlet on high dew-point days.
4 Examine all site power connections and conditions. Document any outages in the site electronic logbook.

5 Verify the computer date and time and GC date and time are ± 1 minute against the NIST-Traceable Clock: Fisherbrand Traceable Big-Digit Radio Atomic Wall Clock. If not, see section 9.12 for corrective action.

Note: DAQ does not observe or correct for daylight savings time on monitoring equipment. All recorded times are displayed in Eastern Standard Time (EST).

4.4 Inlet Probe Residence Time Check

Residence time is obtained by using the purge flow rate of the MIC system method. The PAMS_AutoGC method uses a 100 cc/min purge for two minutes. In 20 seconds, 33.33 cc of gas will have moved through the inlet to the back of the analyzer. The back of the analyzer is considered, in this application, to be the inlet connection at the CIA-Advantage. The inlet is 17 in of ¼-in OD (0.21 in ID) chromatographic grade stainless steel tubing coupled to a 15 µm particulate filter and 207 in of 1/8-in OD (0.085 in ID) chromatographic stainless-steel tubing connected to port 1 on the Markes CIA-Advantage. It has a total volume of 28.88 cc. The total volume of the inlet is replaced in under 20 seconds, meeting the residence time requirement in approved **DAQ-01-007 PAMS Required Network QAPP**. Confirm that the PAMS_AutoGC method is used in the Markes software to sample ambient air through the inlet to continuously meet this requirement.

5.0 DETAILED PROCEDURES

5.1 Laboratory Humid Blank, PAMS Calibration Standard and QC Standard Preparation

Humid blanks, PAMS calibration standards and QC standards will be prepared according to **SOP DAQ-03-006.2 Entech 4700 Precision Diluter Operations** and will not be covered in this document.

5.2 Instrument Nomenclature

Injections will be named via the following format in both the **Markes MIC 2.0 software** and **Agilent Openlab CDS ChemStation**:

1 Filename Format = **PAMSYYYYMMDDHrT**
2 **YYYY** is the 4-digit year
3 **MM** is the 2-digit month (01-12)
4 **DD** is the 2-digit day of the month (01-31)
5 **Hr** is the 2-digit hour of the day in the 24-hour time (00-23)
6 **T** is the type of injection collected. **T** can be **A** (ambient air), **B** (humid blank), **C** (CCV), **I** (initial calibration or ICAL), **M** (method detection limit or MDL standard), **P** (precision standard sample), **S** (second source calibration verification or SSCV), **X** (experimental, troubleshooting, and conditioning)
7 For an ambient air sample collected on June 1st, 2021 at 0:00 the file name format would be PAMS2021060100A.

Sequences are executed at operator discretion. A small sequence may be used to troubleshoot or calibrate the instrument, while standard monitoring sequences will span a week. **Sequences** will be named via the following format in both the **Markes MIC 2.0** software and **Agilent Openlab CDS ChemStation**:

1 Filename Format = **YYYYMMDDA**
2 **YYYY** is the 4-digit year

3 **MM** is the 2-digit month (01-12)
4 **DD** is the 2-digit day of the month (01-31)
5 **A** is the unique sequence identifier if more than one sequence is needed on a given day. This value will increment alphabetically: A, B, C…
6 For sequences initiated on June 1st, 2021 the sequence name would be 20210601A.

5.3 AutoGC System Setup

Note: The instrument was installed at the site by the instrument manufacturer with the aid of the LAB chemist. While installed at the site, the instrument will be maintained by the instrument manufacturer and LAB chemist to ensure functionality. For detailed installation instructions see **future DAQ SOP DAQ-09-001.1 Markes-Agilent Automated Gas Chromatograph ECB Responsibilities.**

1 Open all gas cylinders and set the zero air, helium, and hydrogen manifolds to maintain an outlet pressure of 100 psi. Set the nitrogen manifold to an outlet pressure of 50psi.
2 Open Markes system regulators and set the carrier gas pressure to 60 psi and the purge gas pressure to 60 psi.
3 Power on all systems: computer, monitor, GC, Markes front-end and pump. The GC power button is located on the lower left front corner of the GC. The Markes CIA-Advantage, Kori and Unity power switches are in the back of the units. The Markes system pump power switch is the green switch located on the front of the pump.
4 The GC will try to auto-ignite the FID detectors after they warm up. This can take several minutes to occur. An audible crackle will be heard when the FID is lit. To check the FID ignition manually, use the following keypad button sequence and figure: Select either “Front Det” for the front detector or “Back Det” for the rear detector. Use the up and down arrows to navigate to H2 flow, air flow and make up flow. Press on/yes and then enter to engage the flow if it is not already running. Use the up and down arrow to navigate to flame and press on/yes and enter. The system will switch from off to igniting. Once a popping noise is heard the flame has ignited and the detector will switch to on mode. Repeat the steps for the detector not selected previously. Once both FIDs are ignited the system can be used for analysis after a 30-minute equilibration period.

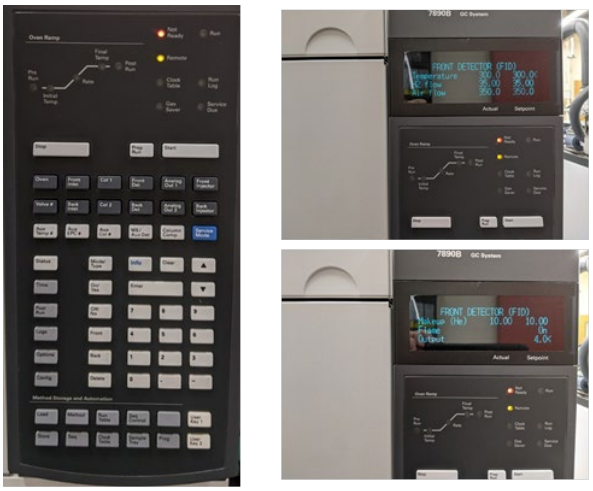

Figure 4: Agilent 7890B GC Keypad and System Detector Screens

5 Connect the AutoGC inlet line to port 1 of the CIA-Advantage heated interface. Document this connection in the electronic logbook.

6 Connect 6-L summa canister(s) to desired port(s) with 1/16 in (0.02 in ID) tubing and appropriate fittings. Log connections to CIA-Advantage ports in the site electronic logbook. Document any canister changes. An example of the site logbook can be seen in appendix F.

5.4 Markes Instrument Controller (MIC) System Operation

1 Open Markes Instrument Controller: MIC 2.0. A dialogue box will appear, and the software will establish communication with the CIA-Advantage, Kori, and Unity. Refer to the applicable subsections of section 9 of this document for troubleshooting of the Markes System. The system dialogue box pictured below should open:

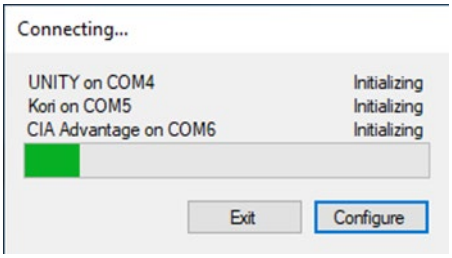

Figure 5: MIC 2.0 System initialization Dialogue

2 Once loaded select from the options shown below: Method Editor, Sequence or Sequence History.

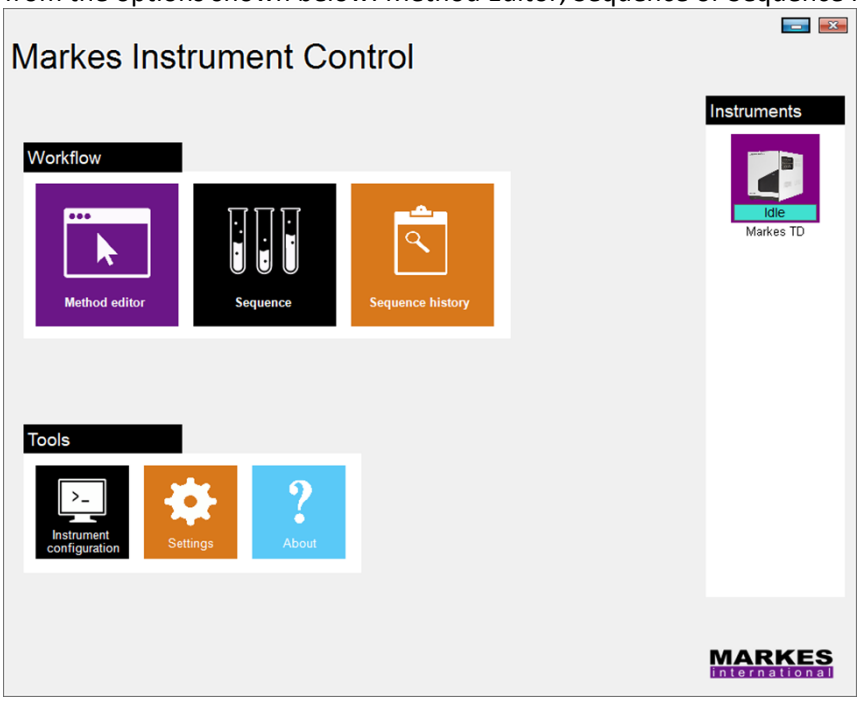

Figure 6: MIC 2.0 Home Screen

3 **Method editor** allows the user to create and alter methods used for trapping PAMS VOCs. The default trapping method is named PAMS_AutoGC. The settings for this method are shown in the figure below:

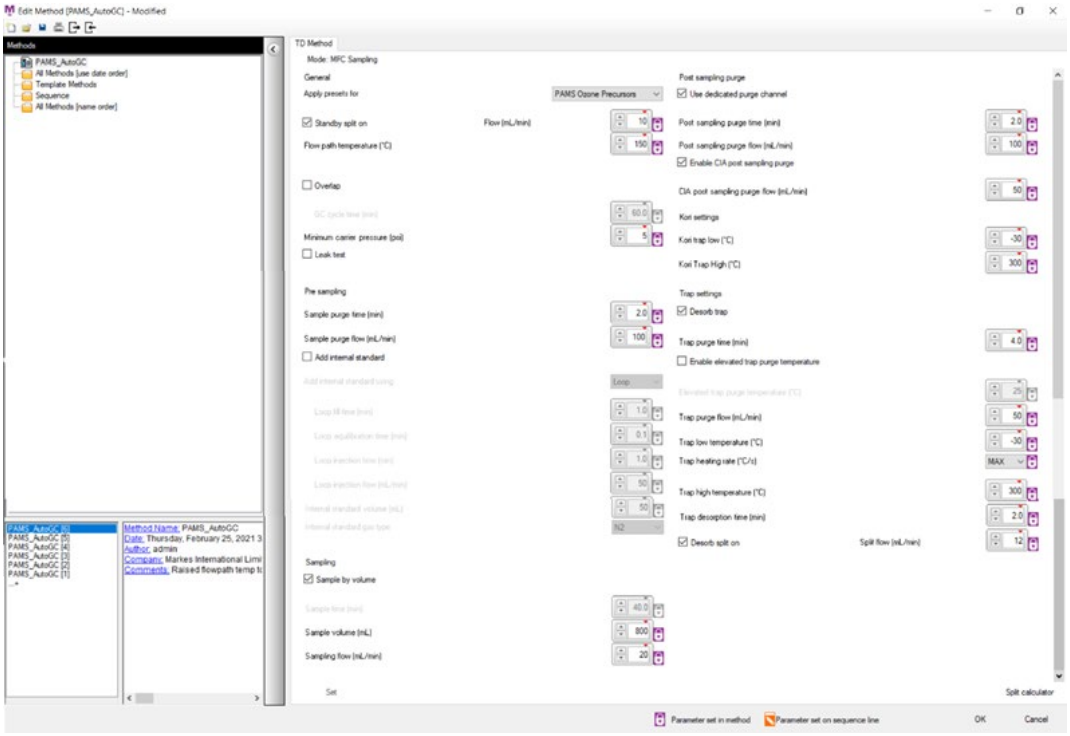

Figure 7: MIC Method Editor for PAMS_AutoGC Trapping Method

4 **Sequence** allows the user to create an acquisition or troubleshooting sequence. It yields useful read back information about the status of the GC and Markes system that can be used for diagnostic or troubleshooting purposes. See figure below of the sequence generation screen:

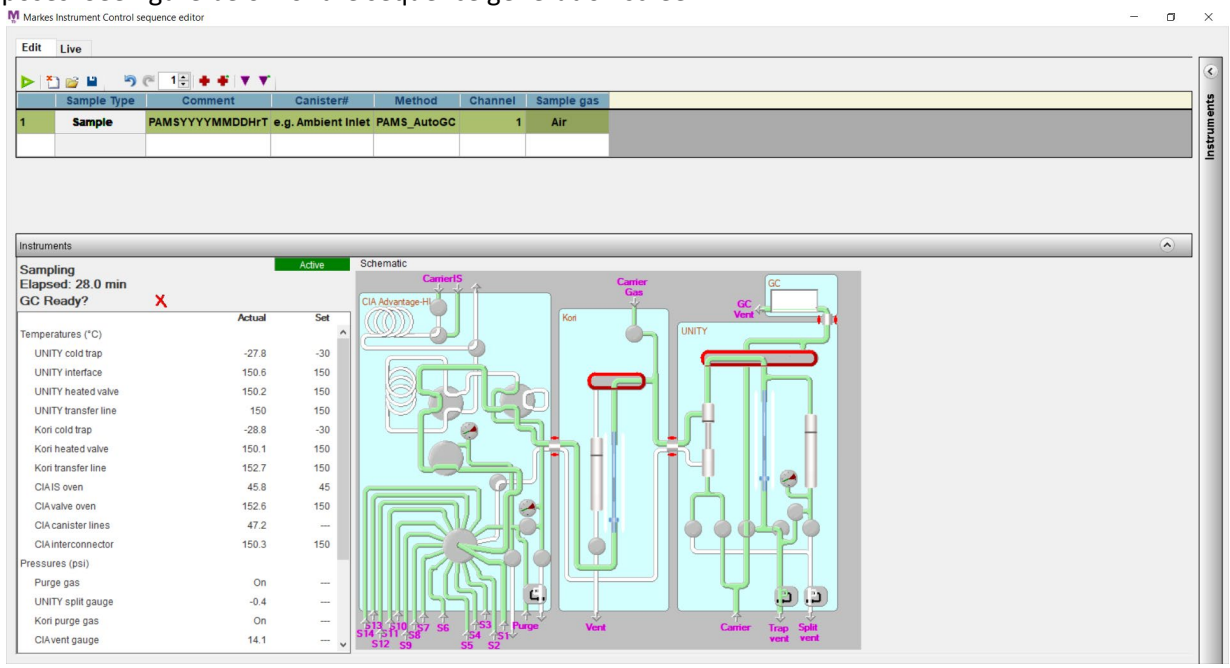

Figure 8: MIC Sequence Table

5 Name the **injection** following the sample nomenclature outlined in Section 5.2 of this document in the **Comment** field.

6 Double click in the method column and select the **PAMS_AutoGC** method from the **All Methods** folder.

7 Select the desired channel (1-16) for the injection. Enter this value in the **Channel** field.
8 Select the sample matrix for the mass flow controller: **Helium**, **Nitrogen**, or **Air** in the **Sample Gas** field.
9 To populate more injections, type the desired number in the box left of the red plus sign in the menu bar.
10 Click the red plus sign to add that many boxes to the sequence list. Follow steps 5-8 above for all added injections to the sequence. Alternatively, the purple, fill down, arrow can be clicked, and the entire column will be populated with first cell input and edited appropriately.
11 Press the blue floppy disk icon to save the **sequence** following the sequence nomenclature outlined in Section 5.2 of this document.
12 **Sequence History** allows the user to view past injection data with an option to export the data. Each sequence, after it is complete, creates a log that is exported by entering this menu and inputting the analysis date windows. The system will automatically find sequences related to that time window and allow the user to export data as a .csv file for review and archive. Completed analytical sequences are exported and saved as **Sequence Name Markes Export**. See figure below for example of past sequence:

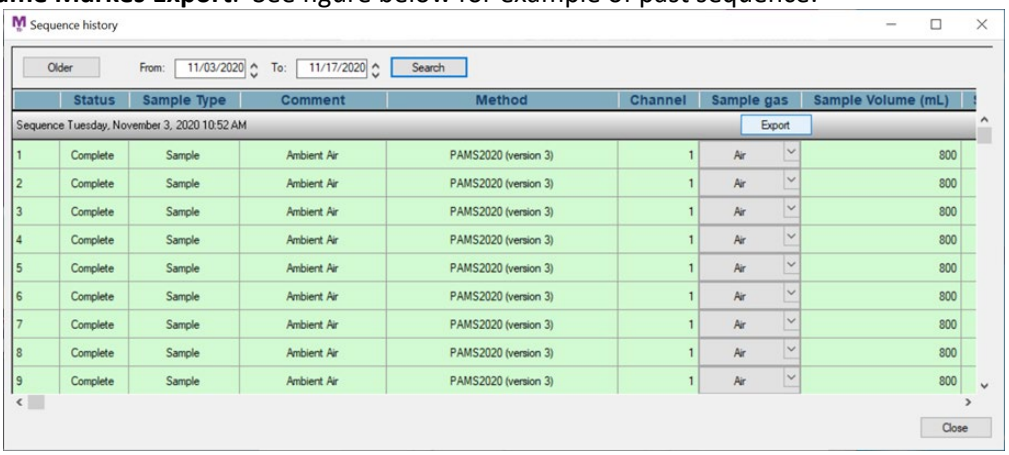

Figure 9: MIC Sequence History Viewer

13 To run an injection, select **Sequence** and fill in the columns with the desired selections. Select the **PAMS_AutoGC** method to capture 800mL of gas at 20 cc/min for 40 min. The 800 mL sample will begin collection at the top of the hour and run each subsequent collection hourly (e.g., collection times 0:00-0:40, 01:00-01:40, 02:00-02:40...).

