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STANDARD OPERATING PROCEDURE

SOP Title: Standard Operating Procedure for Analysis of Volatile Organic Compounds in Whole Air Samples Using the Entech 7200A Preconcentrator and Agilent 8890/5977B Gas Chromatograph–Mass Selective Detector

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Revision History

Revision No.	Name	Date of Revision	Description of Change(s)
0		8/24/23	Initial approval/issuance. This SOP is applicable to a methods development research project. As such we are continuing to experiment with the MS source and quad temperatures to determine the optimum settings. This SOP will be updated as soon as the optimum temperatures are decided.

Standard Operating Procedure for Analysis of Volatile Organic Compounds in Whole Air Samples Using the Entech 7200A Preconcentrator and Agilent 8890/5977B Gas Chromatograph–Mass Selective Detector

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Contents

1.0 Scope and Application

This standard operating procedure (SOP) is applicable to the determination of volatile organic compounds (VOC) using an Entech 7200A universal preconcentrator interfaced with an Entech 7016D autosampler and an Agilent 8890/5977B inert plus extractor electron impact (EI) source gas chromatograph–mass selective detector (GC-MSD) system. VOCs in whole air samples collected in specially prepared sampling canisters from various vendors are preconcentrated onto the Entech focusing trap, injected into the GC, and identified and quantified by mass spectrometry (MS).

The current analysis methods applicable to this SOP are the Entech cold trap dehydration (CTD) method "EtO Short.7200A.CTD" (Appendix A) and the Agilent selected ion monitoring (SIM) method "Short EtO_SegGF25.m" (Appendix A). An alternative longer Entech method "EtO Long.7200A.CTD" (Appendix B) and Agilent SIM method "Long EtO.m" (Appendix B) have also been prepared and are available for use.

The canister analysis method is based on EPA Method TO-15A procedures (U.S. EPA, 2019). In general, the target VOCs are those from the TO-14A (U.S. EPA, 1999a), TO-15 (U.S. EPA, 1999b), TO-15A, Photochemical Assessment Monitoring Stations (PAMS), and National Air Toxics Trends Stations (NATTS) lists with a focus on ethylene oxide (EtO).

2.0 Summary of Method

The Entech 7200A VOC preconcentrator–Agilent 8890/5977B inert plus extractor EI source GC-MSD system is used to determine VOCs in whole air samples collected in specially prepared canisters. The preconcentrator and the GC-MSD have separate instructions for initiating sample analysis on each instrument as specified below. An analysis sequence must be initiated on each instrument to facilitate analysis.

As discussed in Entech's Application Note A-3742-01 (Entech Instruments, 2019), the Entech 7200A universal preconcentrator uses the three-stage extended CTD method for rapid and splitless injection into the GC: dehydration of the sample in Module 1 (dehydration trap), direct trapping of the sample onto a Tenax trap in Module 2, and finally focusing of the sample onto a precolumn in Module 3 (focusing trap). After the sample has been preconcentrated from the canister onto the focusing trap, it is ready to be injected onto the GC column and the Entech sends a start signal to the GC-MSD to begin data acquisition. Once injected into the GC, the compounds undergo further separation. Compounds are transferred to the MS where they undergo ionization and fragmentation in order to identify and quantify compounds. The acquired data are then processed using the ChemStation data analysis software. SIM or SIM/scan mode and internal standards are used in the analytical procedures.

3.0 Definitions

3.1 Acronyms and Abbreviations

amu	atomic mass unit(s)
CB	calibration blank
cc	cubic centimeter(s)
CCV	continuing calibration verification
CGA	Compressed Gas Association
CTD	cold trap dehydration
DQO	data quality objective
EI	electron impact
EtO	ethylene oxide
FB	field blank
FS	field spike
GC	gas chromatograph
HSA	humidified scientific air
HZA	humidified zero air
IB	instrument blank
ICAL	initial calibration
ID	identification
LB	laboratory blank
LS	laboratory spike
MB	method blank
MDL	method detection limit
min	minute(s)
MS	mass spectrometer/spectrometry
MSD	mass selective detector
NATTS	National Air Toxics Trends Stations
PAMS	Photochemical Assessment Monitoring Stations
PFTBA	perfluorotributylamine, a tuning compound
PI	principal investigator
ppbv	parts per billion by volume
ppmv	parts per million by volume
pptv	parts per trillion by volume
psia	pounds per square inch atmosphere
psid	pounds per square inch differential
psig	pounds per square inch gauge
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
RF	response factor
SIM	selected ion monitoring
SOP	standard operating procedure
SSCV	secondary source calibration verification
VOC	volatile organic compound

3.2 Parameter Description and Details

Note: Terminology in this SOP reflects the terminology used in EPA Method TO-15A. In particular, these previously used Ambient Air Branch VOC Laboratory terms are now denoted differently: Helium blank/system blank is instrument blank (IB) and external standard is continuing calibration verification (CCV) standard. Other terms used are study specific and will depend on the data quality objectives (DQO) of the study, as discussed in section 14.9.

CB Calibration blank: a canister filled with clean, humidified diluent gas; indicates that diluent gas and dilution apparatus do not contribute target VOCs, imparting a positive bias to the ICAL (see ICAL description below); may also serve as zero point in the ICAL.

CCV Continuing calibration verification: analysis of a known standard in the lower third of the calibration curve to verify ongoing instrument calibration for each target analyte.

FB Field blank: a canister filled with clean, humidified diluent gas transported to the field site(s) with field collected samples; indicates that field sample handling practices do not contaminate samples.

FS Field spike: a canister filled with humidified standard gas at a concentration in the lower third of the calibration curve transported to the field site(s) with field collected samples; indicates that field sample handling practices do not deteriorate sample integrity.

IB Instrument blank: analysis of an injection where no sample or standard is introduced to the preconcentrator to preliminarily demonstrate the carrier gas and instrument are sufficiently clean to begin analysis.

ICAL Initial calibration: analysis of a minimum of five calibration levels (minimum eight levels if using quadratic regression) covering approximately 20 to 5000 pptv.

LB Laboratory blank: a canister filled with clean, humidified diluent gas that has remained in the laboratory; indicates that laboratory sample handling practices do not contaminate samples.

LS Laboratory spike: a canister filled with humidified standard gas at a concentration in the lower third of the calibration curve that has remained in the laboratory; indicates that laboratory sample handling practices do not deteriorate sample integrity.

MB Method blank: a canister filled with clean, humidified gas; indicates that target VOCs and potential interferences are at acceptably low levels in the system as a whole; the MB is to help assess overall quality of the data.

MDL Method detection limit: establishes the minimum amount of a target analyte distinguishable above background with 99% confidence; determined from spiked canisters and MB canisters.

SSCV Secondary source calibration verification: analysis of a secondary source standard in the lower third of the calibration curve to verify ICAL accuracy for each target analyte.

4.0 Health and Safety Warnings

4.1 Use standard laboratory personal protective equipment, including safety glasses and lab coats, in accordance with the health and safety protocol. Standard laboratory safety procedures should be employed.

4.2 High-pressure cylinders containing gases and dewars of liquid nitrogen for cryogenic cooling are used in this procedure. Exercise extreme caution when working with high-pressure gas cylinders and liquid nitrogen. Cylinders and cryogenic liquids must be handled according to health and safety protocols.

4.3 The oven, inlet, and detector zones can get hot enough to cause burns. Heated areas should be allowed to cool before touching.

4.4 When attaching the VOC sampling canisters to the model 7016D canister autosampler, the operator should use proper lifting techniques to avoid personal injury.

5.0 Interferences

5.1 The research helium cylinder pressure should be checked prior to running a batch of samples to ensure adequate carrier gas for the GC (500 psig minimum).

5.2 The 50 psig liquid nitrogen dewars must be checked prior to running a batch of samples to ensure adequate cryogen for the GC (half tank minimum). Abnormally low pressure in the liquid nitrogen dewar might result in delayed cool-down of the GC oven and failure to inject sample onto the Entech traps.

5.3 Loss of a filament in the MS system during an analysis sequence is not communicated electronically to the Entech. The potential result of this is sample preconcentration without data collection (sample loss). Thorough review by the operator of every chromatographic run at the end of each sequence provides verification that the system is continuing to run well; if a filament has failed in the current analytical sequence, then appropriate actions can be taken so that no additional sample loss occurs.

5.4 All canisters must be tested for cleanliness before use by filling clean, evacuated canisters (J-AMCD-AAB-SOP-3914-2 or J-AMCD-AAB-SOP-3915-2) with humidified scientific air (HSA) (J-AMCD-AAB-SOP-3907-1 or J-AMCD-AAB-SOP-3920-1), allowing the humidified air mixture to age in the canister for a minimum of 24 hours, and analyzing an air sample from the canister according to the procedures outlined in this SOP.

5.5 An IB and a minimum of one MB should be analyzed at the beginning of every sample sequence to check the cleanliness of the analytical system.

5.6 The database for the Entech 7200A run data should be replaced monthly to ensure it does not become full. The replacement of the database is recorded in the laboratory notebook. In the event the database becomes full, an error will appear on the Entech preconcentrator computer screen and the system will not complete any analytical runs until the database is replaced. See the database replacement instructions in the *Entech Model 7200A Preconcentrator User Service Manual*, version 1.0, page 4.

5.7 Prior to installation, the GC column should be conditioned either according to the manufacturer's instructions or by using the suggested column conditioning procedure as outlined in Appendix C to ensure column integrity and to minimize system contamination.

6.0 Personnel Qualifications

6.1 Personnel must have knowledge of laboratory safety practices and have completed any required EPA Safety, Health, and Environmental Management (SHEM) program training.

6.2 Personnel should have sufficient experience in VOC analysis by GC-MS to perform the procedures in this SOP without supervision. New personnel will receive one-on-one training on the specific procedures in this SOP by the principal investigator (PI) or the VOC laboratory lead. The training will be documented on the ORD Training and Demonstration of Capability Form, version 1.0, dated August 11, 2023, which subsequently will be included in the laboratory notebook.

6.3 This procedure requires a thorough understanding of gas chromatography, mass spectrometry, data analysis and validation, flow meters, mass flow controllers, computer spreadsheets, and general instrument troubleshooting.

6.4 Substantial knowledge of the operation of the Entech 7200A preconcentrator, the Agilent GC-MSD system, and Mass Hunter Workstation and ChemStation software is required.

7.0 Equipment and Supplies

7.1 Instrumentation, Software, and Peripherals

Entech 7200A preconcentrator (Entech Instruments Inc., Simi Valley, CA) and associated computer and software:

- Dell OptiPlex 5080 Tower XCTO and Dell P2719H monitor
- Entech 7200A software, version 1.0.2.53 (Entech Instruments Inc.)
- Entech 7200A Report Viewer software, version 1.0.0.4 (Entech Instruments Inc.)
- Entech 7200A Diagnostics software, version 1.19 (Entech Instruments Inc.)