5.5 Agilent Openlab CDS ChemStation Operation

1 To connect to the Agilent 7890B GC, double click on the **PAMS-Millbrook (online)** icon on the site computer. The following initialization screen will appear upon establishing a connection with the GC via the network interface card (NIC):

Figure 10: Agilent OpenLab CDS ChemStation Initialization Dialogue

2 Load the **PAMS_AutoGC.m** method. The method can be changed by selecting one from the **Master Method** menu located on the left-hand side of the software as depicted below:

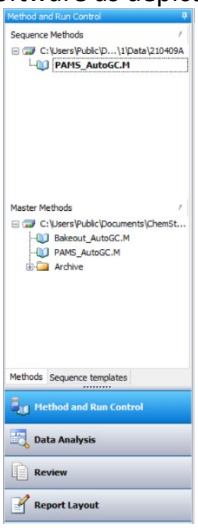

Figure 11: Agilent OpenLab CDS Chemstation Master Methods

3 Verify that the baseline of both FID detectors is flat and below 10 pA. If it is not, see section 9.2 for troubleshooting.

4 To enter analysis information, open the sequence table by selecting **Sequence** from the menu bar and **Sequence Table** from the dropdown box. Enter information into the sample table as follows:

Sequence Table: PAMS-Millbrook

Line	Sample Location	Sample Name	Method Name	Injector Location	Injection Source	Injection Volume	Inj/Loc	Sample Type	Cal Level	Update RF	Update RT	Cal Inte...	Sample Amount	Dilution	Sample Information	Data File	Lims ID1
1	1	PAMS2021040907X	PAMS_AutoGC	Front	As Method	800	1	Sample						1	Ambient Air	PAMS2021040907X	Ambient Air
2	1	PAMS2021040908X	PAMS_AutoGC	Front	As Method	800	1	Sample						1	Ambient Air	PAMS2021040908X	Ambient Air
3	1	PAMS2021040909X	PAMS_AutoGC	Front	As Method	800	1	Sample						1	Ambient Air	PAMS2021040909X	Ambient Air
4	1	PAMS2021040910X	PAMS_AutoGC	Front	As Method	800	1	Sample						1	Ambient Air	PAMS2021040910X	Ambient Air
5	1	PAMS2021040911X	PAMS_AutoGC	Front	As Method	800	1	Sample						1	Ambient Air	PAMS2021040911X	Ambient Air
6	1	PAMS2021040912X	PAMS_AutoGC	Front	As Method	800	1	Sample						1	Ambient Air	PAMS2021040912X	Ambient Air
7	1	PAMS2021040913X	PAMS_AutoGC	Front	As Method	800	1	Sample						1	Ambient Air	PAMS2021040913X	Ambient Air
8	1	PAMS2021040914X	PAMS_AutoGC	Front	As Method	800	1	Sample						1	Ambient Air	PAMS2021040914X	Ambient Air
9	1	PAMS2021040915X	PAMS_AutoGC	Front	As Method	800	1	Sample						1	Ambient Air	PAMS2021040915X	Ambient Air
10	1	PAMS2021040916X	PAMS_AutoGC	Front	As Method	800	1	Sample						1	Ambient Air	PAMS2021040916X	Ambient Air

Figure 12: Agilent OpenLab CDS Chemstation Sequence Table Example

5 The **Sample Location** will match the port number on the CIA advantage that is selected for the injection.

6 The **Sample Name** will be entered in the format of Section 5.2. The **Sample Name** column will match the **Data File** column. The instrument will save a unique data file for each hourly injection.

7 The **Method Name** column will use the **PAMS_AutoGC** method.

8 The **Injection Location** should be filled in with **Front** to indicate the front electronic pressure control (EPC) unit will run the GC method.

9 The **Injection Source** column is filled by default with **As Method**.

10 The **Inj/Loc** column is not used and is filled by default with **1**.

11 Fill the **Sample Type** drop down menu with the applicable type: select **Sample** (default), **Blank**, **Calibration** or **Control Sample**.

12 **Cal Level**, **Update RF**, and **Update RT** is only used during calibration. Enter the **Cal Level**, if applicable and select **Replace** for the **Update RF** and **Update RT** fields. This is only done to recalibrate an already calibrated instrument.

13 **Sample Amount** is unused and left blank.

14 **Dilution** should be filled with **1** to indicate the sample is undiluted.

15 **Lims ID1** can include details about the injection: whether it is ambient air, a humid blank, or the nominal concentration of a standard are some examples of applicable information for this column.

16 Press **Ok** and save the **Sequence** with the nomenclature described in Section 5.2 by selecting **File** from the menu bar. Select **Save As** and then **Sequence Template**.

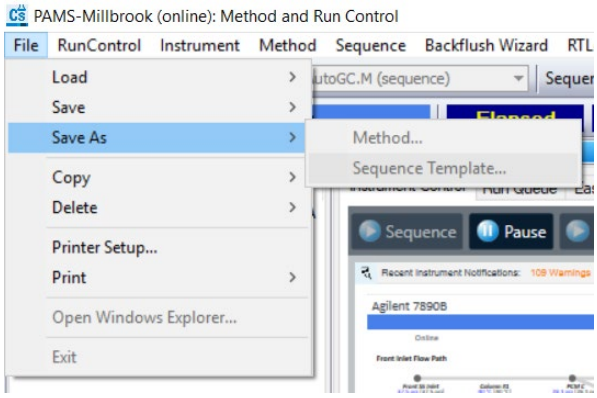

Figure 13: Agilent OpenLab CDS ChemStation Sequence Save

17 To edit and view the analytical method loaded, select **Method** from the menu bar and click on "**Edit Entire Method** from the drop-down menu. The **PAMS_AutoGC.m** method details are shown below:

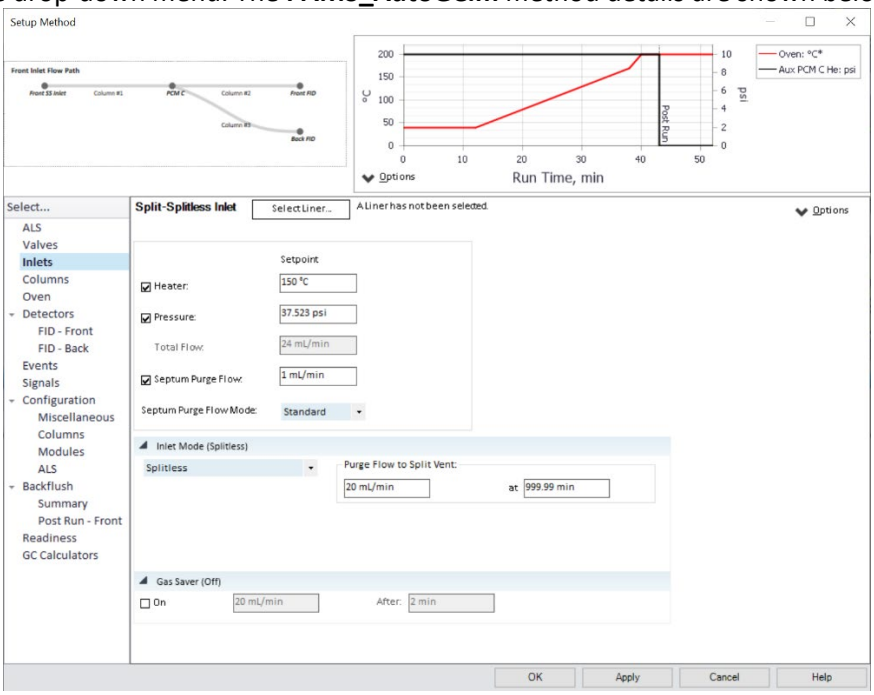

Figure 14: Agilent OpenLab CDS ChemStation Method Editor: GC Inlet Settings

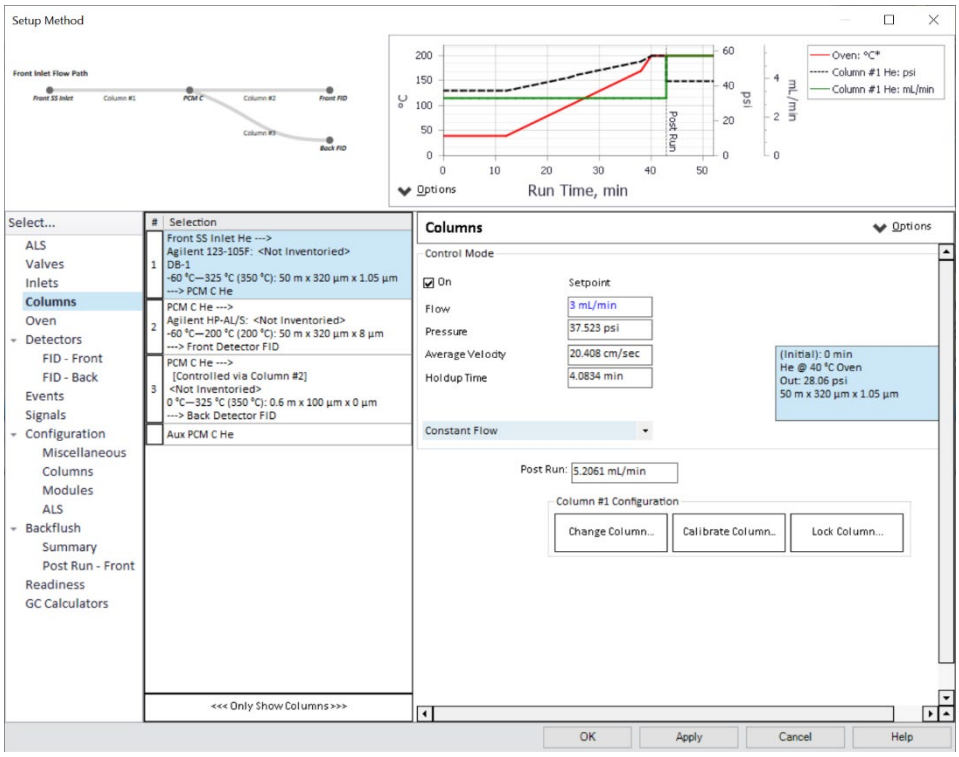

Figure 15: Agilent OpenLab CDS ChemStation Method Editor: Column Settings

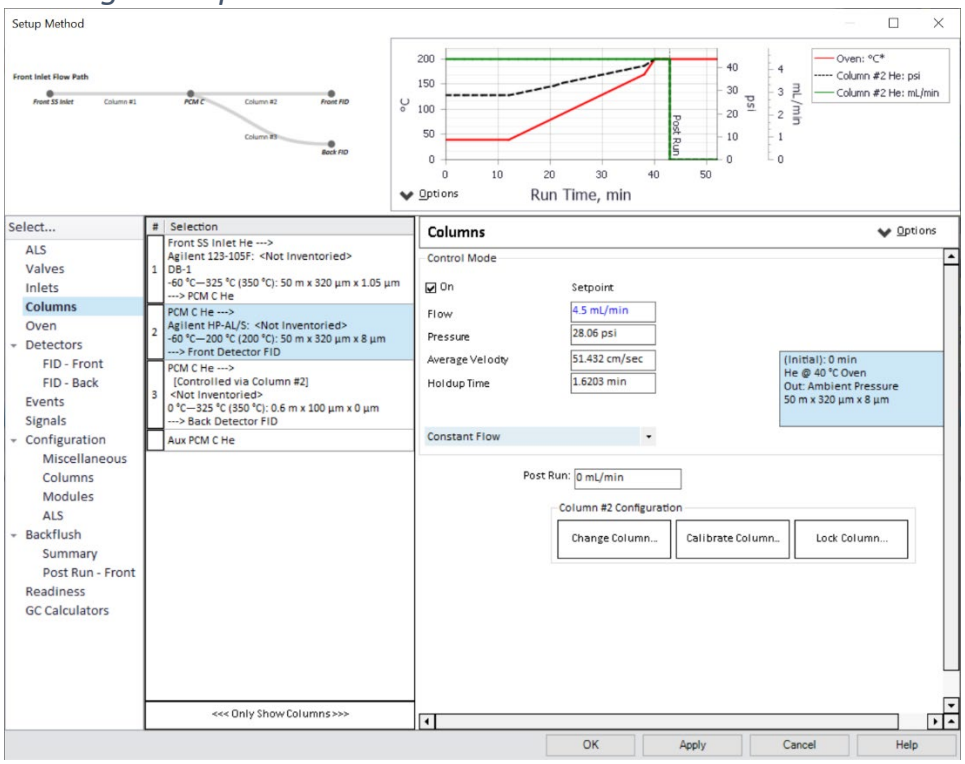

Figure 16: Agilent OpenLab CDS ChemStation Method Editor: Column Settings 2

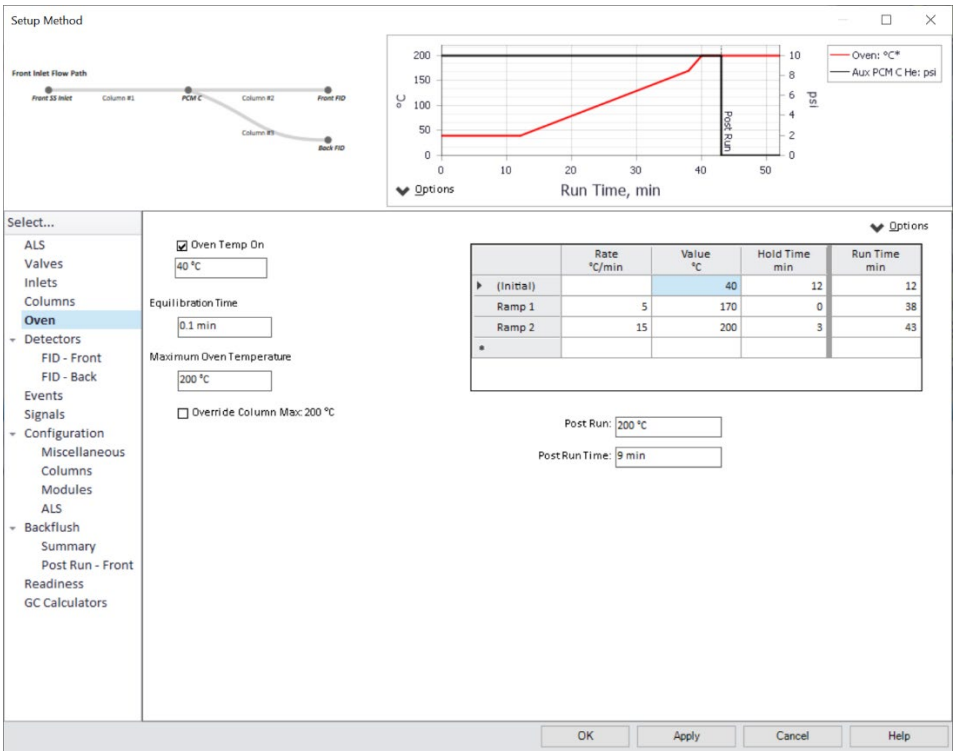

Figure 17: Agilent OpenLab CDS ChemStation Method Editor: Oven Programming

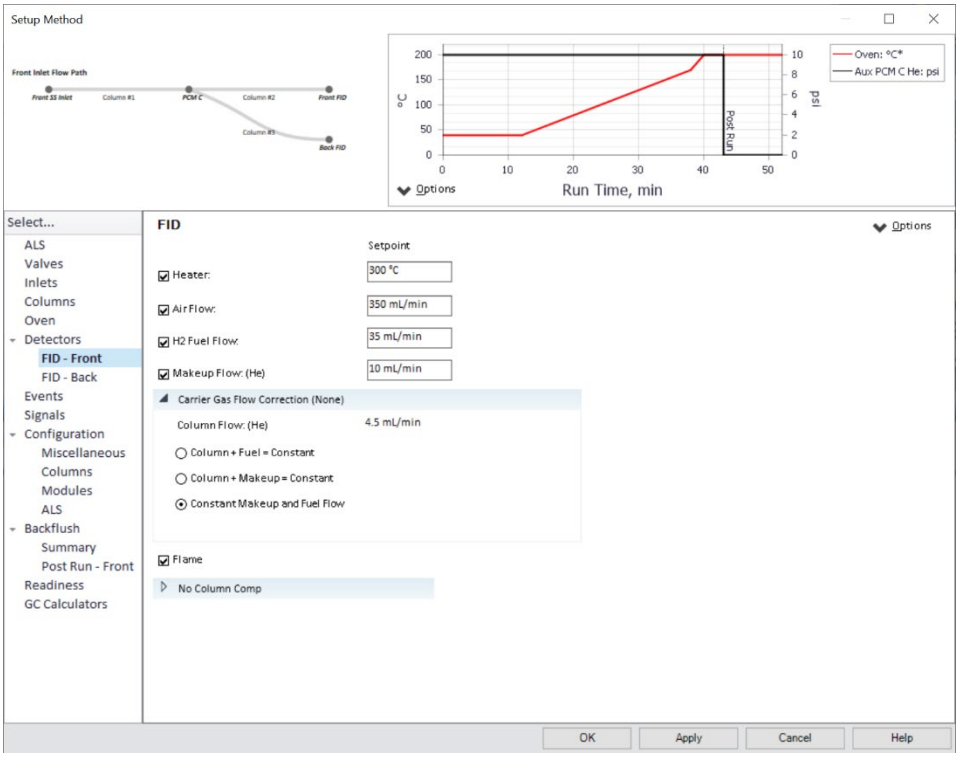

Figure 18: Agilent OpenLab CDS ChemStation Method Editor: Detector Settings

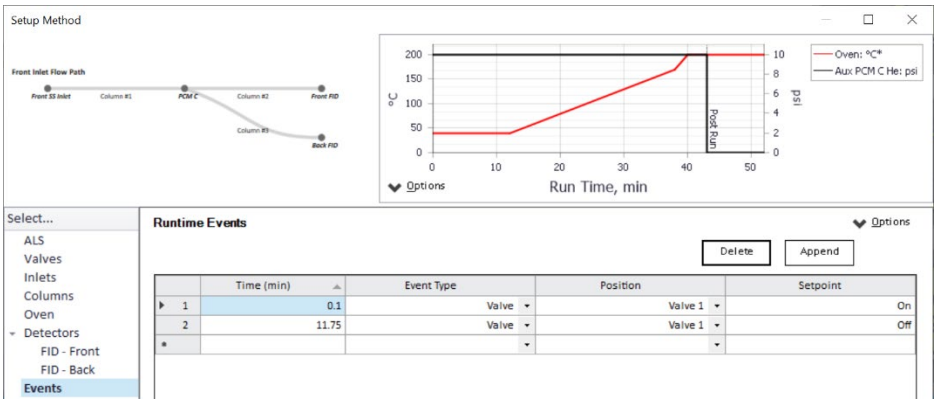

Figure 19: Agilent OpenLab CDS Chemstation Method Editor: Deans Switch Timing

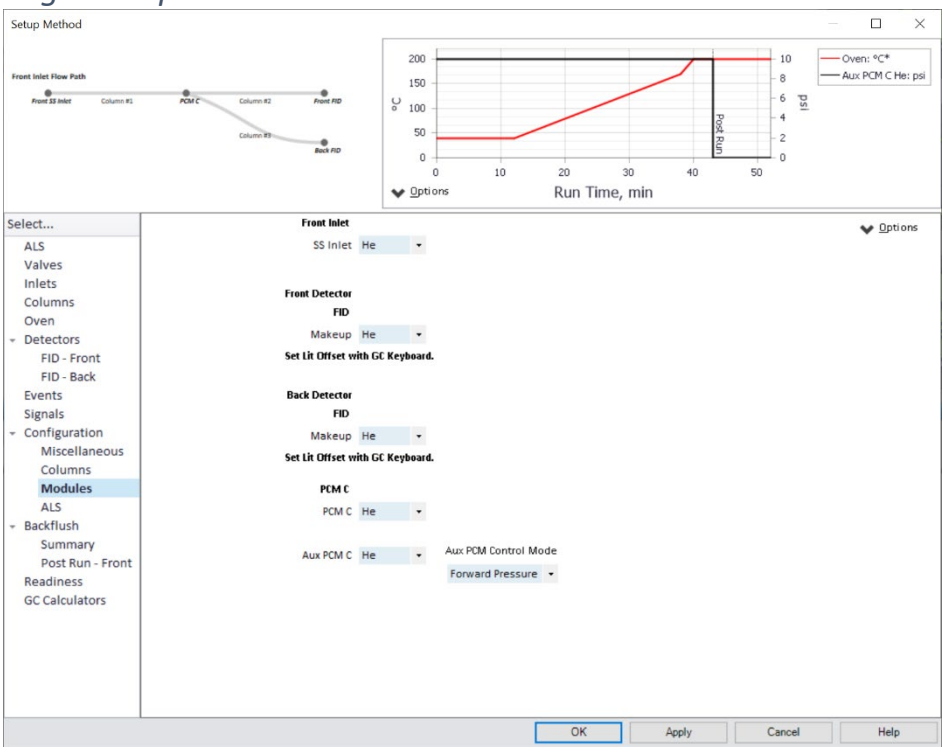

Figure 20: Agilent OpenLab CDS Chemstation Method Editor: Module Gas Settings

18 Press **Apply** to set changes and **OK** to save the changes applied to the method. If any settings differ, they can be altered to the settings in the preceding step. This is the default analytical GC method, and no other GC programming should be used for PAMS analysis.

5.6 Analytical Sequence Creation and Execution

1 Create sequences that have matching injection numbers and sample names in both the **MIC 2.0** and **Agilent ChemStation** software as detailed in the previous two Sections: 5.4-5.5; Confirm there are the same number of rows in each sequence and that hourly times and types of sample match. E.g., line 10 is hour 10 of Ambient Air on June 1st, 2021 in both the **MIC 2.0** and **ChemStation** sequence.

2 In **MIC 2.0** press the green play button in the top left corner of the software to engage the sequence. The instrument will validate the sequence before starting collection.

3 In **ChemStation** select **RunControl** from the top menu bar and select **Run Sequence**. This will execute the loaded sequence. ChemStation will indicate when the GC is ready and the status box will eventually turn purple and display, **Waiting for Injection**.
4 Allow the systems to run the sequences and periodically check on AutoGC operation as outlined in this SOP.
5 At the conclusion of an analytical sequence export the **MIC 2.0** sequence history and save it as the run name in the following file nomenclature: ***Sequence Name* Markes Export**
e.g., June 1st, 2021, the first run of the day would be named 20210601A Markes Export.
6 It is recommended that weekly sequences be created and executed by the operator. The **MIC 2.0** software does not handle well with extremely large sequences and 7-days is a stable span of time for the software. This covers 168 injections. Sequences can also be premade by the operator such that switching week-to-week analyses is not cumbersome or results in a missed sample and/or instrument idle downtime.

5.7 Annual System Shakedown

1 Prior to the start of the PAMS season, create a sequence and run the AutoGC system using the ambient air inlet for at least 14 days to condition the system.
2 The system shakedown period is required prior to the start of the PAMS season, June 1st, of the calendar year 2021.
3 For Calendar Years 2022 and beyond DAQ will begin monitoring on March 1st yearly to correspond with ozone monitoring
4 The shakedown should be done after yearly preventive maintenance has occurred by Agilent Technologies. The scheduled target date is for the preventive maintenance is for December/January of each year and is subject to engineer availability.
5 Log the dates of the annual system shakedown in the electronic logbook. Data from the annual system shakedown is not to be reported to AQS.

5.8 AutoGC Calibration

1 Create a humid blank in a 6-L Silco-treated canister on the Entech 4700 Precision Diluter via **DAQ SOP-03-006.2.**
2 Create discrete standards in 6-L Silco-treated canisters at 10 ppb_v, 2 ppb_v, and 0.25 ppb_v using the Airgas 56 compound VOC standard blend on the Entech 4700 Precision Diluter via **DAQ SOP-03-006.2.**
3 Create a discrete SSCV standard at 2 ppb_v in a 6-L Silco-treated canister using the Linde 61 compound VOC standard blend on the Entech 4700 Precision Diluter via **DAQ SOP-03-006.2.**
4 Connect the standards and blank to the CIA-advantage using the 1/16-in inlet lines. Log which canisters are connected to which port in the site electronic logbook.
5 Open the canisters. Use snoop to check for leaks if desired.
6 Create a **MIC 2.0 sequence** in the order as follows using the **PAMS_AutoGC_Calibration** method. The calibration method decreases the purge flow rate to 40 cc/min to preserve standards as the dead volume of the 1/16-in canister inlet lines is negligible relative to the ambient air inlet. All other trapping conditions are the same as the PAMS_AutoGC method.
Calibration Analytical Sequence:
- Humid Blank (800cc nominal load)
- 10ppb_v PAMS Standard (800cc nominal load, Level 3 Standard)
- 2ppb_v PAMS Standard (800cc nominal load, Level 2 Standard)
- 0.25ppb_v PAMS Standard (800cc nominal load, Level 1 Standard)
- 2ppb_v PAMS SSCV (800cc nominal load)

7 Analyze the sequence as detailed in section 5.6.

8 Process the calibration as detailed in Section 5.12.
9 AutoGC calibration will occur annually prior to the start of PAMS season in each calendar year and as failing QC criteria dictates. Corrective action for failing calibration curves and QC is discussed in sections 9.15-9.19.

5.9 Method Detection Limit (MDL) Determination

1 After a successful calibration has occurred via Section 5.8, analyze three humid blanks and three 0.25 ppb_v standards three times over three non-consecutive days. There will be nine total humid blank analyses and nine total 0.25 ppbv standards analyses. Verify the instrument calibration each time with a passing humid blank and CCV or SSCV prior to conducting the MDL determination. The CCV/SSCV must be ± 30% of nominal value. The humid blank must be ≤ 0.5ppb_c.
2 Process the data as detailed in section 5.10.
3 Reduce the processed data to an MDL by calculating an MDL from the 9 replicates via the following equations for each compound:

$$(1)\ Compound_{0.25ppb_vMDL} = (\sigma[9\ 0.25ppb_v\ Replicates] * Student\ t_{n=9})$$

$$(2)\ Compound_{SpikeMDL} = (\sigma[9\ 0.25ppb_v\ Replicates] * Student\ t_{n=9}) + Mean[9\ 0.25ppb_vReplicates]$$

The student t value for n=9 degrees of freedom is t = 2.896; σ is the standard deviation of the MDL injections.

MDL Values can also be entered into the PAMS MDL Workbook. An example for ethylene is included below in figure 21:

PAMS MDL Workbook

Student's T (n=9) 2.896

Nominal MDL Concentration (ppbv) 0.200

		MDL Day 1: 10/2/2020			MDL Day 2: 10/4/2020			MDL Day 3: 10/6/2020							
Compound	Number of Carbon Atoms	MDL 1	MDL 2	MDL 3	MDL 4	MDL 5	MDL 9	MDL 7	MDL 8	MDL 9	Mean	Standard Deviation	Analyte MDL (ppbv)	Analyte MDL (ppbC)	MDL Recovery (%)
Ethylene	2	0.211	0.198	0.201	0.190	0.208	0.205	0.202	0.199	0.201	0.202	0.006	0.0166	0.033	100.8

PAMS MDL Reduction - Blank Analysis

Student's T (n=9) 2.896

		MDL Day 1: 10/2/2020			MDL Day 2: 10/4/2020			MDL Day 3: 10/6/2020						
Compound	Number of Carbon Atoms	MDL 1	MDL 2	MDL 3	MDL 4	MDL 5	MDL 9	MDL 7	MDL 8	MDL 9	Mean	Standard Deviation	Analyte MDL (ppbv)	Analyte MDL (ppbC)
Ethylene	2	0.001	0.007	0.003	0.009	0.011	0.005	0.014	0.003	0.004	0.006	0.004	0.0180	0.036

Figure 21: MDL Workbook Example for Ethylene

4 MDL selection criteria dictates that the lowest MDL be chosen, and that the MDL must be less than 0.5ppb_c.
5 MDLs are to be determined annually prior to the start of PAMS season in each calendar year.

5.10 PAMS Analysis and Sample Collection Schedule

Ambient samples will be collected hourly and a SSCV or CCV and humid blank will be run daily. A weekly precision check of the SSCV will be collected on the weekend. The SSCV is also considered the retention time standard (RTS). This occurs on a fixed weekly schedule and is published in Appendix G. This schedule will be repeated until monitoring is terminated on October 31st annually.

5.11 PAMS AutoGC Data Processing

1 Begin data analysis by reviewing the analytical sequence **Markes Export** file. Invalidate any injections that contain a deviation that would invalidate the integrity of the sample collected. Examples include: no flow (no

sample volume collected), traps not reaching set-points to collect analyte at method settings or heated zone failure. Notate any deviations in the site electronic logbook.

2 Confirm the collected sample volume is within ±2% of the requested value. E.g., 800 ± 16 cc. Invalidate any injection that does not meet this requirement.

3 Open the **PAMS-Millbrook (offline)** Agilent ChemStation to process data.

4 Once loaded select **Data Processing** in the lower left corner of the program window.

5 On the left-hand side, select the analytical sequence for processing by double clicking it. The injections are automatically processed against the current calibration loaded in the **PAMS_AutoGC** method. E.g., 20210601A for the first sequence of the day on June 1st, 2021.

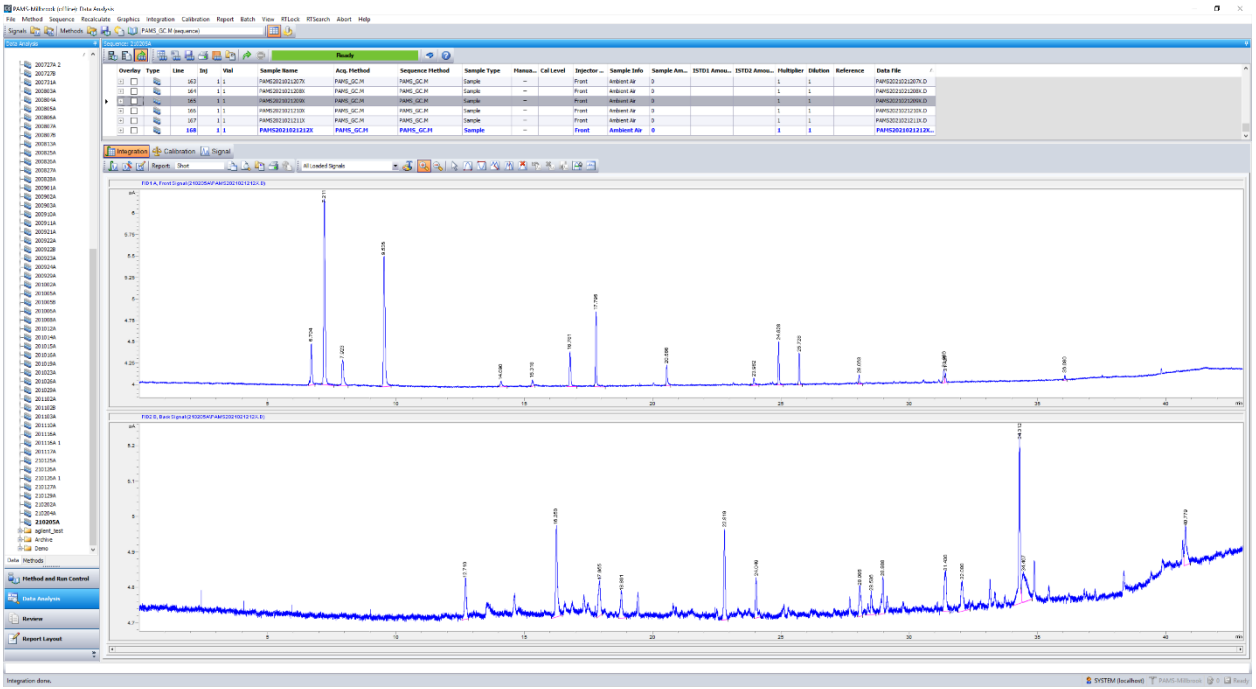

Figure 22: Agilent ChemStation Data Processing on a Sequence

6 Begin review by inspecting the chromatograms: CCV checks, humid blanks, and ambient air injections. The operator will inspect each chromatogram for identification accuracy. If an individual compound peak falls within the retention time window, it will be considered positively identified. The established retention time (RT) windows are fixed in the software as the average of the ICAL RTs ± 4%. **Note**: A mass spectrometer would be required to further quantify the ambient air collected for positive quantification of the speciated VOCs at the individual retention times detected and does not fall under the purview of the PAMS AutoGC.

7 Manual integration can occur at operator discretion when the software incorrectly integrates the peak – e.g., not split, too much base line included. To manually integrate a peak, select the peak with the toolbar zoom tool (the + magnifying glass). Other functions of the toolbar include (from left to right): the peak selection tool (the white cursor), manually integrate a peak, integrate a negative peak, integrate a peak with a tangent skim, split a co-eluting peak, delete a peak, undo integration changes to the original processing, delete integration changes, save integration changes (blue floppy disk). The drop-down menu can be used to select both FID signals, the front FID signal, or the back FID signal. This may be useful for the operator depending on the goals of processing.

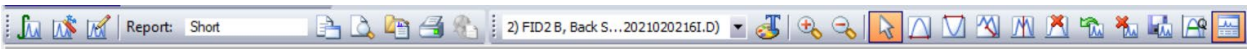

Figure 23: Agilent ChemStation Data Processing Toolbar

8 Delete the poor integration using the peak deletion tool.

9 Select the integration tool and draw a baseline-to-baseline integration for the peak as demonstrated in figure 24:

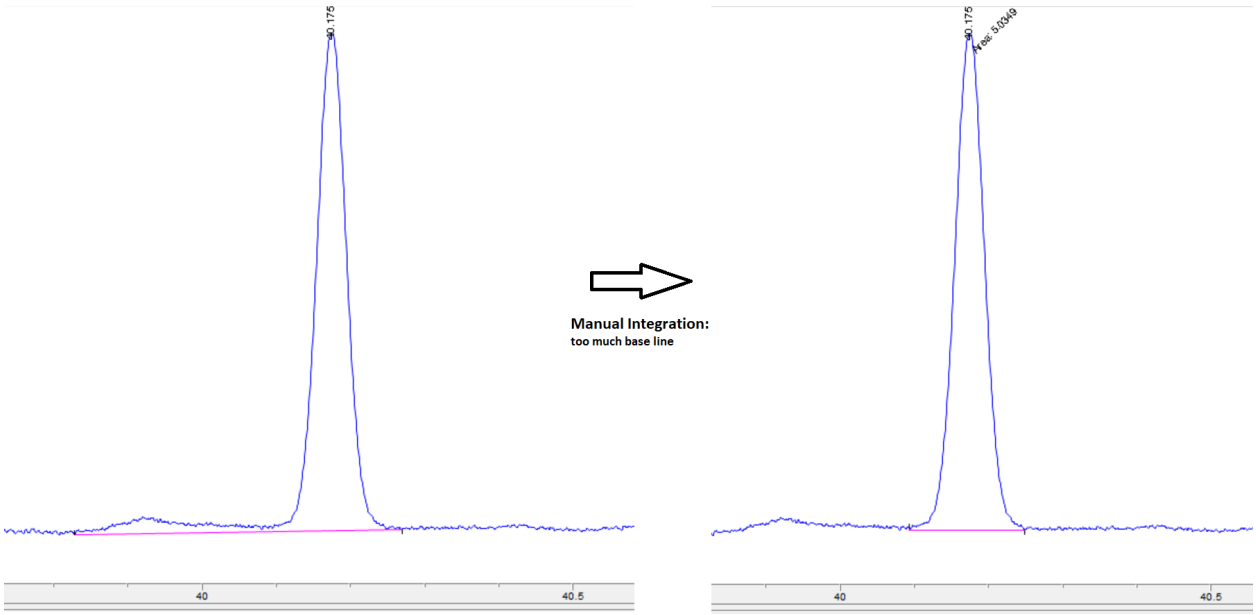

Figure 24: Agilent ChemStation Data Processing: Manual Integration Example

10 Accept the changes by hitting the save button. This saves all changes conducted on the sample.

11 After chromatograms have been reviewed for the given sequence, generate reports for the injections by selecting the **Review** tab in the lower corner of the ChemStation software.

12 In the bottom of the left-hand sequence list select the **Report Templates** tab.

13 Click on the first injection of the sequence in the **Review** table and press ctrl + a to select all injections.

14 Double click on the **Sample Report.rdl** to generate reports for the sequence. It may take several minutes to generate all report pages.

15 Save as PDF, .XLSX and .CSV with the name format: ***Sequence Name***

5.12 PAMS AutoGC Calibration Data Processing

5.12.1 Initial AutoGC Calibration Data Processing

1 Begin data analysis by reviewing the analytical sequence Markes Export file. Invalidate any injections that contain a deviation that would invalidate the integrity of the sample collected. Examples include: no flow (no sample volume collected), traps not reaching set-points to collect analyte at method settings or heated zone failure. Notate any deviations in the site electronic logbook.