Agilent 8890/5977B inert plus GC-MSD turbo EI bundle with extractor source and associated computer and software:

- HP Z2 computer and monitors
- ChemStation software, GC/MS Environmental and Data Analysis software, version F.01.03.2357 (Agilent Technologies, Santa Clara, CA)
- Mass Hunter Workstation software, version 10.0.368 (Agilent Technologies)
- NIST 20 Mass Spectral Library software, version 20 (Agilent Technologies)

HP LaserJet Enterprise M507 printer

Entech 7016D canister autosampler (Entech Instruments Inc.)

Specially prepared stainless-steel canisters (various vendors) such as SilcoCan (Restek Corporation, Bellefonte, PA), Silonite (Entech Instruments, Inc., Simi Valley, CA), or legacy SUMMA-polished (Scientific Instrumentation Specialists, Moscow, ID) canisters

Cylinder regulators for the helium and nitrogen cylinders (CGA 580)

Entech DDS gauge assembly, part no. 03-32030 (Entech Instruments Inc.)

Entech canister regulator, part no. 01-40-03000 (Entech Instruments Inc.)

Vacuum/pressure gauge for measuring canister pressure, part no. PGS-35L-30V/100 or PGS-35L-30V/60 (Omega Engineering, Inc., Norwalk, CT), or similar

7.2 Supplies

Rxi-624Sil 60 m × 0.25 mm × 1.4 µm capillary GC column (catalog number 13869, Restek Inc., Bellefonte, PA)

Assorted brass, Teflon, and stainless-steel Swagelok tube fittings

Assorted wrenches

Vacuum pump oil

7.3 Standards and Reagents

Cylinder gases and cryogen from AirGas (Morrisville, NC):

- Research grade helium, 99.9999% purity
- Liquid nitrogen dewar at 50 psig head pressure
- Ultra-high-purity nitrogen, 99.999% purity

Internal standard canister consisting of 4-bromofluorobenzene, chlorobenzene-d5, 1,4-difluorobenzene, and bromochloromethane standards prepared in-house (SOP J-AMCD-AAB-SOP-3907-1)

Custom canister standards of target VOCs at various concentrations prepared in-house (J-AMCD-AAB-SOP-3907-1 or J-AMCD-AAB-SOP-3920-1)

8.0 Method Procedures

The Entech 7200A universal preconcentrator interfaced with the Entech 7016D autosampler and the Agilent 8890/5977B inert plus extractor EI source GC-MSD is used for determining VOCs in whole air samples in specially prepared sampling canisters from various vendors. The Entech preconcentrator and GC-MSD instruments do not communicate directly with respect to the sample sequence table, so separate operating instructions are given here.

To conduct analyses using these units, first check the support gases and liquid nitrogen required to run the system (8.1); set up the preconcentrator and autosampler, prepare an analysis sequence on the preconcentrator, and conduct a leak check, a canister line flush, and a system bakeout (8.2); and set up the analysis on the Agilent 8890/597B GC-MSD (8.3). Before conducting sample analyses, generate a calibration curve per section 9.2.

8.1 Support Gases and Liquid Nitrogen

8.1.1 Gas Cylinders

The system requires helium as the carrier gas and nitrogen as the Entech sweep and injection gas. The gas cylinders must be monitored regularly to ensure that the cylinders have sufficient pressure (> 500 psig) to operate the system. Prior to changing the helium cylinder, turn off the GC oven temperature, front inlet temperature, back detector temperature, and the Entech 7200A. See the Agilent 8890 user's manual for further details.

8.1.2 Liquid Nitrogen

The system requires one dewar of liquid nitrogen. Liquid nitrogen cryogenically cools the traps of the Entech preconcentrator and cools the GC oven. The dewar must be at least one-half tank full to operate the system as noted by a visual check of the fill gauge on the top of the dewar. The liquid nitrogen valves attached to the transfer lines of the preconcentrator should remain open during these procedures.

8.2 Entech 7200A Preconcentrator and 7016D Autosampler

Prior to conducting analyses, retrieve a copy of the Entech 7200A Preconcentrator and Agilent 8890/5977B GC-MSD Canister Analysis Setup Sheet (Appendix D) from the analysis sheet three-ring binder and fill out all of the canister numbers and sampling identification information on the form. ***Note:*** Canister numbers are stamped on the front of the canister and recorded on the canister hang tag.

8.2.1 Prepare Canisters for Analysis – Pressure Check

Canister samples must be pressure checked to ensure there is adequate pressure in the canister to complete the analysis. Canisters with pressures greater than 10 psig should not be analyzed on the preconcentrator single canister lines without a canister regulator. Canisters with pressures greater that 10 psig should not be analyzed on the 7016D canister autosampler. Check the pressure of one sample canister at a time using the following steps:

1. With the canister valve closed, remove the brass Swagelok cap from the canister using a backing wrench on the square valve body of the canister to hold the can valve steady while using a smaller wrench to remove the nut (Figure 1).

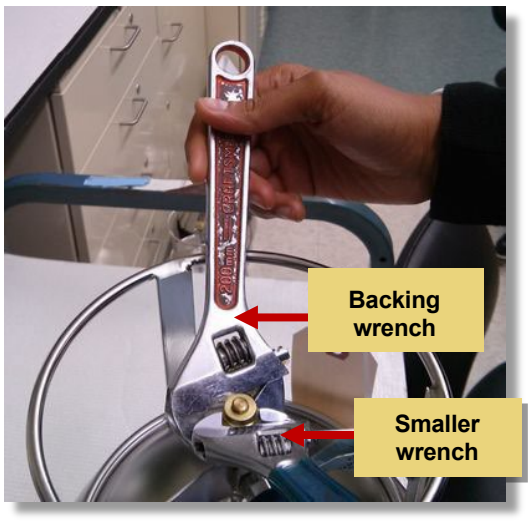


Figure 1. Removal of canister nut using two wrenches.

2. Retrieve a pressure gauge, thread the nut of the gauge onto the canister inlet, and finger tighten to secure the connection (Figure 2). If it is difficult to attach the gauge to the canister, make sure that threads are not damaged or cross threaded. If the gauge threads are damaged, the nut should be replaced or another gauge used. If the canister valve threads are damaged, the sample is likely lost but consult with the PI on how to proceed.

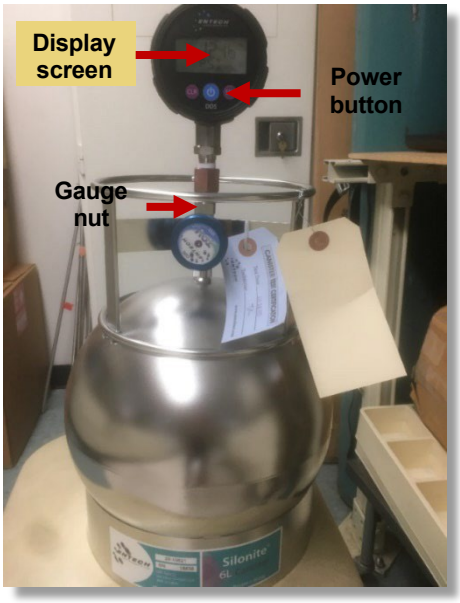


Figure 2. Entech gauge securely connected to canister inlet.

3. Visually inspect the mounting of the gauge on the canister to ensure a secure fit.
4. Power on the gauge by holding down the blue power button, shown in Figure 2, for 2–3 seconds, and record the initial gauge display reading on the analysis sheet in the ambient air pressure column next to the corresponding canister number and in the laboratory notebook.
5. Open the canister valve (Figure 3), allow the gauge reading to settle for 10 seconds, and record the canister pressure on the analysis sheet.
6. Close the canister valve and remove the gauge.
7. Repeat steps 1–6 for all canisters to be analyzed prior to loading them onto the canister autosampler.

Figure 3. Opening canister valve.

Note: The preconcentrator canister autosampler does not support analysis of canister samples at pressures greater than 10 psig. If the canister pressure is greater than 10 psig, contact the PI for further instructions (e.g., venting can).

8.2.2 Load Internal and Calibration Standards and Method Blank Canisters

8.2.2.1 Internal Standard

The dedicated internal standard canister is installed on the dedicated Entech internal standard port that is attached directly to the Entech 7200A preconcentrator (Figure 4). For every analytical run, 50 cc of standard is loaded from the canister into the preconcentration system. The value of 50 is entered by the operator on the Entech sequence table (refer to section 8.2.4, Figure 10). The internal standard consists of four components: 4-bromofluorobenzene, chlorobenzene-d5, 1,4-difluorobenzene, and bromochloromethane. (See J-AMCD-AAB-SOP-3907-1 for internal standard preparation.)

Figure 4. Internal standard canister (first on left), calibration standard canister (second from left), SSCV canister (third from left), and method blank canister (far right) installed on Entech 7200A.

8.2.2.2 Calibration Standard

The calibration standard is installed on the dedicated Entech 7200A calibration port (Figure 4). For the initial calibration (ICAL), this standard generally will be a canister at 500 pptv. Once the ICAL is established, the CCV canister is installed on the dedicated calibration port, replacing the calibration standard used for the ICAL as appropriate. Note that the CCV can be the ICAL standard until that canister is exhausted.

The CCV standard is prepared according to J-AMCD-AAB-SOP-3907-1 or J-AMCD-AAB-SOP-3920-1. The standard is a 500 pptv concentration level canister from which a 250 cc sample volume is collected to generate a 500 pptv effective sample concentration.

8.2.2.3 Method Blank

The MB canister is installed on an autosampler port or one of the four Entech sampler inlets. In our laboratory, the MB is prepared exactly as a calibration standard canister, as described in section 9, but with no calibration standard gas added during the preparation process. (Refer to section 9.3.1 in this SOP and section 15.3.3.2 of EPA Method TO-15A for additional discussion on MBs.)

Note: See the project-specific quality assurance project plan (QAPP) for a given field study to determine the number of CCVs run in an analysis sequence. In general, for Method TO-15A–type analyses, CCV standards and MBs should be analyzed every 10 samples, ending with a CCV.

8.2.3 Load Autosampler

Note: When loading canisters on the 7016D canister autosampler, it is easier to load the canisters and tighten the connections on the bottom row of the autosampler first and then continue to the next lowest row of canisters, ending with the top-most row. Figure 5 shows the fully loaded autosampler.

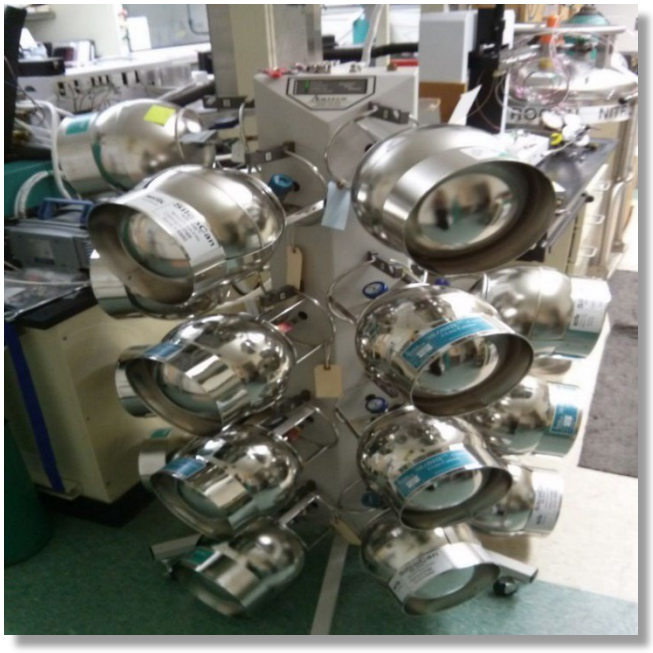


Figure 5. Fully loaded autosampler.