2 Confirm the collected sample volume is within ±2% of the requested value. E.g., 800 ± 16 cc. Invalidate any injection that does not meet this requirement.

3 Open the **PAMS-Millbrook (offline)** Agilent ChemStation to process data.

4 Once loaded select **Data Processing** in the lower left corner of the program window.

5 On the left-hand side, select the analytical sequence for processing by double clicking it.

6 Begin review by inspecting the sequence chromatograms. The operator will inspect each chromatogram for integration accuracy. If an individual compound peak has an improper integration, then a manual integration can be performed.

7 To manually integrate a peak, select the peak with the toolbar zoom tool (the + magnifying glass). Other functions of the toolbar include (from left to right): the peak selection tool (the white cursor), manually integrate a peak, integrate a negative peak, integrate a peak with a tangent skim, split a co-eluting peak, delete a peak, undo integration changes to the original processing, delete integration changes, save integration changes (blue floppy disk). The drop-down menu can be used to select both FID signals, the front FID signal, or the back FID signal. This may be useful for the operator depending on the goals of processing.

8 Delete the poor integration using the peak deletion tool.

9 Select the integration tool and draw a baseline-to-baseline integration for the peak.

10 Accept the changes by hitting the save button. This saves all changes conducted on the sample.

11 The operator may delete any known impurity peaks in the standard and only integrate the target compounds of interest detailed in the **DAQ-01-007 PAMS Required Network QAPP**.

12 Select the first processed calibration standard by double clicking on the injection name.

13 Generate a new **Calibration Table** by selecting **Calibration** from the menu bar and clicking **New Calibration Table**. The following will appear:

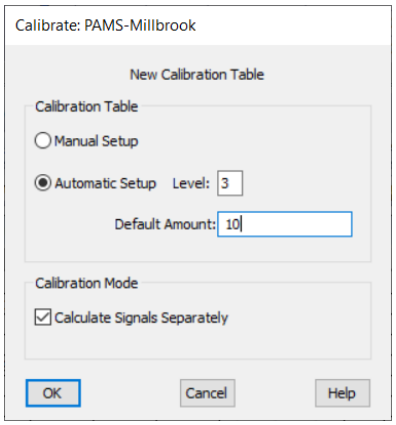

Figure 25: Agilent ChemStation New Calibration Table

14 Fill in the **Level** field with the level of the standard and the **Default Amount** field with the nominal concentration of the standard. Select the **Calculate Signals Separately** box. Press **OK.**

15 Select the next calibration standard by double clicking on it and selecting the **Add new level from current chromatogram** button as depicted below:

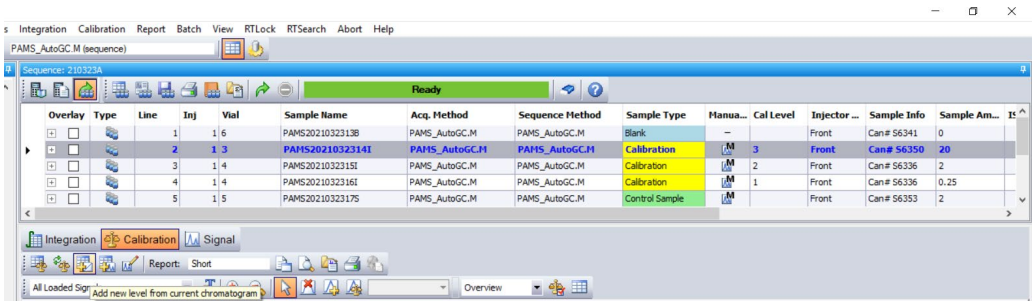

Figure 26: Agilent ChemStation Add New Calibration Level Button

16 The **Add Level** window will appear:

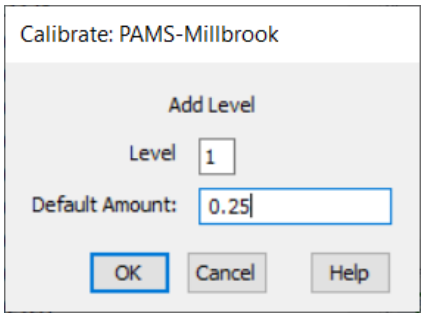

Figure 27: Agilent ChemStation Add New Calibration Level

17 Fill in the **Level** field with the level of the standard and the **Default Amount** field with the concentration of the standard. Repeat for the remaining calibration standard.

18 The **Calibration Table** will be populated with all the integrated peaks from the calibration standards, but no peaks will be labeled. The established RT order is detailed in Appendix H. Fill in each peak with the correct identification. Enter the compound name following by the AQS compound ID in parathesis. E.g., Ethylene (43203). Press OK when finished.

19 In the ChemStation menu bar select **Menu** and click **Update Master Method**. This will push the current **Calibration Table** into the **PAMS_AutoGC** method.

20 Reprocess the data using the new calibration by selecting the green **Start sequence reprocessing**:

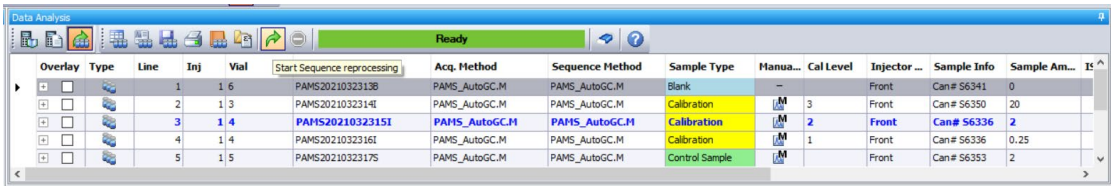

Figure 28: Agilent ChemStation Sequence Reprocessing

21 After data has been reprocessed, generate reports for the calibration by selecting the **Review** tab in the lower corner of the ChemStation software.

22 In the bottom of the left-hand sequence list select the **Report Templates** tab.

23 Ctrl + Click on the three calibration standards of the sequence in the **Review** table.

24 Double click on the **ICAL.rdl** to generate reports for the calibration. It may take several minutes to generate all report pages.

25 Save as PDF and .CSV with the name: ***Sequence Name* ICAL**.

26 Click on the first injection of the sequence in the **Review** table and press ctrl + a to select all injections.

27 Double click on the **Sample Report.rdl** to generate reports for the sequence. It may take several minutes to generate all report pages.

28 Save as PDF, .XLSX and .CSV with the same name of the analytical sequence.

29 Acceptance Criteria:

- Linearity coefficient of determination (R^2) ≥ 0.99.
- The absolute value of the y-intercept/slope must be ≤ 0.5ppb$_c$ or ≤ MDL, whichever is greater.
- The RSD% of each analyte RF in the calibration curve must be ≤ 10%.
- The concentration of each analyte in the calibration curve must be ± 20% of nominal value.
- The humid blank must by ≤ 0.5ppb$_c$ or ≤ MDL, whichever is lower.
- 2ppb$_v$ PAMS SSCV must be ± 30% of nominal value.

30 Corrective action for an invalid calibration curve can be referenced in section 9.15.

5.12.2 Subsequent AutoGC Calibrations

1 Begin data analysis by reviewing the analytical sequence Markes Export file. Invalidate any injections that contain a deviation that would invalidate the integrity of the sample collected. Examples include: no flow (no sample volume collected), traps not reaching set-points to collect analyte at method settings or heated zone failure. Notate any deviations in the site electronic logbook.
2 Confirm the collected sample volume is within ±2% of the requested value. E.g., 800 ± 16 cc. Invalidate any injection that does not meet this requirement.
3 In the calibration analytical sequence use the **Sample Type** field in the ChemStation sequence table. Enter the calibration type and the appropriate level for each standard. Select **Replace** from the **Update RT** and **Update RF** field in the sequence table. This will use the established RT windows to recalibrate the system and the AutoGC ChemStation data system will process the data automatically for the user and import it into the calibration table for review.
4 Open the **PAMS-Millbrook (offline)** Agilent ChemStation to process data.
5 Once loaded select **Data Processing** in the lower left corner of the program window.
6 On the left-hand side, select the analytical sequence for processing by double clicking it.
7 Begin review by inspecting the sequence chromatograms. The operator will inspect each chromatogram for integration accuracy. If an individual compound peak has an improper integration, then a manual integration can be performed.
8 To manually integrate a peak, select the peak with the toolbar zoom tool (the + magnifying glass). Other functions of the toolbar include (from left to right): the peak selection tool (the white cursor), manually integrate a peak, integrate a negative peak, integrate a peak with a tangent skim, split a co-eluting peak, delete a peak, undo integration changes to the original processing, delete integration changes, save integration changes (blue floppy disk). The drop-down menu can be used to select both FID signals, the front FID signal, or the back FID signal. This may be useful for the operator depending on the goals of processing.
9 If any sort of manual reprocessing occurred: In the ChemStation menu bar, select **Menu** and click **Update Master Method**. This will push the current **Calibration Table** into the **PAMS_AutoGC** method. Reprocess the data using the new calibration by selecting the green **Start sequence reprocessing**.
10 Generate reports for the calibration by selecting the **Review** tab in the lower corner of the ChemStation software.
11 In the bottom of the left-hand sequence list select the **Report Templates** tab.
12 Ctrl + Click on the three calibration standards of the sequence in the **Review** table.
13 Double click on the **ICAL.rdl** to generate reports for the calibration. It may take several minutes to generate all report pages.
14 Save as PDF, .XLSX and .CSV with the name: ***Sequence Name* ICAL**.
15 Click on the first injection of the sequence in the **Review** table and press ctrl + a to select all injections.
16 Double click on the **Sample Report.rdl** to generate reports for the sequence. It may take several minutes to generate all report pages.
17 Save as PDF, .XLSX and .CSV with the same name of the analytical sequence.
18 Acceptance Criteria:
- Linearity coefficient of determination (R^2) ≥ 0.99.
- The absolute value of the y-intercept/slope must be ≤ 0.5 ppb_c or ≤ MDL, whichever is lower.
- The RSD% of each analyte RF in the calibration curve must be ≤ 10%.
- The concentration of each analyte in the calibration curve must be ± 20% of nominal value.

- The humid blank must by ≤ 0.5 ppb_c or ≤ MDL, whichever is lower.
- 2ppb_v PAMS SSCV must be ± 30% of nominal value.

19 Corrective action for an invalid calibration curve can be referenced in section 9.15.

5.13 AutoGC System Shutdown

Upon completion of the monitoring season on October 31st annually, the AutoGC will be brought off-line for annual maintenance. This date will be fluid and determined at the LAB Chemist discretion. Shut down the AutoGC system by first confirming each system, the **GC** and **MIC,** are idle. Close each program window and allow the computer to terminate the connection to the instrument. Once the software windows are closed, power off all instrumentation and pumps. Close all gas cylinders and regulators.

6.0 PAMS AutoGC Data Review

This section of the SOP describes steps required for the primary lab chemist to perform a self/Level 1 review on the AutoGC sampling and analysis data. Additionally, this section describes steps required for the lab chemist not directly involved in the AutoGC data collection or processing to perform a peer/Level 2 data review.

6.1 Self/Level 1 PAMS AutoGC Sampling and Analysis Data Review

6.1.1 Calibration Data Review:

1 Open processed reports and confirm that calibration meets criteria:
- Linearity coefficient of determination (R^2) ≥ 0.99.
- The absolute value of the y-intercept/slope must be ≤ 0.5ppb_c or ≤ MDL, whichever is greater.
- The RSD% of each analyte RF in the calibration curve must be ≤ 10%.
- The concentration of each analyte in the calibration curve must by ± 20% of nominal value.
- The humid blank must by ≤ 0.5ppb_c or ≤ MDL, whichever is lower.
- 2ppb_v PAMS SSCV must be +/- 30% of nominal value.

2 Ensure standard logbook pages are included with data for NIST-derived standard traceability.

3 Review exported MIC 2.0 sequence history for sequence related to calibration, include it in final report for injection integrity and tractability.

4 Create a final data package with the raw instrument data and chromatograms, instrument sequence data, calibration information and summary information about the curve meeting or failing the criteria outlined above.

5 Submit data package to peer reviewer for approval.

6.1.2 PAMS Seasonal Data Review:

1 DAQ will process data in weekly intervals.

2 Review all injections in MIC 2.0 sequence history export. Invalidate any injections that are anomalous and flagged with errors. Record any such events in the electronic PAMS AutoGC logbook.

3 Review all QC samples for acceptance criteria. Blanks must be <0.5ppb_c or the MDL whichever is greater. CCV or SSCV samples must be ±30% of the compound concentration in the standard.

4 Review weekly precision CCV for RT consistency against the calibration and precision of ≤ 25% absolute relative percent difference for each target VOC. %RPD can be calculated by the following equation:

$$(3)\ Compound_{\%RPD} = \frac{|(Compound\ Concentration - Precision\ Compound\ Concentration)|}{\left(\frac{Compound\ Concentration + Precision\ Compound\ Concentration}{2}\right)} * 100$$

5 Create a final data package with the raw instrument data and chromatograms, Markes Export sequence data, QC sample information and summary information about the QC meeting or failing the criteria outlined above.

6 Submit data package to peer reviewer for approval along with the PAMS AutoGC Data Review Checklist. See Appendix I for a copy of the review checklist.

6.2 Peer/Level 2 PAMS AutoGC Sampling and Analysis Data Review

Peer review can be completed using the check list in Appendix I. The peer reviewer will be provided all the files by the LAB Chemist.

6.3 Level 3 PAMS AutoGC Sampling and Analysis Data Validation

At the time of this publication, the DAQ will be using ERG via the EPA National Contract to validate PAMS data collected. No in-house level 3 validation of the data will be conducted. More details about the level 3 validation of the DAQ PAMS data will published in subsequent revisions of this document as they are made available. The DAQ is actively working with ERG to obtain this information and the details of secure data transmission for validation purposes.

7.0 PAMS AutoGC File Management

This section of the SOP describes the different files generated during the instrument data processing and the individual required to manage the file, either the primary LAB chemist or level 2 data reviewer, or both. Files include the AutoGC Analysis Data Files, Markes Export Files, exported Sample Reports, exported ICAL reports, and the PAMS AutoGC Data Review Checklist.

7.1 Exported AutoGC Data Files (LAB Chemist)

Exported files are generated for each sequence, both the GC and Markes System, and are stored on the instrument computer and backed up to an external hard drive. A final data package will be created for the analytical sequence and stored on the LAB P: drive for peer data review. The final data package will contain: Sample reports for all injections, initial calibration information, standard information, and the Markes Export files for the sequence.

7.1.1 AutoGC Analysis Files (LAB Chemist)

The chromatograms are exported via the sample report from the Agilent ChemStation software. Reports include both channel chromatograms and calibrated sample concentrations compound-by-compound. The instrument calibration is exported in the same manner using the Agilent ChemStation software ICAL report. Files are generated for each sequence and are stored on the instrument computer and backed up to an external hard drive. Create a folder in the LAB P: drive PAMS folder and create a data package folder with the same name as the analytical sequence. Place the AutoGC data and reports in the report folder.

7.1.2 AutoGC Sequence (LAB Chemist)

Files are generated for the Markes System sequence and are stored on the instrument computer and backed up to an external hard drive. The entered sequences, via the **MIC 2.0** or **Agilent ChemStation** software are saved on the instrument computer and backed up to an external hard drive. The Markes Export file generated for each

sequence is placed in the final data package folder in the LAB P: drive PAMS folder with the same name as the analytical sequence.

7.2 Primary Analyst Generated Data Review Files (LAB Chemist)

Data is manipulated by the analyst to convert the on-column results of ppb_v to ppb_c via the following calculation shown in equation 4:

$$(4)\ [ppb_c] = [ppb_v] * [\#\ of\ Carbon\ Atoms\ in\ Compound]$$

The number of carbons per target compound is shown below in Table 1:

Table 1 - PAMS Target VOCs Carbon Count

Compound	Number of Carbon Atoms
Ethylene	2
Acetylene	2
Ethane	2
Propylene	3
Propane	3
Isobutane	4
1-Butene	4
n-Butane	4
trans-2-Butene	4
cis-2-Butene	4
Isopentane	5
1-Pentene	5
n-Pentane	5
Isoprene	5
trans-2-Pentene	5
cis-2-Pentene	5
2,2-Dimethylbutane	6
Cyclopentane	5
2,3-Dimethylbutane	6
2-Methylpentane	6
3-Methylpentane	6
n-Hexane	6
Methylcyclopentane	6
2,4-Dimethylpentane	7
Benzene	6
Cyclohexane	6
2-methylhexane	7
2,3-Dimethylpentane	7
3-Methylhexane	7
2,2,4-Trimethylpentane	8

n-Heptane	7
Methylcyclohexane	7
2,3,4-Trimethylpentane	8
Toluene	7
2-Methylheptane	8
3-Methylheptane	8
n-Octane	8
Ethylbenzene	8
m/p-Xylene	8
Styrene	8
o-Xylene	8
n-Nonane	9
Isopropylbenzene	9
n-Propylbenzene	9
m-Ethyltoluene	9
p-Ethyltoluene	9
1,3,5-Trimethylbenzene	9
o-Ethyltoluene	9
1,2,4-Trimethylbenzene	9
n-Decane	9
1,2,3-Trimethylbenzene	9
m-Diethylbenzene	10
p-Diethylbenzene	10
n-Undecane	11
Carbon Tetrachloride	1
Ethanol	2
Tetrachloroethylene	2
1,3-Butadiene	4

Data is also manipulated to calculate QC recovery via equation 5:

$$(5)\ \%\ Recovery = \frac{[Compound\ Concentration\ on\ Instrument]}{[Nominal\ Standard\ Compound\ Contration]} * 100$$

Weekly SSCV/CCV precision is evaluated via RPD described in equation (4).

Print the results in PDF and insert into the final data packaged located in the LAB P: Drive PAMS folder with the same name as the analytical sequence.

7.3 PAMS AutoGC Data Review Checklist (LAB Chemist/Peer Level 2 Reviewer)

The Level 2 data reviewer will review the data assembled by the LAB Chemist on the LAB P: Drive PAMS folder using the PAMS AutoGC Data Review Checklist. A complete copy of the checklist should be stored with the final data package.