1. Load the 7016D autosampler ports 1 through 16 with the pressure-checked canister samples to be analyzed by attaching the ¼-inch Swagelok canister outlet fitting to the Swagelok stainless-steel union on the Entech autosampler inlet port(s) (Figure 6). (Autosampler ports are labeled from left to right beginning at the top row shown in Figure 5.)

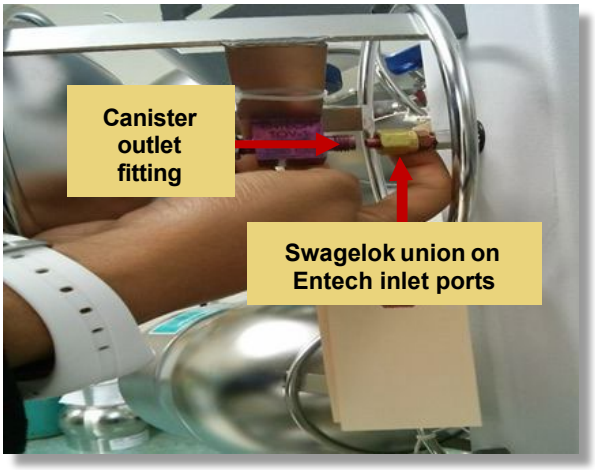


Figure 6. Connecting the canister outlet fitting to the Entech autosampler ports.

2. Finger tighten the connections and then gently snug them by placing a backing wrench on the canister valve body to provide stability and tightening the connection between the canister outlet fitting and the autosampler port using a smaller wrench (Figure 7). Take care not to tighten the fittings too much since they will distort.

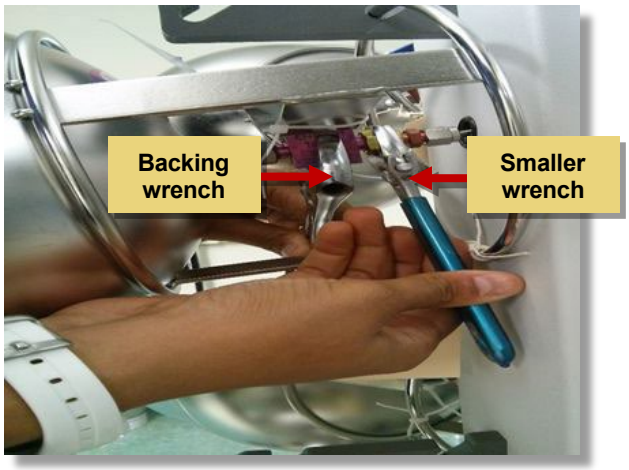


Figure 7. Tightening the canister connection to the autosampler port.

Caution: **The operator must take care to ensure that the appropriate canister is loaded onto the corresponding sample port as recorded on the analysis sheet (Appendix D).**

8.2.4 Preconcentrator Analysis Sequence Setup

The steps of this procedure are order dependent to ensure that the GC-MSD is ready to analyze samples prior to the Entech 7200A preconcentrator injection of the VOCs from the trap onto the GC column. Always open the software in the order given below to avoid software errors. The Entech CTD method used is always **Smart\TO15A_Hybrid Method_042722.7200A.CTD**. Refer to the Entech user's manual for an in-depth discussion of the steps of the CTD method. Set up a sequence in the Entech software as follows:

1. Double click the **Entech 7200A Shortcut** icon on the computer desktop (Figure 8) to establish communication between the Entech computer and the Entech system.

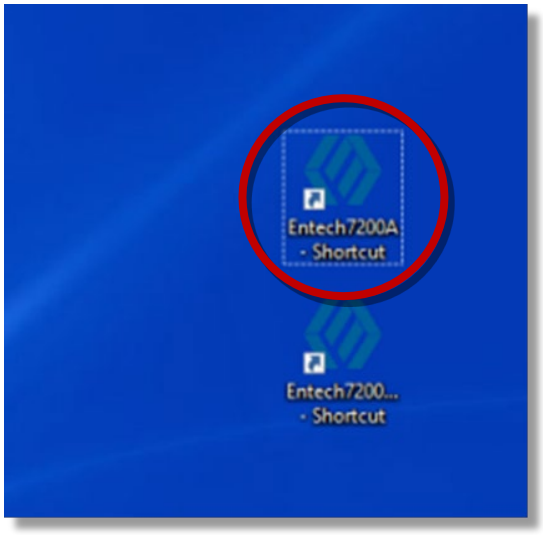


Figure 8. Entech 7200A Shortcut icon on desktop.

2. When the empty sample list appears on the screen, click **File > Load Sequence** at the upper left side of the screen (Figure 9) and choose a recently dated *.SEQ sequence file to use as a template. As shown in the example sequence table in Figure 10, an analysis sequence is generally set up in the following order: IB(s), CCV, MB, and canister sample runs.

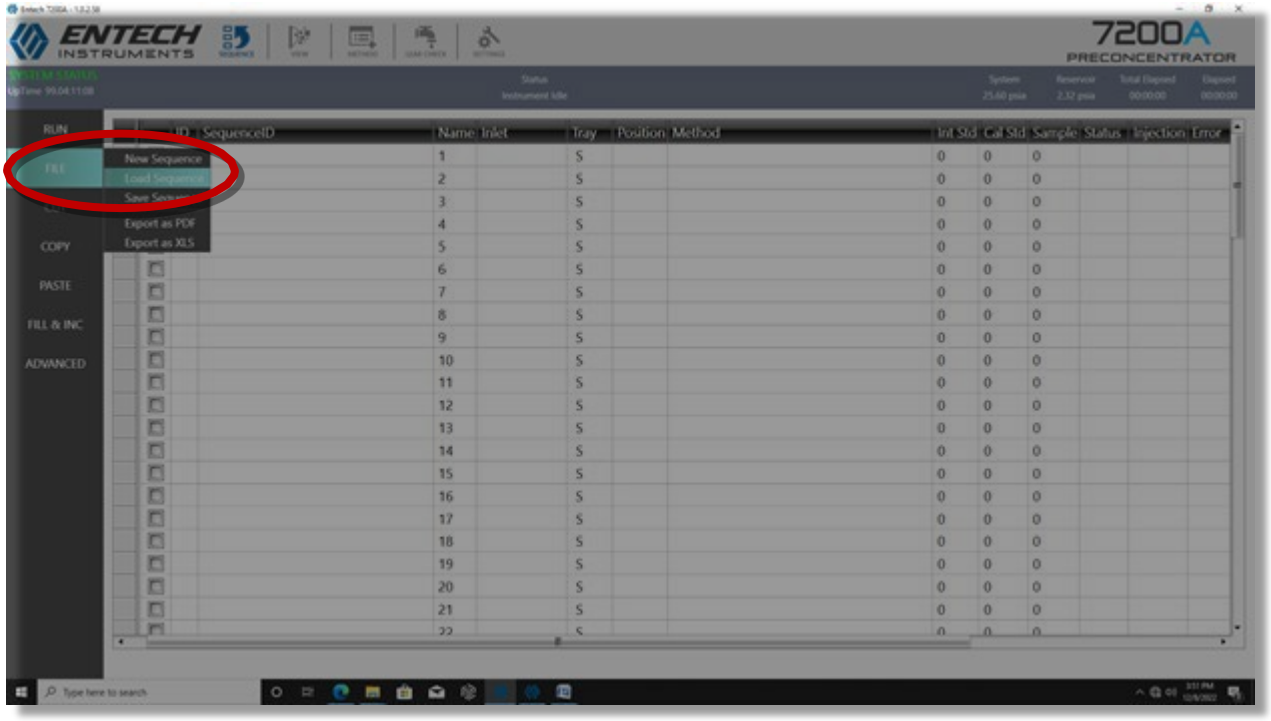
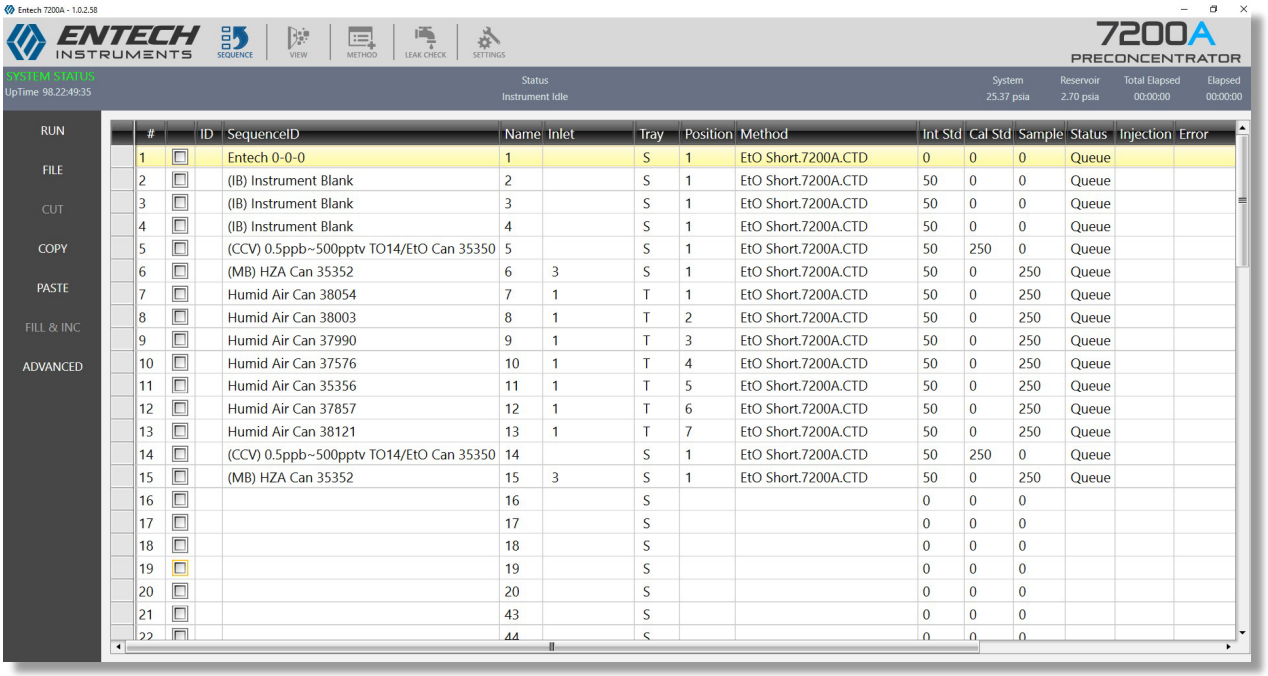


Figure 9. Opening an existing sequence file.



#	ID	SequenceID	Name	Inlet	Tray	Position	Method	Int Std	Cal Std	Sample	Status	Injection	Error
1		Entech 0-0-0	1		S	1	EtO Short.7200A.CTD	0	0	0	Queue		
2		(IB) Instrument Blank	2		S	1	EtO Short.7200A.CTD	50	0	0	Queue		
3		(IB) Instrument Blank	3		S	1	EtO Short.7200A.CTD	50	0	0	Queue		
4		(IB) Instrument Blank	4		S	1	EtO Short.7200A.CTD	50	0	0	Queue		
5		(CCV) 0.5ppb~500pptv TO14/EtO Can 35350	5		S	1	EtO Short.7200A.CTD	50	250	0	Queue		
6		(MB) HZA Can 35352	6	3	S	1	EtO Short.7200A.CTD	50	0	250	Queue		
7		Humid Air Can 38054	7	1	T	1	EtO Short.7200A.CTD	50	0	250	Queue		
8		Humid Air Can 38003	8	1	T	2	EtO Short.7200A.CTD	50	0	250	Queue		
9		Humid Air Can 37990	9	1	T	3	EtO Short.7200A.CTD	50	0	250	Queue		
10		Humid Air Can 37576	10	1	T	4	EtO Short.7200A.CTD	50	0	250	Queue		
11		Humid Air Can 35356	11	1	T	5	EtO Short.7200A.CTD	50	0	250	Queue		
12		Humid Air Can 37857	12	1	T	6	EtO Short.7200A.CTD	50	0	250	Queue		
13		Humid Air Can 38121	13	1	T	7	EtO Short.7200A.CTD	50	0	250	Queue		
14		(CCV) 0.5ppb~500pptv TO14/EtO Can 35350	14		S	1	EtO Short.7200A.CTD	50	250	0	Queue		
15		(MB) HZA Can 35352	15	3	S	1	EtO Short.7200A.CTD	50	0	250	Queue		
16			16		S			0	0	0			
17			17		S			0	0	0			
18			18		S			0	0	0			
19			19		S			0	0	0			
20			20		S			0	0	0			
21			43		S			0	0	0			
22			44		S			0	0	0			

Figure 10. Completed Entech sequence table.

Note: More than one MB may be needed to clear the system of any contaminants if the system is not being used on a daily basis. Of additional note, if the system has not been used in the past week, it is advisable to run a series of humidified zero air (HZA) canister samples to clean up the system prior to setting up the ICAL sequence.

Canister sample sequences may include laboratory blanks (LB) and laboratory spikes (LS) loaded on the autosampler in addition to the field blanks (FB) and field spikes (FS) that may have been collected with the field samples as discussed in section 14.9. Note that in this laboratory, MBs, LBs, and calibration blanks (CB) are all prepared in the same manner using the same standards preparation system that is used to prepare standards for a particular study.

In general, for Method TO-15A–type analyses, CCV standards and MBs should be analyzed every 10 samples, ending with a CCV. An MB may be added after the CCV by the operator if desired. Note that the number and types of samples, blanks, and standards will vary depending on the data quality objectives (DQOs) of the current task. See project-specific QAPPs for explicit DQOs.

3. Click on a sample line in the sequence file to edit it. The line to be edited will be highlighted in yellow.
4. In the first row of the sequence file, click inside each field to edit the contents as outlined below:

- **SequenceID:** Enter the sample descriptor or identification (ID) code and canister number (Can #####) for all samples as appropriate for the sequence. See project-specific QAPPs for sample ID codes. Standard practice in this laboratory is to enter the QA sample types in parentheses for easy identification, as shown in Figure 10. IBs, MBs, CCVs, SSCV standards, ICAL, LSs, LBs, FSs, and FBs should be entered as specified below:
  - Entech 0-0-0, where the volumes for the Int Std, Cal Std, and Sample are set to 0 to verify no initial background contribution from the Entech system
  - IB Instrument Blank
  - MB HZA Can #####
  - CCV (effective concentration in pptv) (gas standard type) Can #####
  - SSCV (effective concentration in pptv) (gas standard type) Can ##### (Note that an SSCV standard is included in the ICAL sequence but not in a standard sample sequence.)
  - ICAL (effective concentration in pptv) (gas standard type) Can #####
  - LS (effective concentration in pptv) (gas standard type) Can #####
  - LB Can #####
  - FS (effective concentration in pptv) (gas standard type) Can #####
  - FB Can #####

  ***Note*:** Humid air samples are labeled "HZA Can #####" when analyzed to certify canister cleanliness or to clean up the preconcentration system.

- **Name: Do not edit.**
- **Inlet:** The four single silicon ceramic-coated stainless-steel lines connected to the back of the 7200A have various purposes. The ICAL/CCV standard should be connected to the dedicated calibration line (tagged as cal) with the inlet entry in the sequence table left blank. Internal standards should be connected to the dedicated internal standards line (tagged as IS). Neither the calibration nor the internal standard line have designated inlet numbers in the software. To select the autosampler, you must select inlet 1-7016D.
    - The IB inlet entry is left blank with both Sample and Cal Std volumes set at 0 such that only a designated aliquot of internal standard gas is loaded from the dedicated internal standard canister shown in Figure 4.
    - The CCV entry is left blank as mentioned above, the Sample volume is set at 0, and the appropriate Cal Std volume is entered such that only an aliquot of calibration gas standard is loaded from the dedicated calibration canister shown in Figure 4 (plus the designated aliquot of internal standard that is loaded with each run).
    - The SSCV entry is set at Inlet 2, with the Sample volume entered such that only an aliquot of secondary source calibration gas standard is loaded from the dedicated canister (plus the designated aliquot of internal standard that is loaded with each run).
    - The MB inlet entry is set at Inlet 3 with the Sample volume entered such that only an aliquot of HZA is loaded from the dedicated canister (plus the designated aliquot of internal standard that is loaded with each run).
- **Tray:** For sample canisters attached to the single canister lines on the side of the preconcentrator, you must select “S” to indicate the single canister line is being used. For sample canisters attached to the autosampler, you must select “T” to indicate the autosampler is being used.
- **Position:** Enter the autosampler port on which the canister is loaded. For the autosampler, the inlet must be set to 1 while the position entry will be a number from 1 to 16 as there are 16 sampling ports on the autosampler. For the canisters on the autosampler, the Sample volume is set at 250 cc and the Cal Std volume is set at 0 such that only an aliquot of sample gas is loaded from the appropriate canister (plus the designated aliquot of internal standard that is loaded with each run).
- **Method:** Select the appropriate method.
- **Int Std:** Enter the volume to be collected from the internal standard canister. For scope and application of the methods mentioned in this SOP, canisters loaded on the autosampler require a 50 cc collection volume. This Int Std entry remains 50 for IBs, MBs, ICAL, CCVs, and SSCVs and should be 0 for the Entech 0-0-0.

- **Cal Std:** For the CCV, enter 250 cc for a 500 pptv calibration canister to generate an effective concentration of 500 pptv. ICAL volumes can be found in "Section 9.0, Instrument Calibration." This entry remains 0 for the Entech 0-0-0, IBs, MBs, and all field samples.
- **Sample:** Enter the volume to be collected from the canister. For scope and application of the methods mentioned in this SOP, canisters loaded on the autosampler (ambient air samples and the SSCV) require a 250 cc collection volume. This entry remains 0 for the Entech 0-0-0, IBs, and CCVs.

Caution: **The operator must make sure the appropriate autosampler position is listed next to the correct canister number in the sequence table in the column labeled "Position."**

5. Repeat step 4 to edit the remaining sample lines as needed.
6. From the **File** drop-down menu, select **Save Sequence** and enter the name for the file with the format YY-MM-DD.7200A.Seq, where YY is year, MM is month, and DD is day. In the event multiple sequences are run in one day, the operator may append a letter or unique identifier to the file name so that files are not overwritten. For example, a file name for a sequence initiated on January 19, 2023 is 23-01-19.7200A.SEQ. Record the Entech file name on the analysis sheet next to "Entech Seq".

8.2.5 Conduct a Leak Check

Note: The canister valves **must be closed** for this portion of the procedure to ensure the sample is not lost. The Entech will only leak check ports 1–16 on the 7016D autosampler. The calibration standard port and internal standard port will not be leak checked.

1. Check canister valves to ensure they are closed.
2. Click **Leak Check** on the top tool bar (Figure 11).
3. Be sure each entry to be leak checked has a check mark in the "Use" column.
4. Click **Run Leak Check** on the left-hand toolbar (Figure 11). A leak check will be performed only on the canister samples listed in the sequence table that are mounted on the 7016D autosampler.

   Note: Leak Check Parameters may be modified by the operator; however, the default settings shown in Figure 12 are currently in use.
5. For each sample port checked, review the Psid values next to the corresponding canister number on the analysis sheet. The system will automatically advance to the next sample until all samples have been checked.
6. Ensure the Psid for each canister is less than 0.2 psia. A difference greater than 0.2 psia indicates a leak in the canister connection (Figure 12).

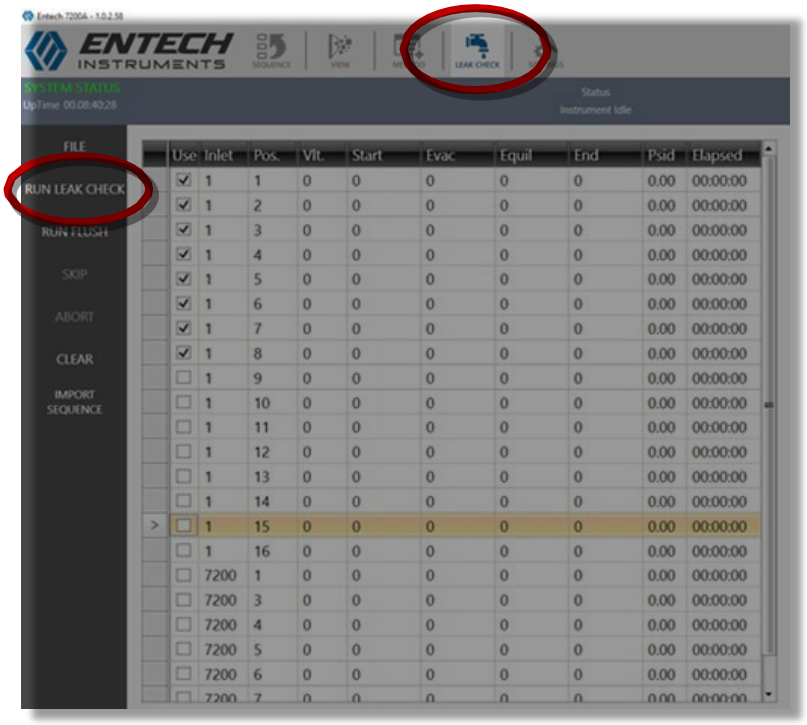


Figure 11. Initiating a leak check.