8.0 File Quality Assurance and Data Handling

8.1 Records Management

All printed records are maintained according to the DAQ document retention plan.

8.1.1 PAMS AutoGC Electronic Logbook

The site operator logbook will document installation, maintenance, or removal of any component of the AutoGC system. Canister standards and blanks connected to the AutoGC will be recorded in the logbook. Completed pages are printed in PDF, reviewed, and stored in the LAB P: drive PAMS folder.

8.1.2 PAMS Standard Preparation Logbook

Standard records prepared at the LAB using the Entech 4700 Precision Diluter are maintained according to **SOP DAQ-03-006.2 Precision Diluter Operation**.

8.2 Monthly Backup of AutoGC Data

At the conclusion of each calendar month all data must be copied to the external hard drive on the site for backup and archival.

9.0 Troubleshooting and Corrective Actions

9.1 Excess Humidity

1 The baseline of the FID detector will have a dip every few minutes if there is too much moisture in the zero-air gas stream supplied to the CIA Advantage, Kori, Unity and GC. See figure below for baseline fluctuations associated with too much humidity:

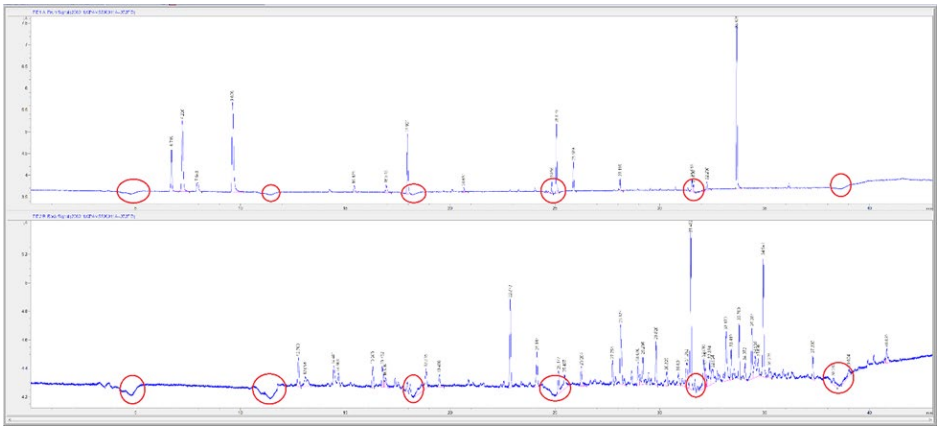

Figure 29: Chromatogram showing water-based interference circled in red

2 Inspect the Kori and Unity windows for moisture droplets. If any are present open the chamber and dry with a lint-free wipe.

3 Inspect the gas-clean filter moisture indicators and make sure they are not depleted. Replace if the indicator has changed to the depleted color.

4 Set the GC oven to 200°C and load up the trap conditioning method on the MIC software. Run it continuously overnight to dry out the traps and system.

5 Analyze a fresh aliquot of ambient air or a QC standard and inspect the system baseline for fluctuations previously observed. In the event the problem is still occurring, a service call can be placed with Agilent Technologies as water might still be trapped in the system and not readily accessible to the operator. Especially, if physical droplets were observed previously.

9.2 Excessive FID Noise

Power off the instrument and allow it to cool to ambient conditions. Inspect the FID jet and spring for clogs and buildup. Maintenance is likely required by way of replacement. See section 9.9 for replacement instructions. In the event the problem is still occurring, a service call can be placed with Agilent Technologies to obtain further support.

9.3 No Peaks, Only Baseline

Inspect transfer lines for breakage. Replacement is likely required and can be done by Agilent Technologies as outlined in section 9.6.

9.4 Low Response/Failing CCV or SSCV

1 Inspect unity trap injection count and replace unity trap with new unity PAMS trap. Injection count is obtained by selecting the settings icon in the **MIC 2.0** software home screen. See figure below:

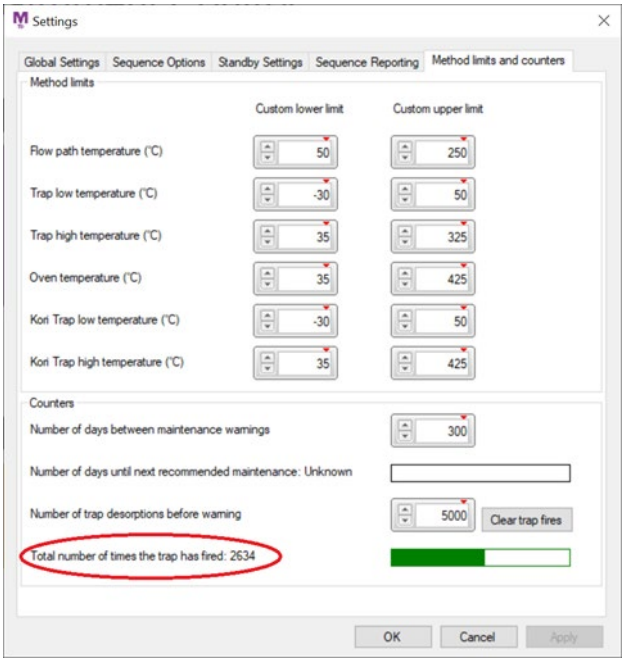

Figure 30: MIC 2.0 Trap Injection Counter

2 Compare trapping ability of benzene via integrated area counts to the first calibration on that trap. If it has reduced significantly replace the PAMS trap as described in section 9.5.

3 Analysis cannot commence if target analytes fail in the SSCV immediately following the ICAL. Investigate any discrepancy between ICAL and SSCV. Investigate chromatogram for retention time shifts which may result in peak misidentification. Investigate for instrument contamination resulting in co-eluting peaks. Investigate for system leaks, section 3.3, or trap malfunction resulting in low recovery. Unless technical justification is provided to explain nonconformance, minimally qualify as “QX” and potentially invalidate as “AS” samples for

affected compounds since the last acceptable SSCV/CCV. Invalidation as "AS" may be required at analyst discretion if compound recovery is exceptionally high or low (outside ±50% recovery).

9.5 Replacing the Traps

9.5.1 Markes Unity TD Trap Replacement

Open the trap housing at center and slide out the trap gently. The black Unity-xr cover, shown below, will have to be removed to access the trap. Replace with a new Unity PAMS (VOC Ozone precursors) trap (P/N MKI-U-T20PAM).

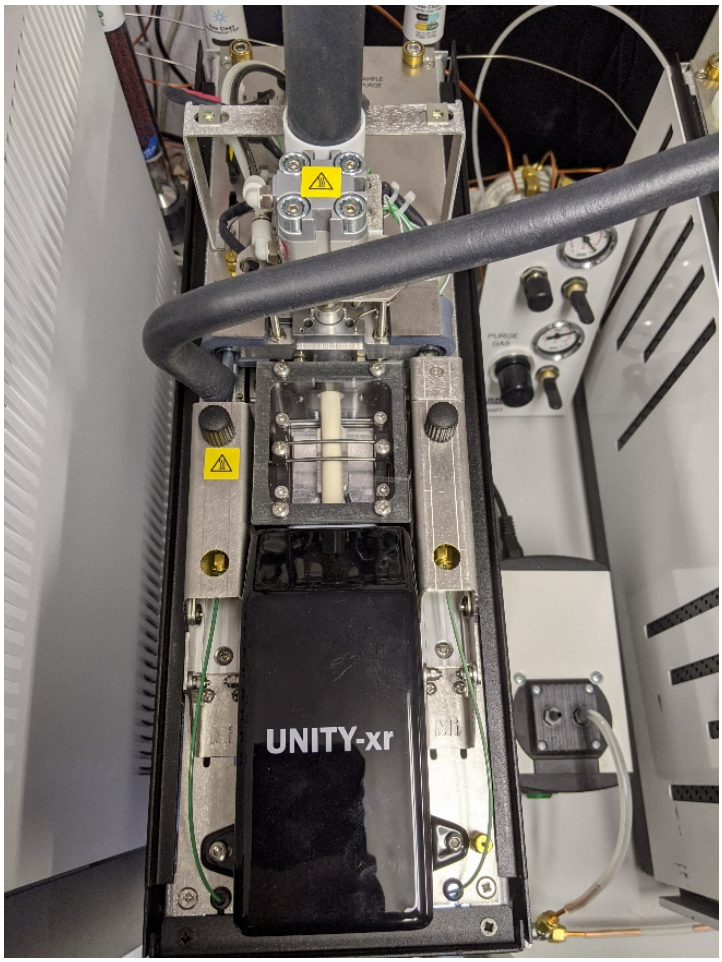

Figure 31: Top-View Shot of Unity Module

Gently slide the new trap in until it slides into the rear O-ring. Then close the trap housing and the trap will secure into place. Do not force this closed. Once the trap is installed, run the **Trap Condition** method in **MIC 2.0** three times and then further condition the trap with ambient air analysis for 24 hours. Document any replacements in the site electronic notebook.

Replace minimally every year, during the preventative maintenance visit. This can be done by the Agilent service engineer at this time.

9.5.2 Markes Kori Trap Replacement

Open the trap housing at center and slide out the trap gently. The white plastic clamp, shown in center frame below, will have to be removed to access the trap with a T20 Torx screwdriver.

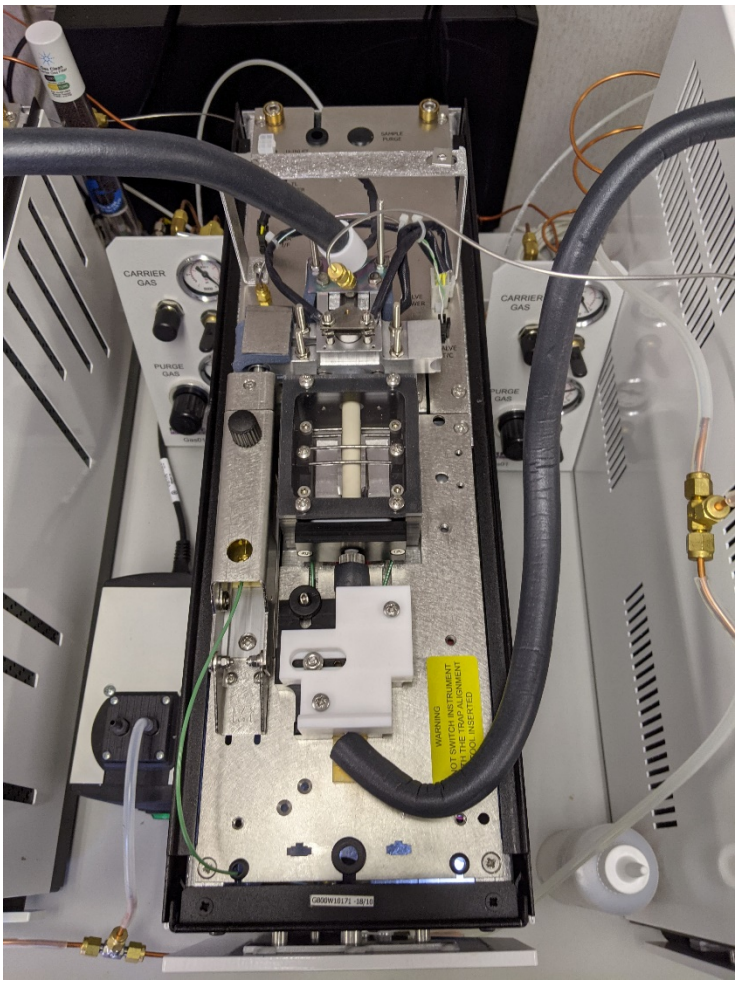

Figure 32: Top-View Shot of Kori Module

The trap is approximately the same size as the cavity it goes into and is a very tight fit. Removing the trap can be difficult and a trap removal and alignment tool was provided by the vendor and should be used to aid the operator. Replace with a new Kori empty cold trap (P/N MKI-U-T1KORI). Once the trap is installed, run the **Trap Condition** method in **MIC 2.0** three times. Document any replacements in the site electronic notebook.

Replace minimally every year, during the preventative maintenance visit. This can be done by the Agilent service engineer at this time.

9.6 Transfer Line Replacement

Parts and labor are covered under the Agilent Crosslab Silver service contract, call into the 1-800-227-9770 number, and create a trouble ticket for the AutoGC. Have Agilent order the line that requires replacement. A service engineer will schedule a repair once the part has been received. Log any repairs in the electronic logbook.

9.7 Markes Heated Zone Failure

Try to reboot the Markes system to reset the trouble state. Sometimes this will allow the heated zone to function again. Confirm any external heated transfer line power connectors are connected and in good physical condition. If the heated zone is still not functional or damage is observed, parts and labor are covered under the Agilent Crosslab Silver service contract, call into the 1-800-227-9770 number, and create a trouble ticket for the

AutoGC. A service engineer will schedule a repair once the part has been received. Log any repairs in the electronic logbook.

9.8 GC Column Replacement

Figure 33: Agilent 7890B Oven and Column Configuration

Power off the GC and open the oven door to allow it to cool to ambient conditions. Remove desired column with ¼-in wrench by loosening its fittings. Open the new replacement column and let out 2-3 in of column from both ends of the column. The ends of the columns are sealed and must be scored with a ceramic column scorer and broken clean. Confirm the cut is clean by holding the column against a white background to aid in inspection. Cut again if the break is not smooth. The fittings and new ferrules can be installed on the column and replaced into its spot in the AutoGC. It is recommended that all columns be replaced during the same maintenance window. The columns must be conditioned at 200°C for at least 8 hours after installation. Log maintenance in the electronic logbook.

Recommended replacement every year, during the preventative maintenance visit. This can be done by the Agilent service engineer at this time. Replacement is required when chromatography is poor, and separation of analytes cannot be achieved that leads to compound identification failures. Column lifetime is a function of the instrument's operational environment and uptime.

9.9 FID Jet Replacement

Power off the GC and allow the system to cool to ambient conditions. Open the top lid of the GC and remove the FID jet via disassembly of the desired housing circled in the picture below:

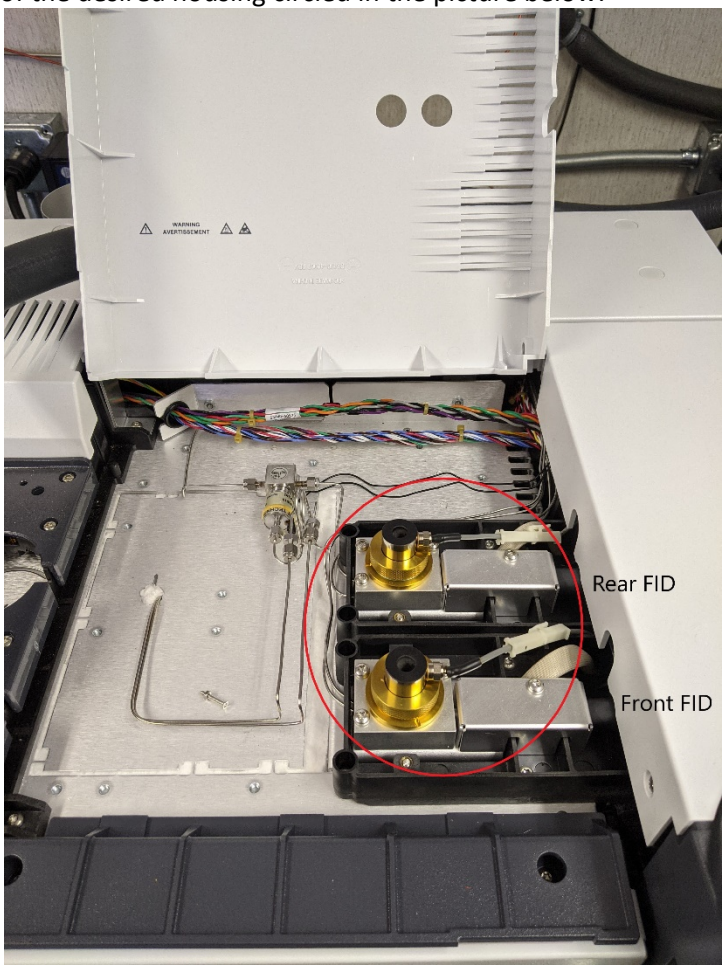

Figure 34: Agilent 7890B FID Access via Top Panel

The jet screws out with a ¼-in hexagonal nut driver. Inspect it for damage and particulate build up and note any in the site electronic logbook. Replace the jet by screwing in a new jet with the nut driver and reassembling the jet housing.

Recommended replacement every year, during the preventative maintenance visit. This can be done by the Agilent service engineer at this time. Replacement is required when baseline noise level is high and exceeds 10 pA.

9.10 Leak Repair

Leaks can occur at any interface and typically are seen at compression fittings when the ferrule has been overtightened. A compression fitting makes a good seal with a quarter turn of the wrench past finger tight. The line installed in the fitting should not be able to slide freely. Once a leak has been identified, disconnect the fitting. Cut the line, if able, and reinstall a nut and ferrule and reseal. If cutting the line is not an option, replace the connection.

Leaks internal to the Markes system are covered under the Agilent CrossLab Silver service contract, call into the 1-800-227-9770 number, and create a trouble ticket for the AutoGC. A service engineer will schedule a repair

once the part required has been received. Log any repairs in the electronic logbook. To trouble check for leaks in the Markes system, run the direct control function from the main menu by right clicking on the **Markes TD** icon and selecting **Direct Control**. Pressurize the system and allow it to equilibrate for 10-15seconds. Click the leak test button and observe the pressure transducer readbacks for 45seconds. A passing manual leak test is defined by the instrument manufacturer as no more than a 7.5% drop in pressure over 45seconds.

9.11 Markes CIA-Advantage 16-Port Valve Pneumatic Failure

The pneumatics system in the Markes CIA-Advantage is pressurized by the supplied zero air gas stream and consumes a large volume of gas when the valve actuates. The valve can fail to actuate fully if the pressure drop in the gas line is too large. This can be reset by turning off the CIA-Advantage and verifying the pressure of the supplied gases is correct: 100 psi at the manifold and 60 psi at the Markes regulator. Turn the system back on and listen for the valve to actuate. The valve can be directly controlled via the **MIC 2.0** software. Right click on the **Markes TD** icon and select **Direct Control**. Click on the picture of the 16-position valve in the CIA-Advantage box and select the port you want to move to. If it still fails, contact Agilent as the Markes system is covered under the Agilent CrossLab Silver service contract. Call into the 1-800-227-9770 number and create a trouble ticket for the AutoGC. A service engineer will schedule a repair once the part required has been received. Log any repairs in the electronic logbook.