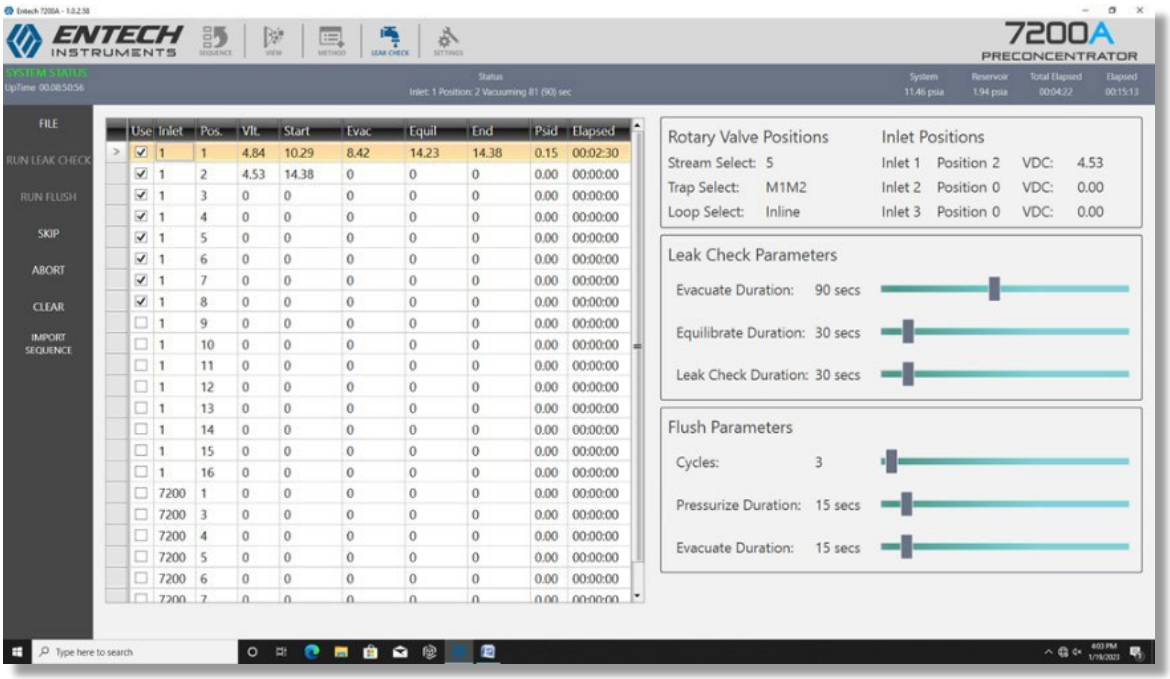


Figure 12. Psid below 0.2.

7. If any canister connection is not leak tight, snug the appropriate fittings slightly using wrenches and repeat the leak check on that port. ***Note:*** If snugging the connection does not remedy the leak, the canister sample cannot be analyzed. At this point, the canister must be removed from the sample queue and repaired, and the sample will be lost.

8. Upon completion of the leak check, click **File > Export as PDF**, print the leak check report, and save the PDF to the desktop folder "Entech Leak Checks."

9. File the leak check report in the three-ring binder labeled "Leak Check." For samples that required a second leak check after snugging the fittings, record the new leak check pressures manually on the original leak check report next to the specific canister number. This will save time because an entire leak check will not have to be repeated to generate a new automatic report.

8.2.6 Flush Canister Lines

When the leak check is finished, the lines to the canisters on the autosampler are flushed with nitrogen. ***Note:*** The flush is not performed when conducting calibration runs as calibration canisters are connected directly to the calibration port on the preconcentrator.

Caution: **The canister valves must remain closed during the flush step or the samples will be lost.**

1. To initiate the flushing of the autosampler lines, ensure the correct inlet and positions are selected (have check marks) and click the **Run Flush** button on the left-hand toolbar (Figure 13).

   Note: Only the selected autosampler lines are flushed. After each line is flushed, the system automatically advances to flushing the next autosampler line. After the lines are flushed, the message "Instrument Idle" appears. Flush Parameters may be modified by the operator; however, the default settings in Figure 13 are currently in use.

2. Indicate on the analysis sheet that the flushing of lines was completed.

3. Click **View** on the top toolbar to exit the **Leak Check** menu (Figure 14).

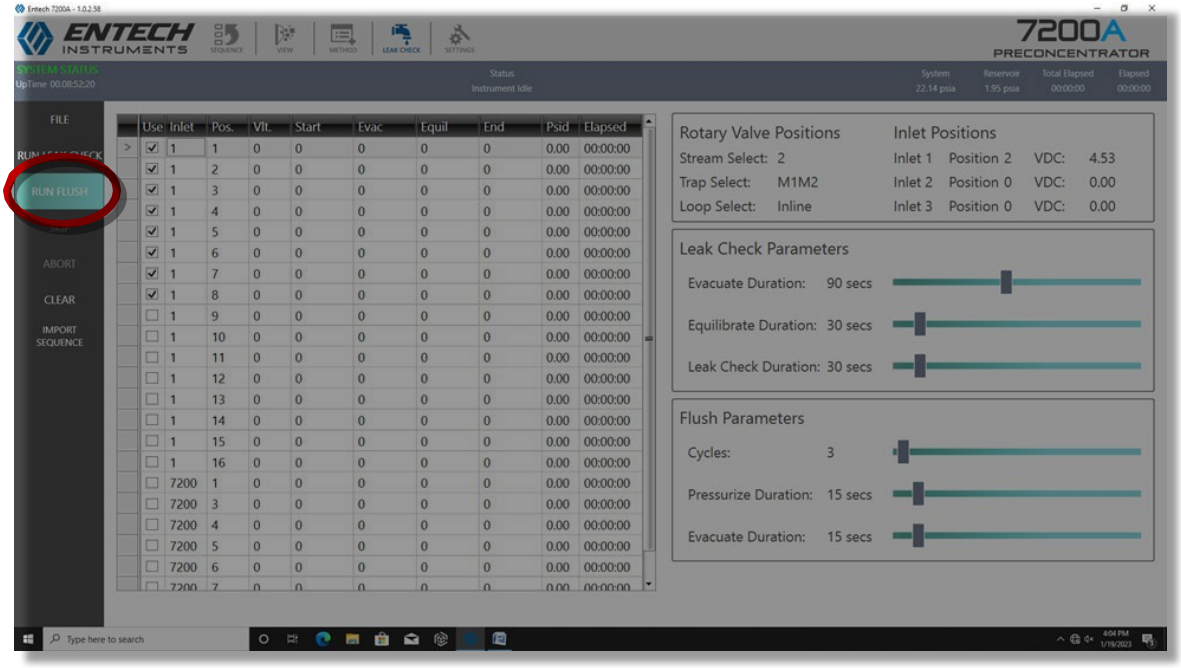


Figure 13. Initiating a canister line flush.

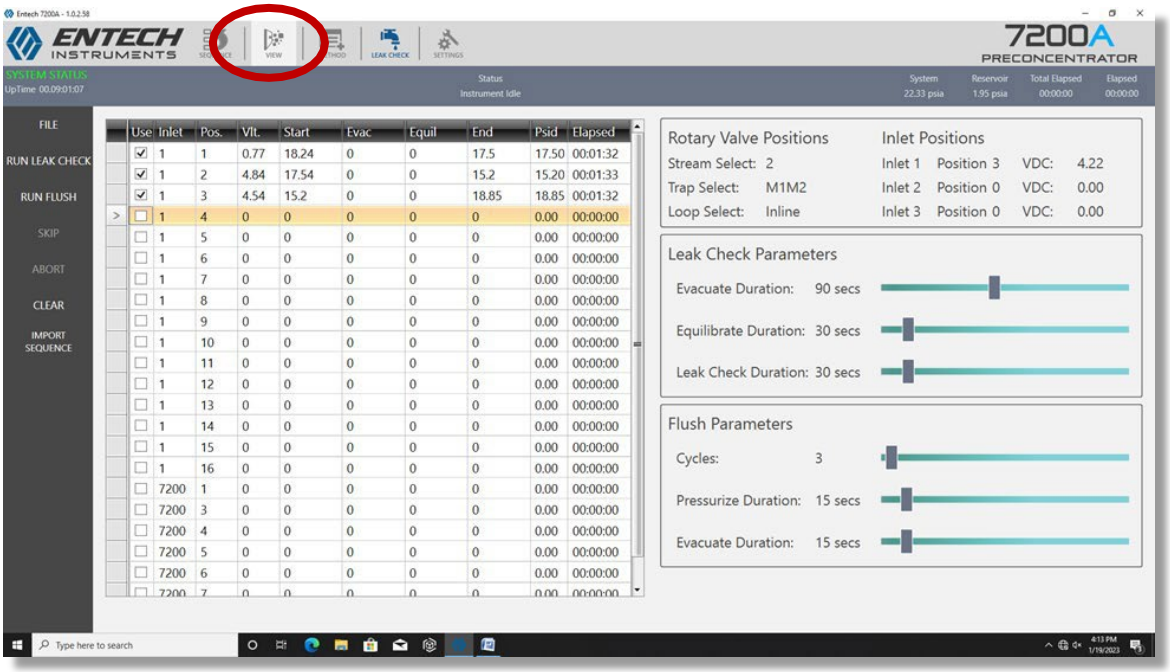


Figure 14. Entech leak check menu.

8.2.7 Perform Entech System Bakeout

An Entech system bakeout should be completed prior to analysis to remove water and any remnants of previous sample remaining in the traps.

1. In the **View** screen, click the **Command** button and select **Bake Out** on the Entech 7200A toolbar (Figure 15). The Entech system will initiate the bake mode, which lasts 10 min.
2. Document "Entech Bakeout" on the analysis sheet by marking **Yes**.
3. Click the **Sequence** button on the top toolbar to return to the instrument view screen.

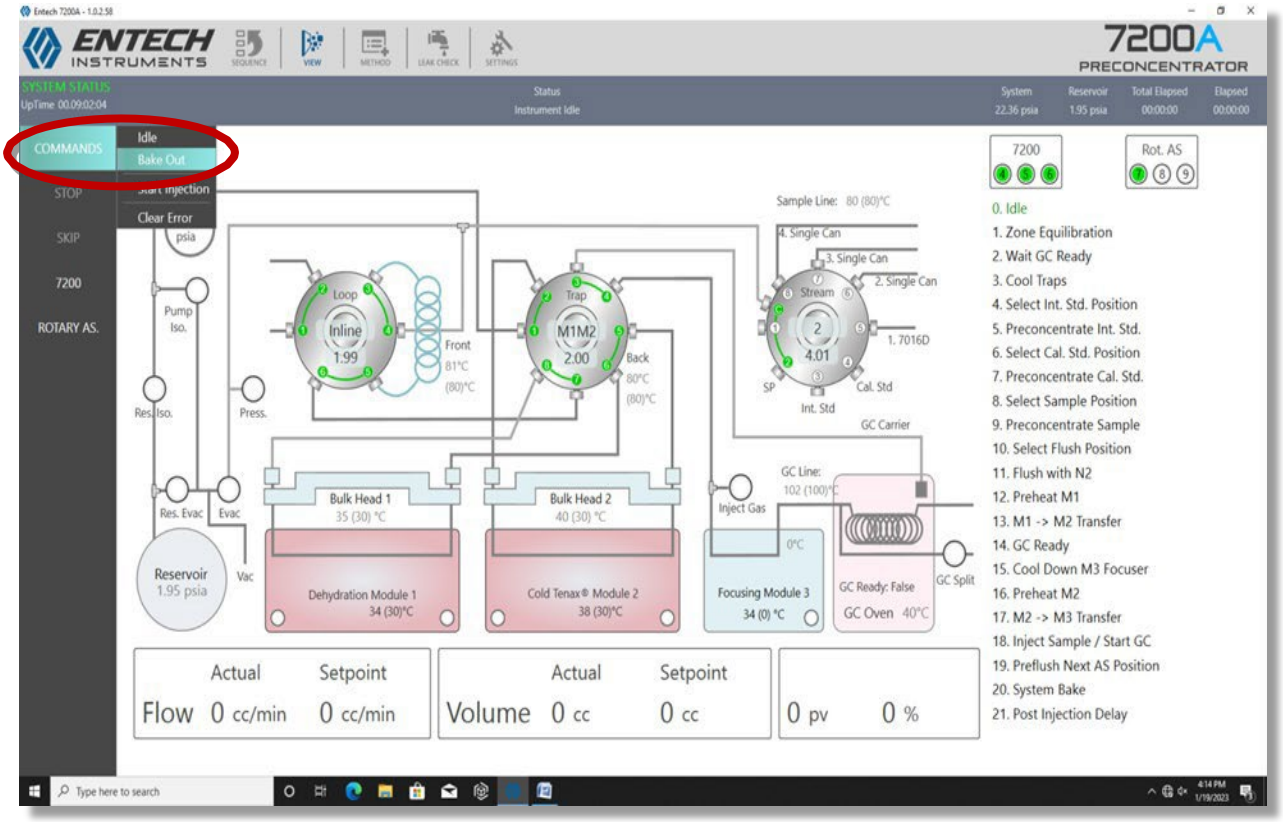


Figure 15. Initiating bake mode.

8.2.8 Initiate Entech Analysis Sequence

1. Open all canister valves for the canisters listed in the Entech sequence table.
2. **Before moving on, follow the procedures in section 8.3** in order to a) prepare the Agilent 8890/5977B GC-MSD for analysis and b) use the Environmental Agilent GC-MS ChemStation software to create an analysis table (sample list) and initiate an analytical sequence before proceeding to step 3 below.

3. To begin the preconcentration of samples using the Entech, **after completing the steps in section 8.3**, click the first sample entry in the Entech sample list to highlight the sample (Figure 16). This ensures the Entech selects the first sample entry once the sequence is initiated.
4. Click **Run** on the toolbar ([1] in Figure 16).
5. Click **View** ([2] in Figure 16) to view the instrument set points and the steps of the analysis, which are shown in Figure 17. The Entech sequence will run until all entries in the sample list have been analyzed, and the system will then stay in standby mode until the operator intervenes. Standby mode is indicated when step **0 Idle** appears in green on the system view screen.
6. After an analysis sequence has been completed, click the Entech 7200A ReportViewer7200A icon on the desktop (Figure 18) to access the quality assurance/quality control (QA/QC) reports pertaining to the Entech 7200A analysis runs. To review canister pressures before and after analysis and collected sample volumes, double click the QA/QC report of interest. Reports are listed by date and time and include all information recorded in the sequence table. After review, record any discrepancies in the laboratory notebook.
7. After all analyses are complete, close the canister valves and remove the canisters from the autosampler ports.
8. **Proceed to section 8.3.3 step 4.**

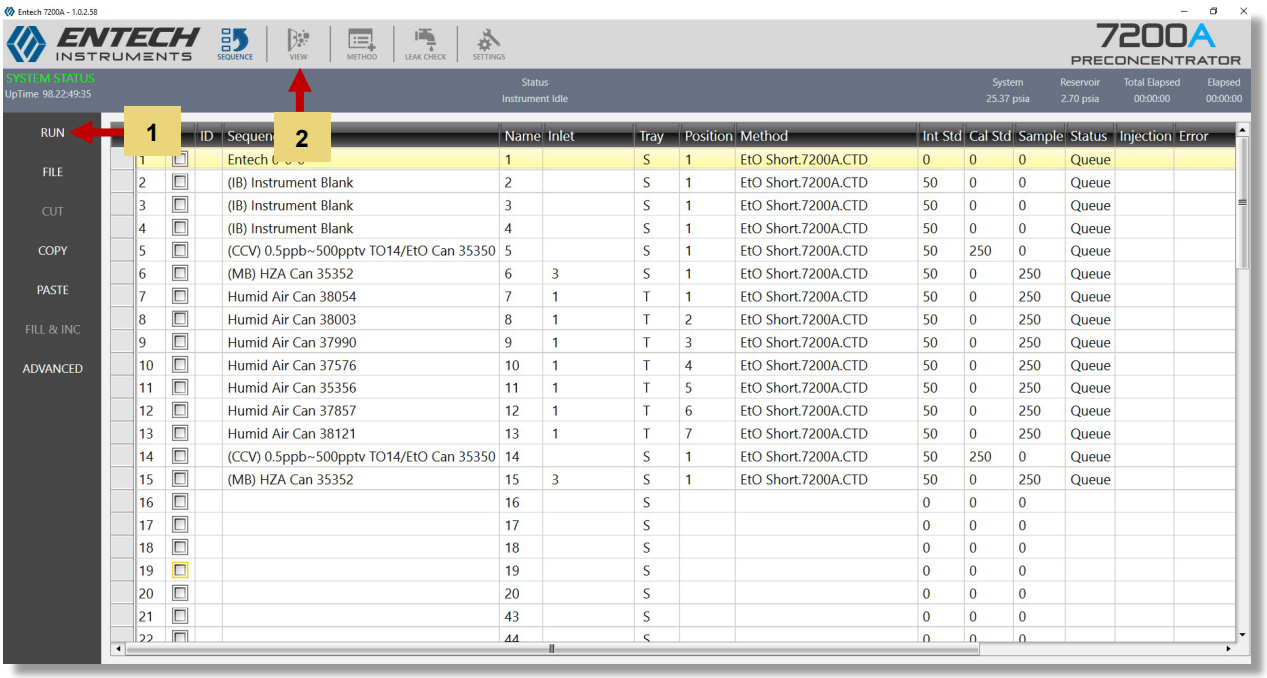


Figure 16. Completed Entech sequence.

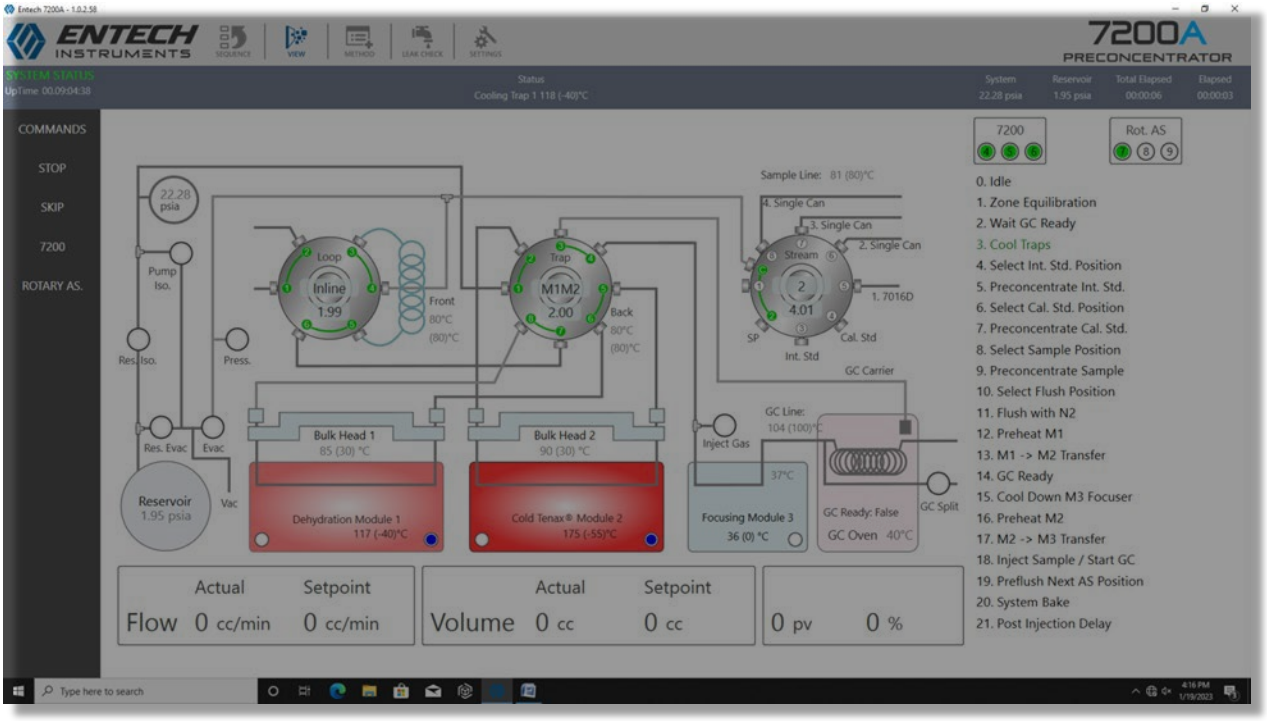


Figure 17. System view.

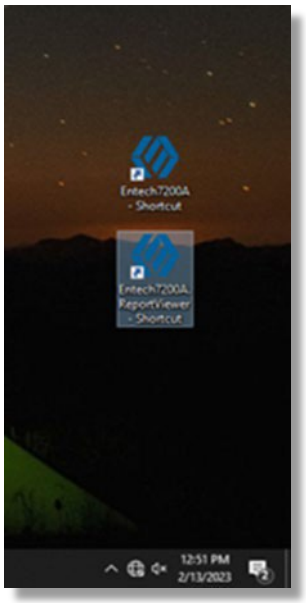


Figure 18. QA/QC reports desktop icon.

8.3 Agilent 8890/5977B GC-MSD Preparation and Analytical Sequence Setup and Initiation

8.3.1 GC-MS Air/Water Check

Prior to analyses, an air/water check is conducted. The air/water check serves as a QC measure to ensure that the system is free of high air and water background levels. When present, high air and water levels indicate a system leak that could compromise the integrity of collected data. Contact the PI if values greater than 5% are detected for masses 28 and/or 18 amu.