9.12 Instrument PC or GC Time Incorrect

The instrument PC time is set by the DIT and cannot be adjusted without an administrator.

Note: DAQ does not observe or correct for daylight savings time when setting monitoring equipment PC times. Administrative rights are required for this step.

The GC time can drift occasionally if the instrument is off-line for extended periods and can easily be resynced. In the **ChemStation** menu select **Instrument** -> **Instrument Menu** -> **synchronize PC and GC time.**

9.13 Kori Purge Flow Correction

With the Agilent ADM Flowmeter still connected to the purge outlet, rotate the dial located to the left. Refer to figure 2, if needed. Counterclockwise rotation will increase the flow, while clockwise rotation will decrease the purge flow outlet. Use the dial to set the flow to 100 cc/min. Document adjustment in the electronic logbook.

9.14 Agilent Gas Clean Filter Replacement

Agilent Gas Clean oxygen-moisture filters utilize a color indicator to alert the operator that the gas stream has depleted the filter cartridge. Both indicators will begin at a green hue. As oxygen depletes the trap, the oxygen indicator will turn black. As moisture depletes the trap, the moisture indicator will turn yellow. The water and oxygen indicators are separate and labeled on each filter.

To replace a spent filter, unscrew the black plastic base to disconnect the filter. The base will leave behind 2 posts with O-rings and an alignment cylinder. Removal of the filter cartridge will also stop flow of the gas stream. Inspect the O-rings prior to trap installation and replace if they are worn. Replace the moisture-oxygen trap with an Agilent in-line gas clean moisture filter (P/N CP17971).

Minimum replacement is yearly during the preventative maintenance visit or as indicator dictates filter is depleted, whichever is sooner.

Hydrocarbon traps are replaced yearly during preventative maintenance visit or as contamination is observed, whichever is sooner. Removal and replacement is the same as detailed above for the gas clean oxygen-moisture filter. Replace with Agilent hydrocarbon filter (P/N CP17972).

Log filter replacement in electronic logbook and be sure to order replacements after employing new gas filters.

9.15 Invalid Calibration Curve Corrective Action

Prepare a new calibration using the Entech 4700 dilution system. It may be necessary to investigate for system contamination or interferences resulting in suppression or enhancement of analytes. System leaks, section 9.10, and trap degradation, section 9.4, may impede a proper calibration as well as carryover from samples or standards. Improperly conditioned traps may contribute chromatographic artifacts. PAMS data monitoring may not commence without a valid calibration curve. Investigate chromatogram for retention time shifts which may result in peak misidentifications by the software. Unless technical justification is provided to explain nonconformance, minimally qualify as “QX” and potentially invalidate as “AS” samples for affected compounds.

9.16 System Humid Blank Corrective Action

Reanalyze the blank, or prepare a new humid blank, to investigate potential carryover from previous samples. Investigate system for contamination. Unless technical justification is provided to explain nonconformance, qualify as “LB” in AQS all samples for affected compounds since the last passing humid blank.

9.17 System CCV Failure Corrective Action

Reanalyze the CCV or SSCV standard. If the reanalysis yields passing results (± 30% of the nominal concentration), monitoring may continue. Any compound outside of these limits, but within ± 50% of the nominal concentration of the standard, can be flagged and monitoring may continue. Compounds outside of this standard range can be invalidated and monitoring can continue, unless it is a priority PAMS compound. Priority compound failure will result in immediate recalibration of the PAMS AutoGC system. The PAMS compound list is shown from the EPA in Appendix J. Investigate chromatograms for retention time shifts which may result in peak misidentifications by the software. Unless technical justification is provided to explain nonconformance, minimally qualify as “QX” and potentially invalidate as “AS” samples for affected compounds since the last passing CCV or SSCV analysis. Invalidation as “AS” may also be required at analyst discretion if compound recovery is exceptionally high or low (outside ± 50% of the nominal concentration of the standard).

9.18 Precision CCV/SSCV Check Failure Corrective Action

Investigate system for carryover, contamination, leaks, or suppression, as indicated by trends in compound behavior. Qualify ambient sample data for affected compounds since the last passing precision check as “QX” in AQS.

9.19 Retention Time Standard (SSCV) Retention Time Shift Corrective Action

Review previous week’s ambient and QC check sample data to evaluate events resulting in retention time shift. May require reassignment or adjustment of retention time windows and reprocessing of data collected since the most recent CCV or RTS. Unless technical justification is provided to explain nonconformance, associated ambient sample data will be invalidated as “BH” for compounds whose identities cannot be confirmed.

10.0 REVISION HISTORY

1. 04/22/2021 **BDV** Original Publication

11.0 REFERENCES

1. North Carolina Department of Environmental Quality, Division of Air Quality (2021). Quality Assurance Project Plan for the North Carolina Division of Air Photochemical Assessment Monitoring Stations (PAMS) Required Site Network for Speciated Volatile Organic Compounds, Carbonyls, and Meteorological Parameters Including Mixing Layer Height. Revision 0. Raleigh, NC. DAQ Document ID: DAQ-01-007. Steger, Joette; Walters, Steven and Velleco, Brian D.
2. United States Environmental Protection Agency: Office of Air Quality Planning and Standards (2019). Technical Assistance Document for the Sampling and Analysis of Ozone Precursors for the Photochemical Assessment Monitoring Station Program. Revision 2. Research Triangle Park, NC. EPA Document ID: EPA-454/B-19-004.
3. United States Environmental Protection Agency: Ambient Monitoring Technology Information Center [AMTIC] 54 PAMS Target Compounds (Hydrocarbons) Listed in Their Elution Sequence (1995). U.S EPA.
4. United States Environmental Protection Agency: Office of Air Quality Planning and Standards (2017). Additional Revision to the Photochemical Assessment Monitoring Stations Compound Target List. Memorandum. Research Triangle Park, NC. Cavender, Kevin

12.0 APPENDICES

1. Appendix A – Arc3 PurityPlus Specialty Gases Grade Specification Sheet
2. Appendix B - Airgas Specialty Gases – 56 VOC compound blend COA
3. Appendix C - Linde SPECTRA Environmental Gases – 61 VOC compound blend COA
4. Appendix D - Agilent ADM Flowmeter Certificate of Calibration
5. Appendix E - FisherBrand Traceable Big-Digit Radio Atomic Wall Clock Certificate of Calibration
6. Appendix F - PAMS-Millbrook AutoGC Electronic Lab Notebook Example
7. Appendix G – PAMS AutoGC Weekly Sample Collection Schedule
8. Appendix H –PAMS Target Compounds List in their Elution Sequence
9. Appendix I – PAMS AutoGC Data Review Checklist
10. Appendix J – PAMS Target List (Priority and Optional Compounds)
11. Appendix K – AQS Qualifier and Null Codes for PAMS

Appendix A – Arc3 PurityPlus Specialty Gases Grade Specification Sheet

PurityPlus Specialty Gases

PURE GAS GRADE SPECIFICATIONS

CONTAMINATE LEVELS (UNLESS OTHERWISE NOTED AS %)

PRODUCT	GRADE	PURITY	PART #	VALVE	O2	THC*	H2O	CO	CO2	N2
ACETYLENE										
ATOMIC ABSORPTION✧	2.6	99.6%	ACE-26-300	510	< 4000 PPM (combined)		-	-	-	-
✧ < 20 PPM PH3										
AIR										
ULTRA ZERO	0.1	-	AIR-UZ-300	590	19.5% - 23.5%	<0.1 ppm	<3 ppm	<1 ppm	<1 ppm	-
ZERO	1.0	-	AIR-ZE-300	590	19.5% - 23.5%	<1 ppm	-	-	-	-
EXTRA DRY	-	-	AIR-ED-300	590	19.5% - 23.5%	-	<8 ppm	-	-	-
ARGON										
RESEARCH	6.0	99.9999%	CDI-50-60	580	<0.2 ppm	<0.1 ppm	<0.2 ppm	<0.1 ppm	<0.1ppm	<0.4 ppm
CHROMATOGRAPH	5.5	99.9995%	ARG-55-XX	580	<1 ppm	<0.1 ppm	<1 ppm	-	-	<3 ppm
NITROGEN FREE	5.0	99.9990%	ARG-NF-XX	580	<2 ppm	<0.5 ppm	<2 ppm	-	-	<4 ppm
UHP	5.0	99.999%	ARG-50-300	580	<1 ppm	<0.5 ppm	<1 ppm	-	-	-
PREPURIFIED	4.8	99.998%	ARG-48-300	580	<5 ppm	<2 ppm	<5 ppm	-	-	-
ZERO	4.8	99.998%	ARG-ZE-300	580	-	<0.5 ppm	-	-	-	-
CARBON DIOXIDE										
RESEARCH	5.0	99.999%	CDI-50-50	320	<1 ppm	<0.5 ppm	<2 ppm	<0.1 ppm	99.999%	<1 ppm
Scientific	4.8	99.998%	CDI-48-50	320	<2 ppm	<2 ppm	<3 ppm	<1 ppm	99.998%	
LASER	4.5	99.995%	CDI-45-50	320	<5 ppm	<1 ppm	<5 ppm	-	99.995%	
COLEMAN/ INSTRUMENT	4.0	99.99%	CDI-40-50	320	<20 ppm	-	<10 ppm	-	99.99%	<50 ppm
ANAEROBIC	3.0	99.9%	CDI-30-50	320	<20 ppm	-	-	-	99.9%	
BONE DRY	2.8	99.8%	CDI-28-50	320	-	-	<20 ppm	-	99.8%	
HELIUM										
GRADE 7	7.0	99.99999%	HEL-70-300	580	<50 **ppb**	<20 **ppb**	<50 **ppb**	<20 **ppb**	<20 **ppb**	<50 **ppb**
RESEARCH	6.0	99.9999%	HEL-60-300	580	<0.2 ppm	<0.1 ppm	<0.2 ppm	<0.1 ppm	<0.1 ppm	<0.4 ppm
CHROMATOGRAPH	5.5	99.9995%	HEL-55-XX	580	<1 ppm	<0.5 ppm	<1 ppm	-	-	<3 ppm
UHP	5.0	99.999%	HEL-50-300	580	<1 ppm	<0.5 ppm	<1 ppm	-	-	-
PREPURIFIED	4.7	99.997%	HEL-47-300	580	<5 ppm	-	<5 ppm	-	-	-
ZERO	4.8	99.998%	HEL-48-300	580	-	<0.5 ppm	-	-	-	-
HYDROGEN										
RESEARCH	6.0	99.9996%	HYD-60-300	350	<0.2 ppm	< 0.1 ppm	<0.5 ppm	<0.1 ppm		<0.3 ppm
Grade 5.5	5.5	99.9995%	HYD-55-300	350	<0.5 ppm	<0.2 ppm	<2 ppm	<0.2 ppm	<0.1 ppm	<2 ppm
UHP^	5.0	99.999%	HYD-50-300	350	<1 ppm	<0.5 ppm	<1 ppm	-	-	<5 ppm
ZERO	4.5	99.995%	HYD-45-300	350	-	<0.5 ppm	-	-	-	-
PREPURIFIED	4.0	99.99%	HYD-40-300	350	<20 ppm		<10 ppm			
NITROGEN										
RESEARCH	6.0	99.9999%	NIT-60-300	580	<0.2 ppm	<0.1 ppm	<0.2 ppm	<0.1 ppm	<0.1 ppm	
CHROMATOGRAPH	5.5	99.9995%	NIT-55-XX	580	<1 ppm	<0.1 ppm	<1 ppm	<1 ppm	<1 ppm	-
UHP	5.0	99.999%	NIT-50-300	580	<1 ppm	<0.5 ppm	<1 ppm	-	-	-
ZERO	4.8	99.998%	NIT-ZE-300	580	-	<0.5	-	-	-	-
PREPURIFIED	4.8	99.998%	NIT-48-300	580	<5 ppm	-	<5 ppm	-	-	-
Oxygen Free	4.8	99.998%	NIT-OF-300	580	<0.5 ppm	-	-	-	-	-
NITROUS OXIDE										
ATOMIC ABSORPTION	2.6	99.6%	N20-26-50	326	*	-	<30 ppm	-	-	*
* N20-AA: AIR<2000 ppm										
OXYGEN										
RESEARCH***	5.0	99.999%	OXY-50-300	540	99.999%	<0.5 ppm	<1 ppm	<1 ppm		<5 ppm
UHP**	4.3	99.993%	OXY-43-300	540	99.993%	<0.5 ppm	<3 ppm	-	-	<10 ppm
ZERO	2.8	99.8%	OXY-28-300	540	99.8%	<0.5 ppm	-	-	-	-
EXTRA DRY	2.6	99.6%	OXY-26-300	540	99.6%	-	<10 ppm	-	-	-
					**O2-UHP <40 ppm Ar		***O2-RESEARCH <5 ppm Ar			
ppm = Parts Per Million					ppb = Parts Per Billion		THC = Total Hydrocarbons			

Appendix B - Airgas Specialty Gases – 56 VOC compound blend COA

Scott

Airgas Specialty Gases
Airgas USA, LLC
6141 Easton Road
Bldg 1
Plumsteadville, PA 18949
Airgas.com

CERTIFICATE OF ANALYSIS

Grade of Product: CERTIFIED HYDROCARBON

Part Number:	X57NI99C15AC003	Reference Number:	160-401659192-1
Cylinder Number:	AAL072554	Cylinder Volume:	144.3 CF
Laboratory:	124 - Plumsteadville - PA	Cylinder Pressure:	2050 PSIG
Analysis Date:	Nov 19, 2019	Valve Outlet:	350SS
Lot Number:	160-401659192-1	Expiration Date:	Nov 19, 2021

Traceability Statement: Hydrocarbon Process standards are NIST traceable either directly by weight or by comparison to Airgas laboratory standards that are directly NIST traceable by weight.

CERTIFIED CONCENTRATIONS

Component	Requested Concentration	Reported Mole %	Accuracy
1 BUTENE	100.000 PPB	108.000 PPB	+/- 10%
1 HEXENE	100.000 PPB	98.000 PPB	+/- 10%
1 PENTENE	100.000 PPB	99.000 PPB	+/- 10%
1,2,3 TRIMETHYL BENZENE	100.000 PPB	105.000 PPB	+/- 10%
1,2,4 TRIMETHYLBENZENE	100.000 PPB	104.000 PPB	+/- 10%
1,3 DIETHYLBENZENE	100.000 PPB	97.000 PPB	+/- 10%
1,3,5 TRIMETHYL BENZENE	100.000 PPB	100.000 PPB	+/- 10%
1,4 DIETHYL BENZENE	100.000 PPB	99.000 PPB	+/- 10%
2 ETHYLTOLUENE	100.000 PPB	104.000 PPB	+/- 10%
2 METHYL PENTANE	100.000 PPB	106.000 PPB	+/- 10%
2 METHYLHEPTANE	100.000 PPB	99.000 PPB	+/- 10%
2 METHYLHEXANE	100.000 PPB	102.000 PPB	+/- 10%
2,2 DIMETHYLBUTANE	100.000 PPB	101.000 PPB	+/- 10%
2,3 DIMETHYL BUTANE	100.000 PPB	104.000 PPB	+/- 10%
2,3 DIMETHYL PENTANE	100.000 PPB	100.000 PPB	+/- 10%
2,3,4 TRIMETHYL PENTANE	100.000 PPB	99.000 PPB	+/- 10%
2,4 DIMETHYL PENTANE	100.000 PPB	102.000 PPB	+/- 10%
3 ETHYLTOLUENE	100.000 PPB	99.000 PPB	+/- 10%
3 METHYL PENTANE	100.000 PPB	105.000 PPB	+/- 10%
3 METHYLHEPTANE	100.000 PPB	102.000 PPB	+/- 10%
3 METHYLHEXANE	100.000 PPB	102.000 PPB	+/- 10%
4 ETHYL TOLUENE	100.000 PPB	95.000 PPB	+/- 10%
ACETYLENE	100.000 PPB	101.000 PPB	+/- 10%
BENZENE	100.000 PPB	100.000 PPB	+/- 10%
CIS 2 BUTENE	100.000 PPB	108.000 PPB	+/- 10%
CIS 2 PENTENE	100.000 PPB	98.000 PPB	+/- 10%
CUMENE	100.000 PPB	96.000 PPB	+/- 10%
CYCLOHEXANE	100.000 PPB	103.000 PPB	+/- 10%
CYCLOPENTANE	100.000 PPB	95.000 PPB	+/- 10%
DODECANE	100.000 PPB	103.000 PPB	+/- 10%
ETHANE	100.000 PPB	107.000 PPB	+/- 10%
ETHYL BENZENE	100.000 PPB	101.000 PPB	+/- 10%
ETHYLENE	100.000 PPB	111.000 PPB	+/- 10%
HEXANE	100.000 PPB	105.000 PPB	+/- 10%
ISOBUTANE	100.000 PPB	108.000 PPB	+/- 10%
ISOOCTANE	100.000 PPB	100.000 PPB	+/- 10%
ISOPENTANE	100.000 PPB	96.000 PPB	+/- 10%
ISOPRENE	100.000 PPB	95.000 PPB	+/- 10%
M,P XYLENE	100.000 PPB	102.000 PPB	+/- 10%
METHYL CYCLOHEXANE	100.000 PPB	102.000 PPB	+/- 10%
METHYL CYCLOPENTANE	100.000 PPB	106.000 PPB	+/- 10%
N BUTANE	100.000 PPB	107.000 PPB	+/- 10%
N DECANE	100.000 PPB	104.000 PPB	+/- 10%

Approved for Release

Scott

Airgas Specialty Gases
Airgas USA, LLC
6141 Easton Road
Bldg 1
Plumsteadville, PA 18949
Airgas.com