The Agilent 8890/5977B GC is operated using the Agilent GC/MS Environmental ChemStation software as follows:

1. Double click the Baby Yoda 2 **GCMS** icon on the computer desktop to launch the software.
2. In the instrument control screen click **Method** and **Load Method.**
3. Select the standby method listed in the drop-down list: **Restek_Hybrid Entech Method_Standby.m**.
4. Set the GC oven temperature to 110 °C by pressing **Oven** on the GC touchscreen to input **110** into the **Value (˚C)** field (Figure 19).

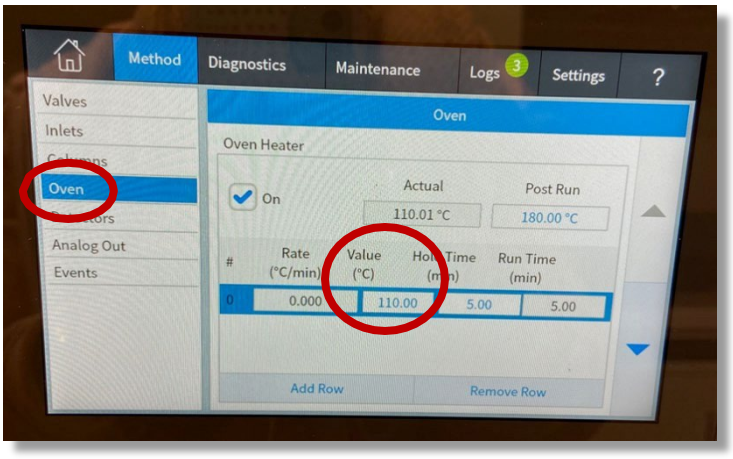


Figure 19. Setting the GC oven temperature to 110 ˚C.

5. When the oven temperature reaches 110 °C on the GC display above the keypad, click **View** on the top toolbar in the GC software and select **Tune and Vacuum Control** (Figure 20).

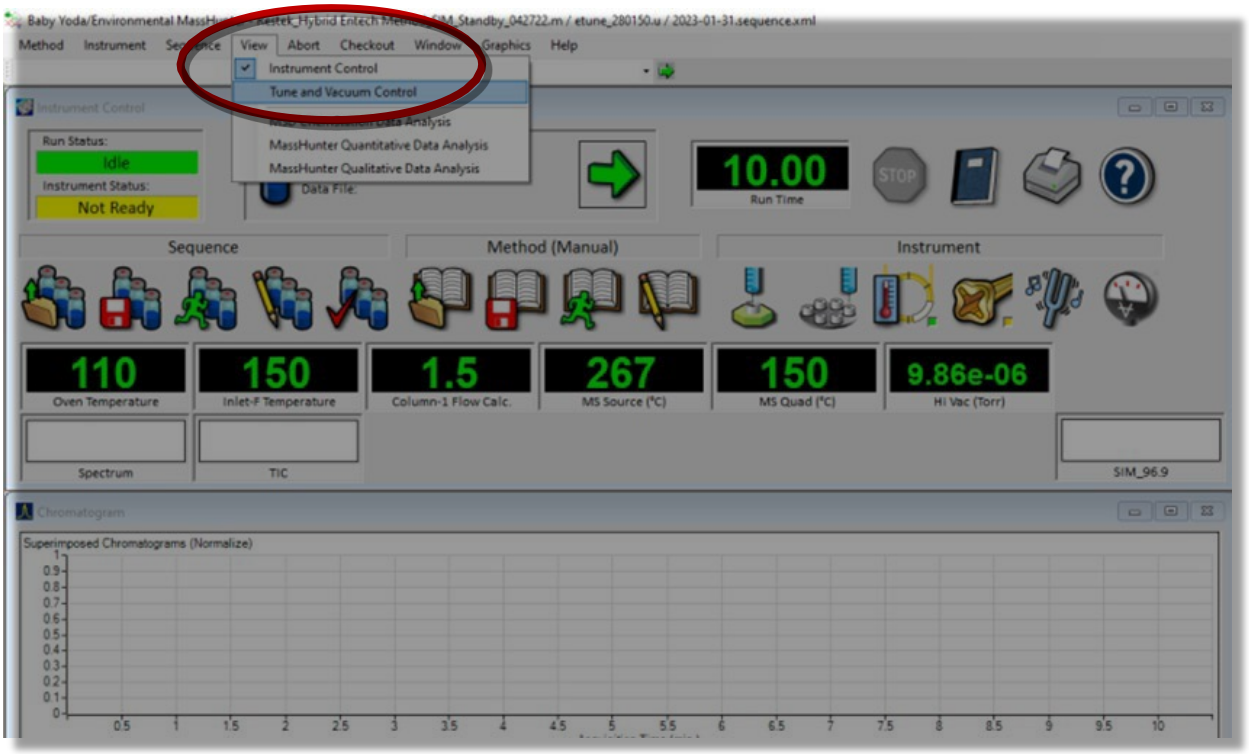


Figure 20. Selecting Tune and Vacuum Control.

6. In the **Tune and Vacuum Control** screen, click **Tune > Air and Water Check** from the drop-down menu (Figure 21). The system will automatically initiate the air/water check and print out a report at the conclusion of the check.

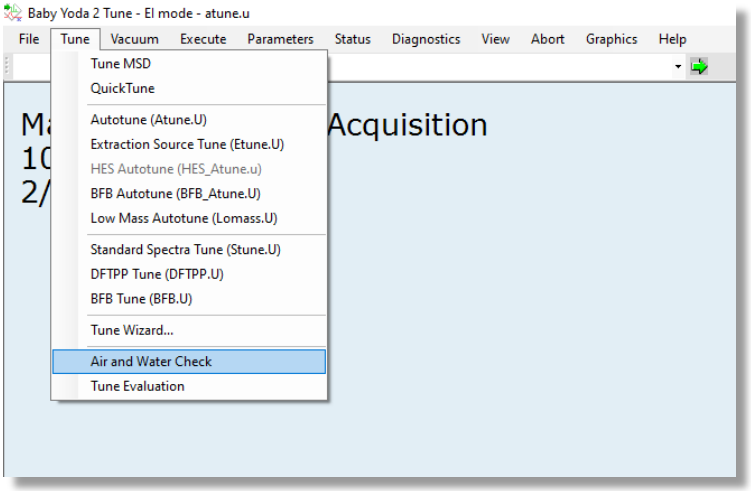


Figure 21. Selecting Air and Water Check.

7. Click **Parameters** in the **Tune and Vacuum Control** screen and select **Manual Tune**.
8. Click the **Profile** tab and enter 69 for Mass 1, 18 for Mass 2, and 28 for Mass 3 (Figure 22).
9. Double click in the **PFTBA** box (Figure 22) to open the calibrant valve.
10. Click the **Profile** button (Figure 22) and allow the profile reading to settle for 5 seconds.
11. Click **Stop** and record **Abundances** and **Relative Abundances** in the **Profile** window into the laboratory notebook.

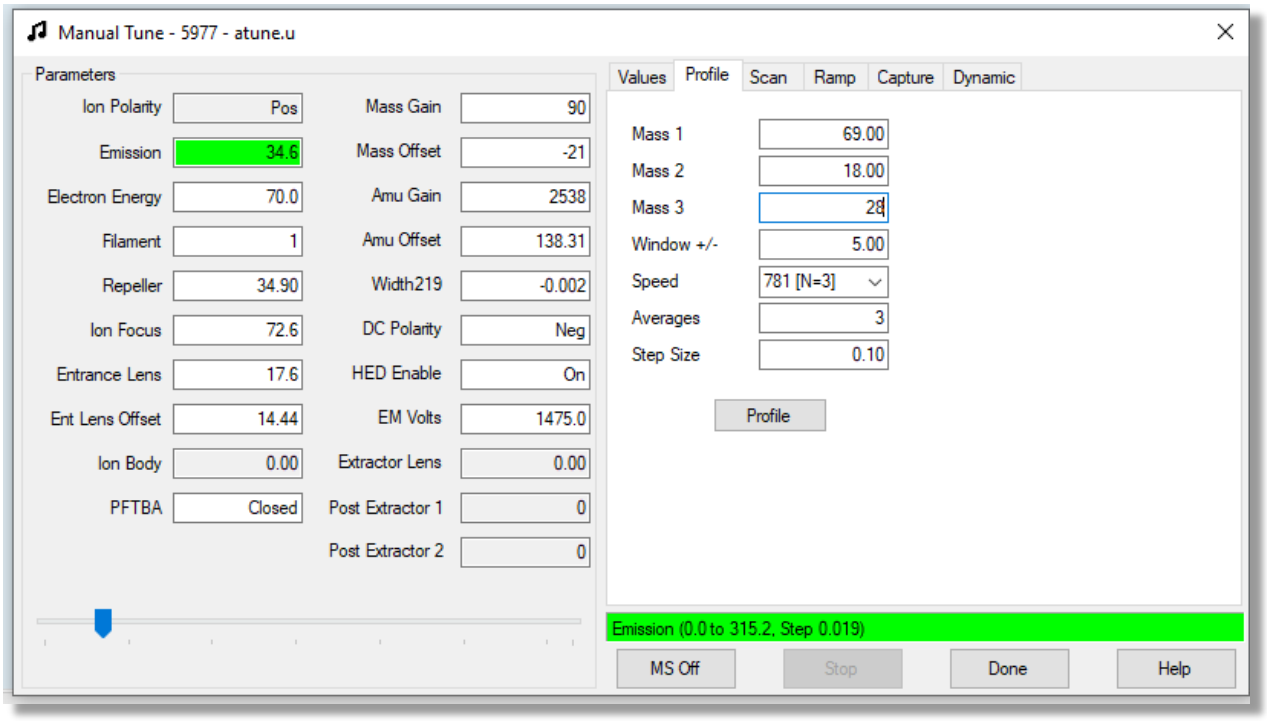


Figure 22. Air/water check initiated by clicking Profile.

12. Review the printout of the air/water check to ensure the relative abundances are optimal. See Table 1 for typical air and water background relative abundances (Agilent, 2022). ***Note:*** If relative abundances exceed typical background readings, contact the study PI for corrective action.
13. Click **View** on the top toolbar and select **Instrument Control** from the drop-down menu to return to the instrument control screen.