N HEPTANE	100.000 PPB	96.000 PPB	+/- 10%
N NONANE	100.000 PPB	102.000 PPB	+/- 10%
N OCTANE	100.000 PPB	101.000 PPB	+/- 10%
N PENTANE	100.000 PPB	101.000 PPB	+/- 10%
N PROPYL BENZENE	100.000 PPB	101.000 PPB	+/- 10%
O XYLENE	100.000 PPB	100.000 PPB	+/- 10%
PROPANE	100.000 PPB	109.000 PPB	+/- 10%
PROPYLENE	100.000 PPB	107.000 PPB	+/- 10%
STYRENE	100.000 PPB	99.000 PPB	+/- 10%
TOLUENE	100.000 PPB	106.000 PPB	+/- 10%
TRANS 2 BUTENE	100.000 PPB	106.000 PPB	+/- 10%
TRANS 2 PENTENE	100.000 PPB	101.000 PPB	+/- 10%
UNDECANE	100.000 PPB	103.000 PPB	+/- 10%
NITROGEN	100.0 %	99.999429 %	+/- 2%

Permanent Notes: STD TO MIX - PAMS

Approved for Release

Appendix C - Linde SPECTRA Environmental Gases – 61 VOC compound blend COA

ISO 9001:2015 Linde **SPECTRA** Environmental Gases, 80 Industrial Drive, Alpha, NJ 08865

THE LINDE GROUP

SHIPPED TO: NC Denr Division of Air Quality
4403 Reedy Creek Rd.
Raleigh, NC 27607

PAGE: 1 of 3

ANALYSIS REPORT

Sales#:	117393630	**Cylinder Size:**	082 (7.2" X 35")
Production#:	1515540	**Cylinder # :**	EY-0001288
Report Date:	Jul-28-2020	**Cylinder Pressure:**	2200 psig
P.O.# :	PDI PO PENDING	**Cylinder Valve:**	CGA 350 / Steel
Blend Type:	QUALIFIED	**Cylinder Volume:**	15.7 Liter
Material#:	24106473	**Cylinder Material:**	Aluminum
Traceability:	NIST by weight	**Gas Volume:**	2367 Liters
Expiration Date:	Jul-28-2021	**Blend Tolerance:**	10% Relative
Do NOT use under:	150 psig	**Analytical Accuracy:**	10% Relative

COMPONENT	CAS NUMBER	REQUESTED CONC	QUALIFIED CONC
Ethylene	74-85-1	100 ppb	97 ppb
Acetylene	74-86-2	100 ppb	97 ppb
Ethane	74-84-0	100 ppb	97 ppb
Propylene	115-07-1	100 ppb	104 ppb
Propane	74-98-6	100 ppb	95 ppb
Isobutane	75-28-5	100 ppb	97 ppb
1-Butene	106-98-9	100 ppb	92 ppb
1,3-Butadiene	106-99-0	100 ppb	93 ppb
n-Butane	106-97-8	100 ppb	96 ppb
Trans-2-Butene	624-64-6	100 ppb	93 ppb
Cis-2-Butene	590-18-1	100 ppb	99 ppb
Ethanol (Analytical Accuracy ± 20%)	64-17-5	100 ppb	85 ppb
Isopentane	78-78-4	100 ppb	99 ppb
1-Pentene	109-67-1	100 ppb	93 ppb
n-Pentane	109-66-0	100 ppb	93 ppb
Isoprene	78-79-5	100 ppb	95 ppb
Trans-2-Pentene	646-04-8	100 ppb	97 ppb
Cis-2-Pentene	627-20-3	100 ppb	91 ppb
2,2-Dimethylbutane	75-83-2	100 ppb	95 ppb
Cyclopentane	287-92-3	100 ppb	96 ppb
2,3-Dimethylbutane	79-29-8	100 ppb	96 ppb
2-Methylpentane	107-83-5	100 ppb	94 ppb
3-Methylpentane	96-14-0	100 ppb	97 ppb
n-Hexane	110-54-3	100 ppb	96 ppb
Methylcyclopentane	96-37-7	100 ppb	96 ppb
2,4-Dimethylpentane	108-08-7	100 ppb	97 ppb
Benzene	71-43-2	100 ppb	97 ppb
Carbon Tetrachloride	56-23-5	100 ppb	98 ppb
Cyclohexane	110-82-7	100 ppb	97 ppb
2-Methylhexane	591-76-4	100 ppb	97 ppb

Linde Gas North America LLC

(908) 329-9700 Main (908) 329-9740 Fax
www.Lindeus.com

ISO 9001:2015 Linde **SPECTRA** Environmental Gases, 80 Industrial Drive, Alpha, NJ 08865

THE LINDE GROUP

Linde

SHIPPED TO: NC Denr Division of Air Quality
4403 Reedy Creek Rd.
Raleigh, NC 27607

PAGE: 2 of 3

ANALYSIS REPORT

Sales#:	117393630	**Cylinder Size:**	082 (7.2" X 35")
Production#:	1515540	**Cylinder # :**	EY-0001288
Report Date:	Jul-28-2020	**Cylinder Pressure:**	2200 psig
P.O.# :	PDI PO PENDING	**Cylinder Valve:**	CGA 350 / Steel
Blend Type:	QUALIFIED	**Cylinder Volume:**	15.7 Liter
Material#:	24106473	**Cylinder Material:**	Aluminum
Traceability:	NIST by weight	**Gas Volume:**	2367 Liters
Expiration Date:	Jul-28-2021	**Blend Tolerance:**	10% Relative
Do NOT use under:	150 psig	**Analytical Accuracy:**	10% Relative

COMPONENT	CAS NUMBER	REQUESTED CONC	QUALIFIED CONC
2,3-Dimethylpentane	565-59-3	100 ppb	98 ppb
3-Methylhexane	589-34-4	100 ppb	97 ppb
2,2,4-Trimethylpentane	540-84-1	100 ppb	97 ppb
n-Heptane	142-82-5	100 ppb	97 ppb
Methylcyclohexane	108-87-2	100 ppb	98 ppb
2,3,4-Trimethylpentane	565-75-3	100 ppb	98 ppb
Toluene	108-88-3	100 ppb	98 ppb
2-Methylheptane	592-27-8	100 ppb	99 ppb
3-Methylheptane	589-81-1	100 ppb	97 ppb
n-Octane	111-65-9	100 ppb	98 ppb
Tetrachloroethylene	127-18-4	100 ppb	97 ppb
Ethylbenzene	100-41-4	100 ppb	99 ppb
p-Xylene	106-42-3	100 ppb	50 ppb
m-Xylene	108-38-3	100 ppb	50 ppb
Styrene	100-42-5	100 ppb	97 ppb
o-Xylene	95-47-6	100 ppb	100 ppb
Nonane	111-84-2	100 ppb	100 ppb
Isopropylbenzene	98-82-8	100 ppb	98 ppb
alpha-Pinene (No Stability Guarantee)	80-56-8	100 ppb	114 ppb
n-Propylbenzene	103-65-1	100 ppb	99 ppb
m-Ethyltoluene	620-14-4	100 ppb	102 ppb
p-Ethyltoluene	622-96-8	100 ppb	99 ppb
1,3,5-Trimethylbenzene	108-67-8	100 ppb	102 ppb
o-Ethyltoluene	611-14-3	100 ppb	100 ppb
beta-Pinene (No Stability Guarantee)	127-91-3	100 ppb	117 ppb
1,2,4-Trimethylbenzene	95-63-6	100 ppb	99 ppb
n-Decane	124-18-5	100 ppb	99 ppb
1,2,3-Trimethylbenzene	526-73-8	100 ppb	98 ppb

Linde Gas North America LLC
(908) 329-9700 Main (908) 329-9740 Fax
www.Lindeus.com

ISO 9001:2015 Linde **SPECTRA** Environmental Gases, 80 Industrial Drive, Alpha, NJ 08865

THE LINDE GROUP

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SHIPPED TO: NC Denr Division of Air Quality
4403 Reedy Creek Rd.
Raleigh, NC 27607

PAGE: 3 of 3

ANALYSIS REPORT

Sales#:	117393630	**Cylinder Size:**	082 (7.2" X 35")
Production#:	1515540	**Cylinder # :**	EY-0001288
Report Date:	Jul-28-2020	**Cylinder Pressure:**	2200 psig
P.O.# :	PDI PO PENDING	**Cylinder Valve:**	CGA 350 / Steel
Blend Type:	QUALIFIED	**Cylinder Volume:**	15.7 Liter
Material#:	24106473	**Cylinder Material:**	Aluminum
Traceability:	NIST by weight	**Gas Volume:**	2367 Liters
Expiration Date:	Jul-28-2021	**Blend Tolerance:**	10% Relative
Do NOT use under:	150 psig	**Analytical Accuracy:**	10% Relative

COMPONENT	CAS NUMBER	REQUESTED CONC	QUALIFIED CONC
m-Diethylbenzene	141-93-5	100 ppb	98 ppb
p-Diethylbenzene	105-05-5	100 ppb	99 ppb
n-Undecane	1120-21-4	100 ppb	98 ppb
Nitrogen	7727-37-9	Balance	Balance

ANALYST: Lou Lorenzetti

DATE: Jul-28-2020

Linde Gas North America LLC

(908) 329-9700 Main (908) 329-9740 Fax
www.Lindeus.com

Appendix D - Agilent ADM Flowmeter Certificate of Calibration

Certificate Of Calibration

Agilent Technologies Flow Meter SN MY20020044

Bayan Lepas Free Industrial Zone, Phase 3, 11900 Bayan Lepas, Penang, Malaysia

Date: 2020 Jan 10
Model: **G6692A**
Serial: **MY20020112** – Flow cartridge
Product Key: **3D3F**
Test Station: E1234

Equipment used:

Flow Measurement System Controller
Manufacturer: Fluke
Model: molbox1+700K
Serial Number: 2347

Low Range Measurement (0-100 ml/min)
Manufacturer: Fluke
Model: 5E1-VCR-V-Q - 5E1 LAMINAR MOLBLOC FLOW ELEMENT
Serial Number: 7054

High Range Measurement (100-750 ml/min)
Manufacturer: Fluke
Model: 1E3-VCR-V-Q - 1E3 LAMINAR MOLBLOC FLOW ELEMENT
Serial Number: 7053

Ambient Temperature(°C): 22.2
Ambient Pressure(MPa): 0.100972
Calibration Gas: Nitrogen
Calibrated by: FMATS
Calibrated Status: NEW

Temperature
Manufacturer: Pico Technologies
Model: PT100 probe (PT104 Data Logger)
Serial Number: CP901/012

Pressure
Manufacturer: Omega Engineering
Model: PX409-26BUSBH
Serial Number: 456451

The above designated flow meter was calibrated to within an absolute accuracy of 0-500 ml/min +/-2% or +/- 0.2 ml/min (whichever is greater) ; 501-750ml/min +/-3% at room temperature using NIST traceable flow rate standards. These flow rate standards are periodically verified to the above listed NIST traceable standards as employed by Agilent and have a maximum aggregate uncertainty of 0.33% percent of the actual flow rate.

Verification Table

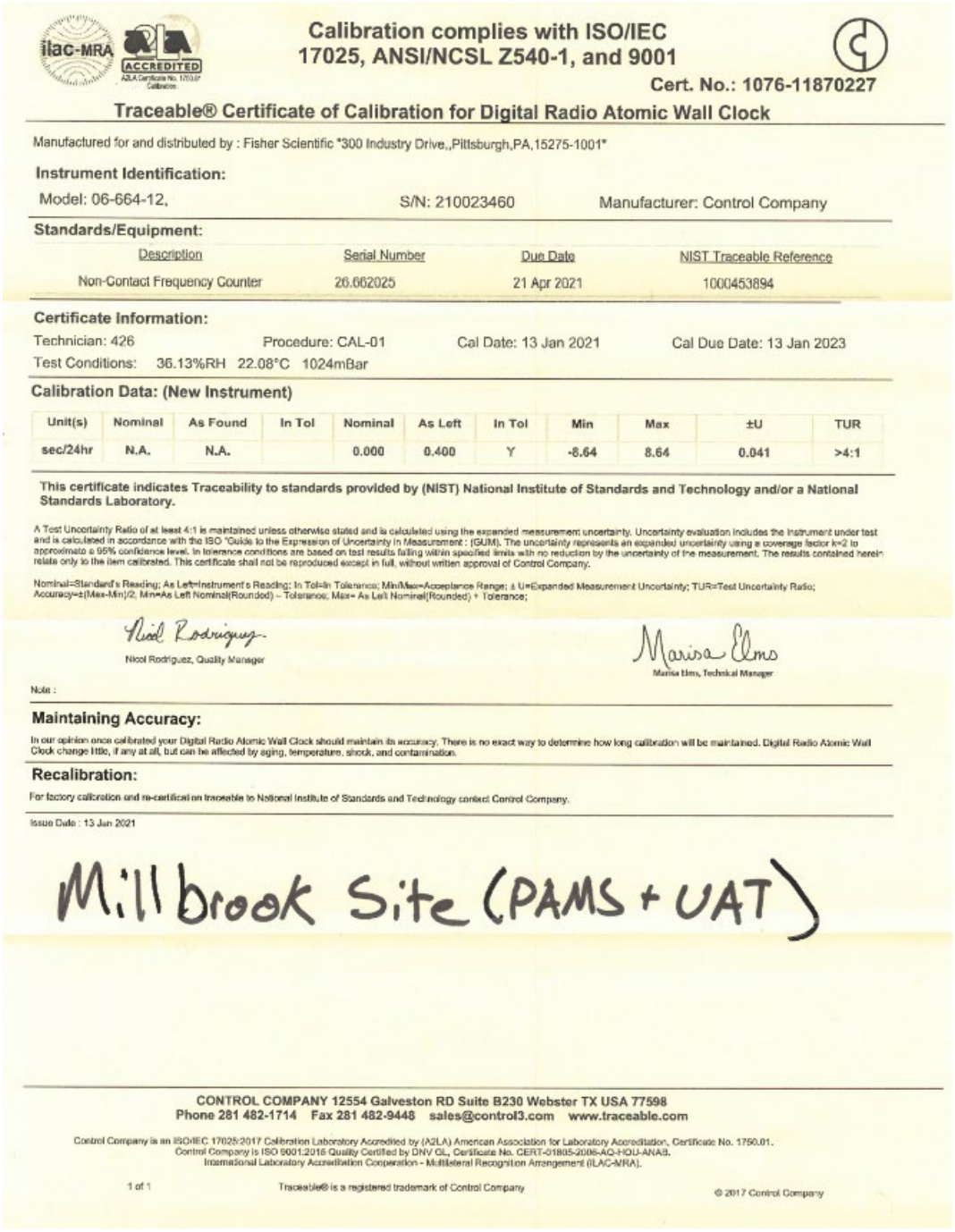
Flow Reference	Flow Measured	Low Limit	High Limit	Pass/Fail
0 [0]	0.01 [0]	-0.17 [-0.17]	0.17 [0.17]	Pass [Pass]
0.5 [0.46]	0.49 [0.46]	0.33 [0.29]	0.67 [0.63]	Pass [Pass]
0.98 [0.9]	0.99 [0.91]	0.81 [0.73]	1.15 [1.07]	Pass [Pass]
4.98 [4.59]	5 [4.61]	4.81 [4.42]	5.15 [4.76]	Pass [Pass]
9.97 [9.18]	9.96 [9.2]	9.8 [9.01]	10.14 [9.35]	Pass [Pass]
50.1 [46.1]	50 [46]	49.29 [45.4]	50.9 [46.9]	Pass [Pass]
99.7 [91.8]	99.4 [91.4]	98.15 [90.4]	101.34 [93.3]	Pass [Pass]
199.9 [184.2]	198.9 [183.3]	196.7 [181.2]	203.1 [187.1]	Pass [Pass]
300 [276.4]	298.2 [274.6]	295.18 [272]	304.78 [280.8]	Pass [Pass]
400.2 [368.6]	397.2 [365.4]	393.77 [362.8]	406.58 [374.6]	Pass [Pass]
510.4 [470.4]	506.9 [464.9]	502.2 [462.8]	518.53 [477.9]	Pass [Pass]
600.3 [553]	596.4 [548.6]	590.7 [544.1]	609.91 [561.8]	Pass [Pass]
700.3 [645.1]	696.3 [639.6]	689.08 [634.8]	711.49 [655.4]	Pass [Pass]
740.1 [681.8]	735.8 [676.4]	728.28 [670.9]	751.97 [692.7]	Pass [Pass]

Top values are in ml/min. [Bottom values] are in sccm

G6692A MY20020112

Page 1 of 1

Appendix E - FisherBrand Traceable Big-Digit Radio Atomic Wall Clock Certificate of Calibration



Calibration complies with ISO/IEC 17025, ANSI/NCSL Z540-1, and 9001

Cert. No.: 1076-11870227

Traceable® Certificate of Calibration for Digital Radio Atomic Wall Clock

Manufactured for and distributed by : Fisher Scientific "300 Industry Drive,,Pittsburgh,PA,15275-1001"

Instrument Identification:

Model: 06-664-12, S/N: 210023460 Manufacturer: Control Company

Standards/Equipment:

Description	Serial Number	Due Date	NIST Traceable Reference
Non-Contact Frequency Counter	26.662025	21 Apr 2021	1000453894

Certificate Information:

Technician: 426 Procedure: CAL-01 Cal Date: 13 Jan 2021 Cal Due Date: 13 Jan 2023

Test Conditions: 36.13%RH 22.08°C 1024mBar

Calibration Data: (New Instrument)

Unit(s)	Nominal	As Found	In Tol	Nominal	As Left	In Tol	Min	Max	±U	TUR
sec/24hr	N.A.	N.A.		0.000	0.400	Y	-8.64	8.64	0.041	>4:1

This certificate indicates Traceability to standards provided by (NIST) National Institute of Standards and Technology and/or a National Standards Laboratory.

A Test Uncertainty Ratio of at least 4:1 is maintained unless otherwise stated and is calculated using the expanded measurement uncertainty. Uncertainty evaluation includes the instrument under test and is calculated in accordance with the ISO "Guide to the Expression of Uncertainty in Measurement : (GUM). The uncertainty represents an expanded uncertainty using a coverage factor k=2 to approximate a 95% confidence level. In tolerance conditions are based on test results falling within specified limits with no reduction by the uncertainty of the measurement. The results contained herein relate only to the item calibrated. This certificate shall not be reproduced except in full, without written approval of Control Company.

Nominal=Standard's Reading; As Left=Instrument's Reading; In Tol=In Tolerance; Min/Max=Acceptance Range; ± U=Expanded Measurement Uncertainty; TUR=Test Uncertainty Ratio; Accuracy=±(Max-Min)/2, Min=As Left Nominal(Rounded) – Tolerance; Max= As Left Nominal(Rounded) + Tolerance;

Nicol Rodriguez, Quality Manager

Marisa Elms, Technical Manager

Note :

Maintaining Accuracy:

In our opinion once calibrated your Digital Radio Atomic Wall Clock should maintain its accuracy. There is no exact way to determine how long calibration will be maintained. Digital Radio Atomic Wall Clock change little, if any at all, but can be affected by aging, temperature, shock, and contamination.

Recalibration:

For factory calibration and re-certification traceable to National Institute of Standards and Technology contact Control Company.

Issue Date : 13 Jan 2021

Millbrook Site (PAMS + UAT)

CONTROL COMPANY 12554 Galveston RD Suite B230 Webster TX USA 77598
Phone 281 482-1714 Fax 281 482-9448 sales@control3.com www.traceable.com

Control Company is an ISO/IEC 17025:2017 Calibration Laboratory Accredited by (A2LA) American Association for Laboratory Accreditation, Certificate No. 1750.01.
Control Company is ISO 9001:2015 Quality Certified by DNV GL, Certificate No. CERT-01805-2006-AQ-HOU-ANAB.
International Laboratory Accreditation Cooperation - Multilateral Recognition Arrangement (ILAC-MRA).

1 of 1

Traceable® is a registered trademark of Control Company

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Appendix F - PAMS-Millbrook AutoGC Electronic Lab Notebook Example

North Carolina Department of Environmental Quality, Division of Air Quality LAB

PAMS-Millbrook AutoGC Electronic Lab Notebook

12/22/2020 BDV – Agilent 7890B (S/N US18403044), Unity-XR (S/N GB00U-33073), Kori-XR (S/N GB00W-10171) and CIA-Advantage (S/N GB00H-33073) installed at the Millbrook Site located at 3801 Spring Forest Rd. Raleigh, NC by Karen Kaikkonen of Agilent Technologies. System failed to pressurize after a leak test. Another service call will be required to complete the installation of the AutoGC system.

1/25/2021 BDV – Gregory Oppenheim of Agilent Technologies at site to repair system. Found clog in the flow path of the Markes front-end (Unity, Kori and CIA-Advantage). Transfer lines were replaced and the system passed leak test and capture of ambient air and analytical standard. The Unity-XR, system, however, fails to hit the temperature set-point of -30°C designated by the manufacturer. Greg will return Friday, 1/29, to replace the Unity-XR trap heater.

1/29/2021 BDV – Gregory Oppenheim of Agilent Technologies at site to replace Unity-XR trap heater. Trap heater was replaced without issue and the system now functions at designed PAMS method specifications. Testing of the new part will occur over the next week.

The inlet was installed for the PAMS AutoGC. The inlet is composed of an inverted conical rain guard and 17in of 1/4" OD (0.21"ID) chromatographic grade stainless steel tubing coupled to a 15um particulate filter and 207in of 1/8" OD (0.085" ID) chromatographic stainless steel tubing that is directly interfaced with the AutoGC. The total length of the inlet is 18.67ft and with a purge rate of 100cc/min for 2minutes, the equipment meets the 20second residence time requirement for PAMS sampling operations.

2/01/2021 BDV – Canisters installed to instrument as follows:

CIA Port 1: Ambient Inlet
CIA Port 2: Humid Blank; Canister# S6341
CIA Port 3: 10ppbv PAMS Standard – Airgas; Canister# S2453
CIA Port 4: 2ppbv PAMS Standard - Airgas; Canister# S2391

All other ports open to shelter.

2/05/2021 BDV – System deemed stable and 14-shakedown period begun consisting of repetitive ambient air capture and analysis. Site inspection and hydrogen gas delivery occurred.

2/15/2021 BDV – Shakedown still occurring. Site inspection and zero air gas delivery occurred.

2/23/2021-2/24/2021 BDV – PAMS AutoGC Training sessions with Eastern Research Group (ERG) conducted by Markes service engineer, Nathan Shafer. ERG members included Mitch Howell and Kameron Singer.

Canisters installed to instrument as follows:

CIA Port 1: Ambient Inlet
CIA Port 2: Humid Blank; Canister# S6341
CIA Port 3: ERG PAMS RT Canister (15L)

All other ports open to shelter.

Leak detected during a leak test demonstration by Nathan. The leak was found within the Kori-XR. Helium was detected behind the trap assembly from the bottom of the pneumatic pin valve using a leak detector.

PAMS-Millbrook AutoGC Electronic Lab Notebook Pg. 1
Self/Level 1 Review: BDV 4/11/2021
Peer/Level 2 Review:_____

Appendix G – PAMS AutoGC Weekly Sample Collection Schedule

PAMS AutoGC Weekly Sample Collection Schedule							
Sample Start Time	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
0:00	CCV	CCV	CCV	CCV	CCV	CCV	CCV
1:00	B	B	B	B	B	B	P
2:00	A	A	A	A	A	A	B
3:00	A	A	A	A	A	A	A
4:00	A	A	A	A	A	A	A
5:00	A	A	A	A	A	A	A
6:00	A	A	A	A	A	A	A
7:00	A	A	A	A	A	A	A
8:00	A	A	A	A	A	A	A
9:00	A	A	A	A	A	A	A
10:00	A	A	A	A	A	A	A
11:00	A	A	A	A	A	A	A
12:00	A	A	A	A	A	A	A
13:00	A	A	A	A	A	A	A
14:00	A	A	A	A	A	A	A
15:00	A	A	A	A	A	A	A
16:00	A	A	A	A	A	A	A
17:00	A	A	A	A	A	A	A
18:00	A	A	A	A	A	A	A
19:00	A	A	A	A	A	A	A
20:00	A	A	A	A	A	A	A
21:00	A	A	A	A	A	A	A
22:00	A	A	A	A	A	A	A
23:00	A	A	A	A	A	A	A

A Ambient air sample
B Humid Blank sample
CCV CCV or SCCV
P Precision check, replicate CCV or SCCV

Appendix H –PAMS Target Compounds List in their Elution Sequence

54 PAMS target compounds (hydrocarbons) listed in their elution sequence.

	Hydrocarbon	AIRS	CAS
1.	Ethylene	43203	74851
2.	Acetylene	43206	74862
3.	Ethane	43202	74840
4.	Propylene	43205	115071
5.	Propane	43204	74986
6.	Isobutane	43214	75285
7.	1-Butene[1]	43280	106989
8.	n-Butane	43212	106978
9.	*t*-2-Butene	43216	624646
10.	*c*-2-Butene	43217	590181
11.	Isopentane	43221	78784
12.	1-Pentene	43224	109671
13.	n-Pentane	43220	109660
14.	Isoprene	43243	78795
15.	*t*-2-Pentene	43226	646048
16.	c-2-Pentene	43227	627203
17.	2,2-Dimethylbutane	43244	75832
18.	Cyclopentane	43242	287923
19.	2,3-Dimethylbutane	43284	79298
20.	2-Methylpentane	43285	107835
21.	3-Methylpentane	43230	96140
22.	n-Hexane	43231	110543
23.	Methylcyclopentane	43262	96377
24.	2,4-Dimethylpentane	43247	108087
25.	Benzene	45201	71432
26.	Cyclohexane	43248	110827
27.	2-Methylhexane	43263	591764
28.	2,3-Dimethylpentane	43291	565593
29.	3-Methylhexane	43249	589344
30.	2,2,4-Trimethylpentane	43250	540841
31.	n-Heptane	43232	142825
32.	Methylcyclohexane	43261	108872
33.	2,3,4-Trimethylpentane	43252	565753
34.	Toluene	45202	108883
35.	2-Methylheptane	43960	592278
36.	3-Methylheptane	43253	589811
37.	n-Octane	43233	111659
38.	Ethylbenzene	45203	100414
39.	*m* & *p*-Xylene[2]	45109	108383/106423
40.	Styrene	45220	100425
41.	*o*-Xylene	45204	95476
42.	n-Nonane	43235	111842
43.	Isopropylbenzene	45210	98828
44.	n-Propylbenzene	45209	103651
45.	*m*-Ethyltoluene	45212	620144
46.	*p*-Ethyltoluene	45213	622968
47.	1,3,5-Trimethylbenzene	45207	108678
48.	*o*-Ethyltoluene	45211	611143
49.	1,2,4-Trimethylbenzene	45208	95636
50.	n-Decane	43238	124185
51.	1,2,3-Trimethylbenzene	45225	526738
52.	*m*-Diethylbenzene[3]	45218	141935
53.	*p*-Diethylbenzene	45219	105055
54.	n-Undecane	43954	1120214

[1]Note that because 1-Butene and Isobutene elute at about the same time, they are difficult to resolve. The coeluting isomers are assigned AIRS Parameter Code 43127. Isobutene is assigned AIRS Parameter Code 43270 and CAS 115117.

[2]These isomers of xylene are also difficult to resolve. Individually, their AIRS Parameter Codes are 45205 & 45206, respectively. Respective CAS numbers are provided in the table.

[3]Also named 1,3-Diethylbenzene.

Note: Additional Compounds in the Airgas standard are n-Dodecane and 1-Hexene.

n-Dodecane elutes after n-Undecane in the calibration standard.

1-Hexene elutes before n-Hexane and is used to determine the microfluidic Dean switch timing.

Appendix I – PAMS AutoGC Data Review Checklist

PAMS AutoGC Data Review Checklist

Sequence Name:	
AutoGC Operator (Initials and Date):	
Level 2 Peer Reviewer (Initals and Date):	

Data Review: Initial Calibration (ICAL)	Self/Level 1 Review (Check One) Y	Self/Level 1 Review (Check One) N	Peer/Level 2 Review (Check One) Y	Peer/Level 2 Review (Check One) N
Markes Export File Reviewed? Confirm that hourly injections occur, at least 75%, during the hour specified. Confirm the captured sample volume is ± 2% of the volume requested				
The humid blank ≤ 0.5ppbc or ≤ MDL, whichever is lower for all compounds?				
Linearity Coefficient of Determination (R^2) > 0.99 for all compounds?				
The absolute value of the y-intercept/slope ≤ 0.5ppbc or ≤ MDL (whichever is lower)?				
The RSD% of each analyte RF in the calibration curve ≤ 10%?				
The concentration of each analyte in the calibration curve ± 20% of nominal value?				
2ppbv PAMS SSCV ± 30% of nominal value for all compounds?				
Raw chromatograms and data files located in LAB P: Drive PAMS folder under the Sequence Name?				
LAB Notes:				
Reviewer Notes:				

Data Review: PAMS Seasonal Data	Self/Level 1 Review (Check One) Y	Self/Level 1 Review (Check One) N	Peer/Level 2 Review (Check One) Y	Peer/Level 2 Review (Check One) N
Markes Export File Reviewed? Confirm that hourly injections occur, at least 75%, during the hour specified. Confirm the captured sample volume is ± 2% of the volume requested.				
2ppbv PAMS daily CCV or SSCV ± 30% of nominal value for all compounds?				
The daily humid blank ≤ 0.5ppbc or ≤ MDL, whichever is lower for all compounds?				
Weekly CCV precision of ≤ 25% RPD for all compounds?				
2ppbv PAMS weekly CCV or SSCV ± 30% of nominal value for all compounds?				
Raw chromatograms and data files located in LAB P: Drive PAMS folder under the Sequence Name?				
LAB Notes:				
Reviewer Notes:				

Appendix J – PAMS Target List (Priority and Optional Compounds)

PAMS Target List

Existing Priority Compounds	Optional Compounds
1,2,3-Trimethylbenzene	1,3 Butadiene
1,2,4-Trimethylbenzene	1,3,5-Trimethylbenzene
1-Butene	1-Pentene
2,2,4-Trimethylpentane	2,2-Dimethylbutane
Acetaldehyde	2,3,4-Trimethylpentane
Benzene	2,3-Dimethylbutane
Cis-2-Butene	2,3-Dimethylpentane
Ethane	2,4-Dimethylpentane
Ethylbenzene	2-Methylheptane
Ethylene	2-Methylhexane
Formaldehyde	2-Methylpentane
Isobutane	3-Methylheptane
Isopentane	3-Methylhexane
Isoprene	3-Methylpentane
M/P Xylene	Acetone
M-Ethyltoluene	Acetylene
N-Butane	Alpha Pinene
N-Hexane	Benzaldehyde
N-Pentane	Beta Pinene
O-Ethyltoluene	Cis-2-Pentene
O-Xylene	Carbon Tetrachloride
P-Ethyltoluene	Cyclohexane
Propane	Cyclopentane
Propylene	Ethanol
Styrene	Isopropylbenzene
Toluene	M-Diethylbenzene
Trans-2-Butene	Methylcyclohexane
	Methylcyclopentane
	N-Decane
	N-Heptane
	N-Nonane
	N-Octane
	N-Propylbenzene
	N-Undecane
	P-Diethylbenzene
	Tetrachloroethylene
	Trans-2-Pentene

Acetaldehyde and Formaldehyde are measured via **DAQ SOP-03.004.2 Thermo Ultimate 3000 Ultra-High Performance Liquid Chromatography Ultra-Violet and Mass Spectrometer Analysis** and are not discussed here.
Acetone and Benzaldehyde are not monitored by AutoGC.
α-Pinene, β-Pinene, Carbon Tetrachloride, Ethanol and Tetrachloroethylene are not monitored or reported as discussed in the approved **PAMS QAPP DAQ-07-001**.

Appendix K – AQS Qualifier and Null Codes for PAMS

AQS Qualifiers and Null Codes for PAMS

Qualifier Code	Qualifier Description	Qualifier Type	Comment
1	Deviation from a CFR/Critical Criteria Requirement	QA	substitute a more descriptive QA qualifier where possible
2	Operational Deviation	QA	substitute a more descriptive QA qualifier where possible
3	Field Issue	QA	substitute a more descriptive QA qualifier where possible
4	Lab Issue	QA	substitute a more descriptive QA qualifier where possible
5	Outlier	QA	
7	Below Lowest Calibration Level	QA	
DI	Sample was diluted for analysis	QA	applies to carbonyls only
EH	Estimated; Exceeds Upper Range	QA	
FB	Field Blank Value Above Acceptable Limit	QA	
HT	Sample pick-up hold time exceeded	QA	applies to carbonyls only
LB	Lab blank value above acceptable limit	QA	applies to carbonyls only
LJ	Identification Of Analyte Is Acceptable; Reported Value Is An Estimate	QA	most common qualifier when an estimate is needed
LK	Analyte Identified; Reported Value May Be Biased High	QA	
LL	Analyte Identified; Reported Value May Be Biased Low	QA	
MD	Value less than MDL	QA	
ND	No Value Detected	QA	
NS	Influenced by nearby source	QA	rare – in most situations such data should be invalidated
QX	Does not meet QC criteria	QA	
SQ	Values Between SQL and MDL	QA	
SS	Value substituted from secondary monitor	QA	rare – most sites will not have collocated instruments
SX	Does Not Meet Siting Criteria	QA	should require invalidation, but no associated null code exists

Qualifier Code	Qualifier Description	Qualifier Type	Comment
TB	Trip Blank Value Above Acceptable Limit	QA	applies to carbonyls only
TT	Transport Temperature is Out of Specs.	QA	applies to carbonyls only
V	Validated Value	QA	
VB	Value below normal; no reason to invalidate	QA	
AC	Construction/Repairs in Area	NULL	
AD	Shelter Storm Damage	NULL	
AE	Shelter Temperature Outside Limits	NULL	
AF	Scheduled but not Collected	NULL	
AG	Sample Time out of Limits	NULL	
AH	Sample Flow Rate out of Limits	NULL	
AI	Insufficient Data (cannot calculate)	NULL	should be used in situations where the 75% of the hour is not met or the sampling period for VOCs is not 40 minutes
AM	Miscellaneous Void	NULL	substitute a more descriptive code where possible
AN	Machine Malfunction	NULL	
AP	Vandalism	NULL	
AQ	Collection Error	NULL	
AR	Lab Error	NULL	
AS	Poor Quality Assurance Results	NULL	substitute a more descriptive QA qualifier where possible
AT	Calibration	NULL	
AU	Monitoring Waived	NULL	
AV	Power Failure	NULL	
AW	Wildlife Damage	NULL	
AX	Precision Check	NULL	
AY	QC Control Points (zero/span)	NULL	
AZ	QC Audit	NULL	used for analysis of the VOCs PT sample & TTP audit for ozone & NO_2
BA	Maintenance/Routine Repairs	NULL	
BB	Unable to Reach Site	NULL	
BE	Building/Site Repair	NULL	
BH	Interference/co-elution/misidentification	NULL	applies to auto-GC parameters only
BI	Lost or damaged in transit	NULL	applies to carbonyls only
BJ	Operator Error	NULL	
BK	Site computer/data logger down	NULL	
DA	Aberrant Data (Corrupt Files, Aberrant Chromatography, Spikes, Shifts)	NULL	
DL	Detection Limit Analyses	NULL	
MC	Module End Cap Missing	NULL	applies to carbonyls only
SC	Sampler Contamination	NULL	
TC	Component Check & Retention Time Standard	NULL	

Qualifier Code	Qualifier Description	Qualifier Type	Comment
TS	Holding Time Or Transport Temperature Is Out Of Specs.	NULL	recommend use of "HT" QA qualifier instead
XX	Experimental Data	NULL	used for troubleshooting, instrument conditioning, MDL determination, etc.
IC	Chem. Spills & Indust Accidents	INFORM	rare
ID	Cleanup After a Major Disaster	INFORM	rare
IE	Demolition	INFORM	rare
IH	Fireworks	INFORM	rare
II	High Pollen Count	INFORM	rare
IJ	High Winds	INFORM	rare, may apply to wind speed and direction data
IK	Infrequent Large Gatherings	INFORM	rare
IM	Prescribed Fire	INFORM	rare
IP	Structural Fire	INFORM	rare
IQ	Terrorist Act	INFORM	rare
IR	Unique Traffic Disruption	INFORM	rare
IS	Volcanic Eruptions	INFORM	rare
IT	Wildfire-U. S.	INFORM	rare
J	Construction	INFORM	rare