Table 1. Air/water check recommended parameters (Agilent, 2022)

Time after pump down and thermal stability	Water *m/z* 18 relative abundance	Nitrogen *m/z* 28 relative abundance	Oxygen *m/z* 32 relative abundance
2 hours	< 20%	< 5%	< 1.5%
> 12 hours	< 2.5%	< 2.5%	< 1%

8.3.2 GC Sequence Table Setup

1. Click the **Sequence** tab on the toolbar and select **Load Sequence** from the drop-down menu (Figure 23).

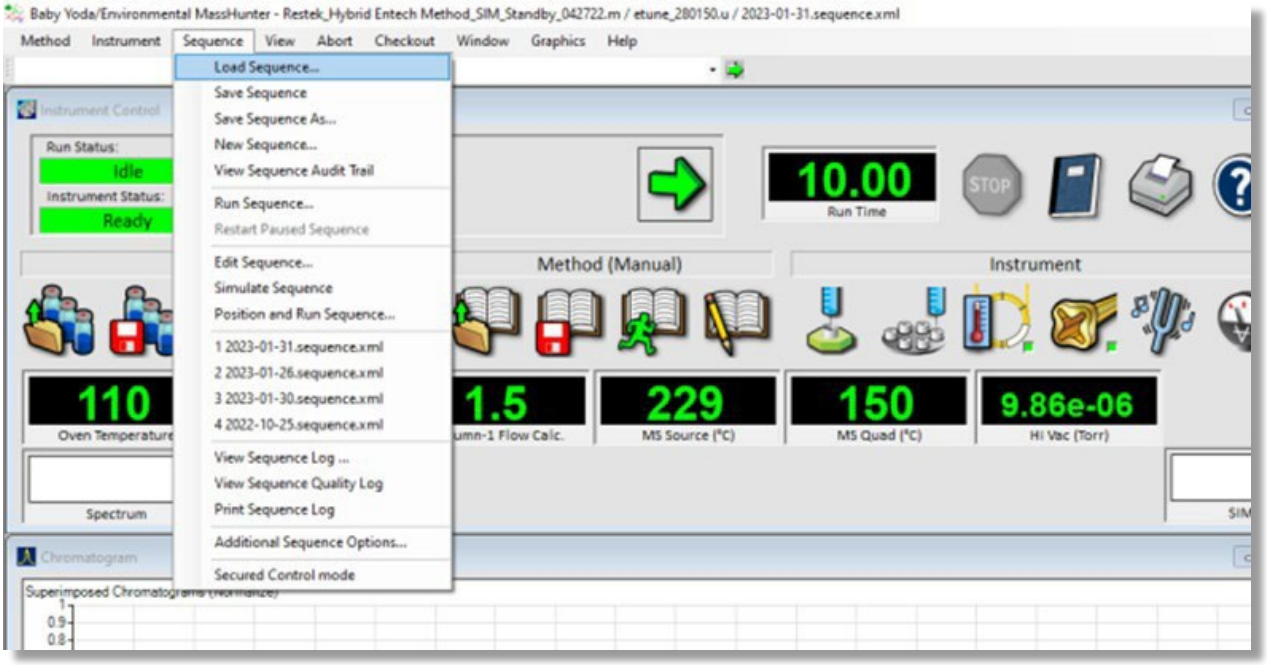


Figure 23. Select Load Sequence.

2. Highlight a sequence from a previous analysis (e.g., YYYY-MMDD.S, where YYYY is year, MM is month, and DD is day) and click **Select**.
3. Click **Sequence** and select **Edit Sequence** from the drop-down menu (Figure 24).

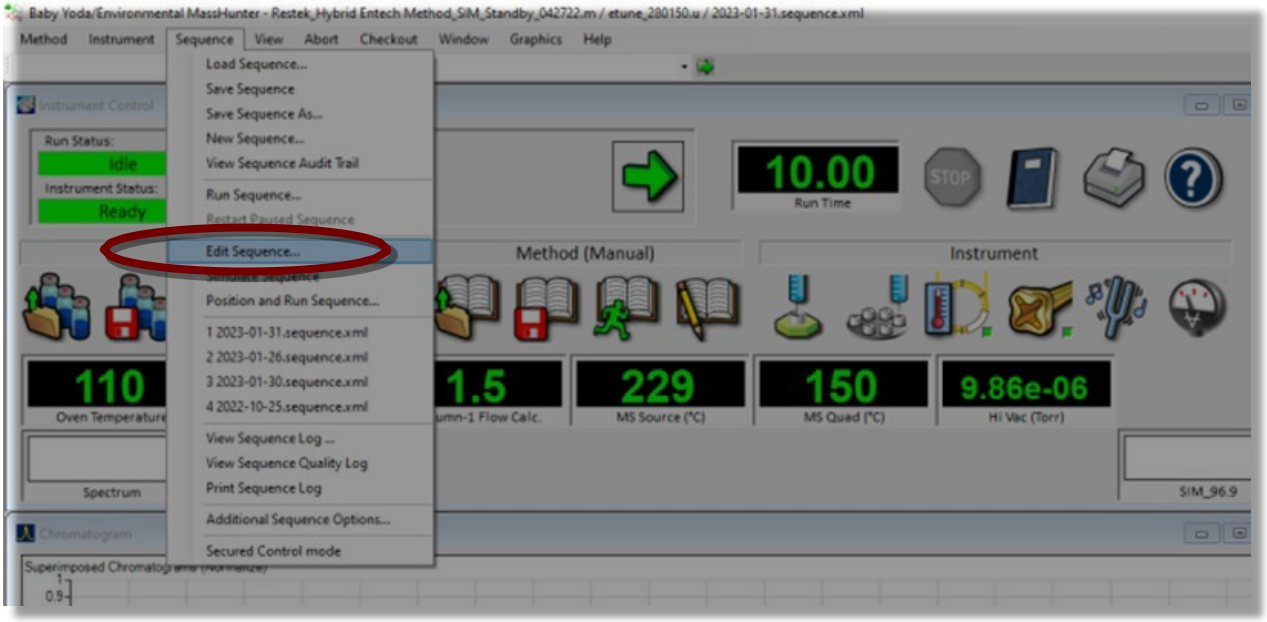
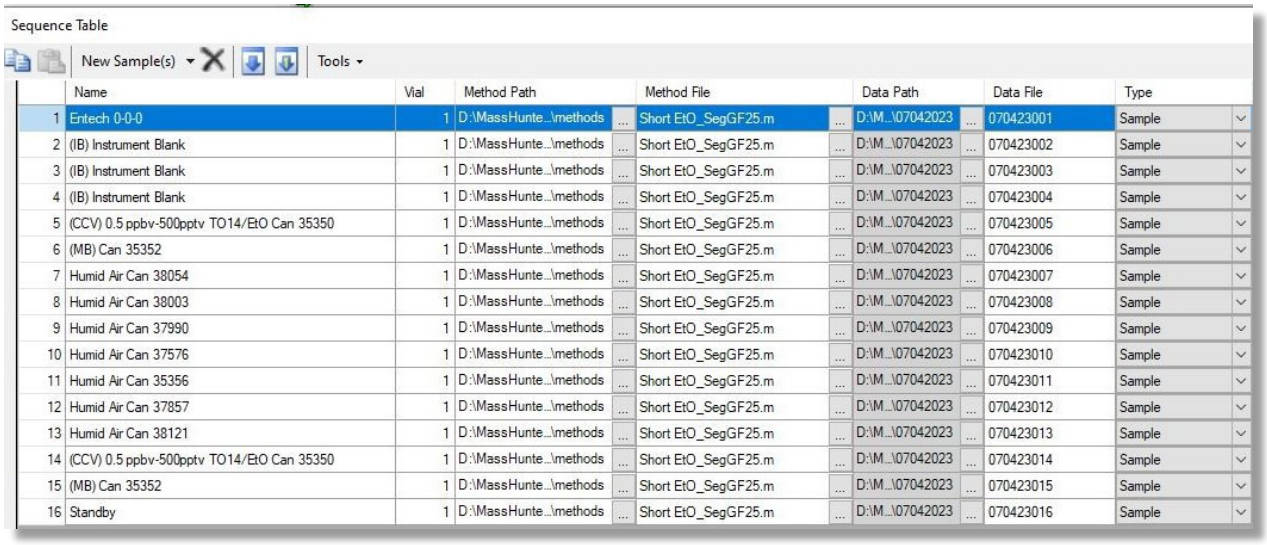


Figure 24. Edit Sequence dialog box.

4. When the **Sequence Table** appears (Figure 25), the following comments should be entered in the **Name** column for the following sample types:

   - Blank: **Entech 0-0-0**, **Instrument blank** or **IB, Method blank** or **MB** plus **Can #####**, or **Calibration blank** or **CB** plus **Can #####.**
   - DailyCal: CCV (effective concentration in pptv) (gas standard type) Can #####, where effective concentration refers to the volume of standard pulled from the external canister standard by the Entech (volume entered when setting up the Entech sample sequence table in section 8.2.4); pptv denotes the concentration of standard loaded into the canister (J-AMCD-AAB-SOP-3907-1 or J-AMCD-AAB-SOP-3920-1); and gas standard type refers to the gas mixture used in the CCV. ***Example:*** **(CCV) 0.5 ppbv-500 pptv TO14/EtO Can 37746.**
   - Sample: **Sample ID** where applicable (determined from project-specific QAPP) and **Can #**. The Name column should also be populated with the details of each calibration standard concentration for the ICAL or the SSCV being analyzed or any LSs or FSs included in a sample sequence, as in the CCV example above.

     Note: Use the information recorded on the Entech 7200A Preconcentrator and Agilent 8890/5977B GC-MSD Canister Analysis Setup Sheet from section 8.2 to assist with entering canister sample information into the sequence table in Figure 25.



	Name	Vial	Method Path	Method File	Data Path	Data File	Type
1	Entech 0-0-0	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423001	Sample
2	(IB) Instrument Blank	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423002	Sample
3	(IB) Instrument Blank	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423003	Sample
4	(IB) Instrument Blank	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423004	Sample
5	(CCV) 0.5 ppbv-500pptv TO14/EtO Can 35350	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423005	Sample
6	(MB) Can 35352	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423006	Sample
7	Humid Air Can 38054	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423007	Sample
8	Humid Air Can 38003	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423008	Sample
9	Humid Air Can 37990	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423009	Sample
10	Humid Air Can 37576	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423010	Sample
11	Humid Air Can 35356	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423011	Sample
12	Humid Air Can 37857	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423012	Sample
13	Humid Air Can 38121	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423013	Sample
14	(CCV) 0.5 ppbv-500pptv TO14/EtO Can 35350	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423014	Sample
15	(MB) Can 35352	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423015	Sample
16	Standby	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423016	Sample

Figure 25. Editing Sequence Table.

5. Next click the ··· button in the **Method Path** field in row 1 (Figure 25). Select the folder that contains the analytical method of choice. Choosing this folder creates the file path **D:\MassHunter\GCMS\3\methods\Optimizing Methods\Etune Methods** in the **Method Path** field.

6. Click in the **Method Path** field and click the fill-down button to populate the remaining rows with the method path.

7. Click the ··· button in the **Method File** field in row 1 (Figure 25). Select the correct analytical method from the drop-down list and use the fill-down button shown above to populate the remaining rows with the analytical method. ***Method Note:*** The method currently in use in this laboratory is **Short EtO_ SegGF25.m**; details of this method are given in Appendix A.

8. Click the ··· button in the **Data Path** field in row 1 (Figure 25).

9. Click the YYYY folder relevant to the current year and click **Make New Folder** (Figure 26).

10. Rename the new folder with the date in the **MMDDYY** format.

11. Click on the folder to select it and click **OK**. This new folder is where data generated for the current sequence will be stored. ***Note:*** The data path should be an iteration of D:\MassHunter\GCMS\1\data\YYYY\MMDDYY, where YYYY indicates the current year and MMDDYY indicates the date the sequence was initiated.

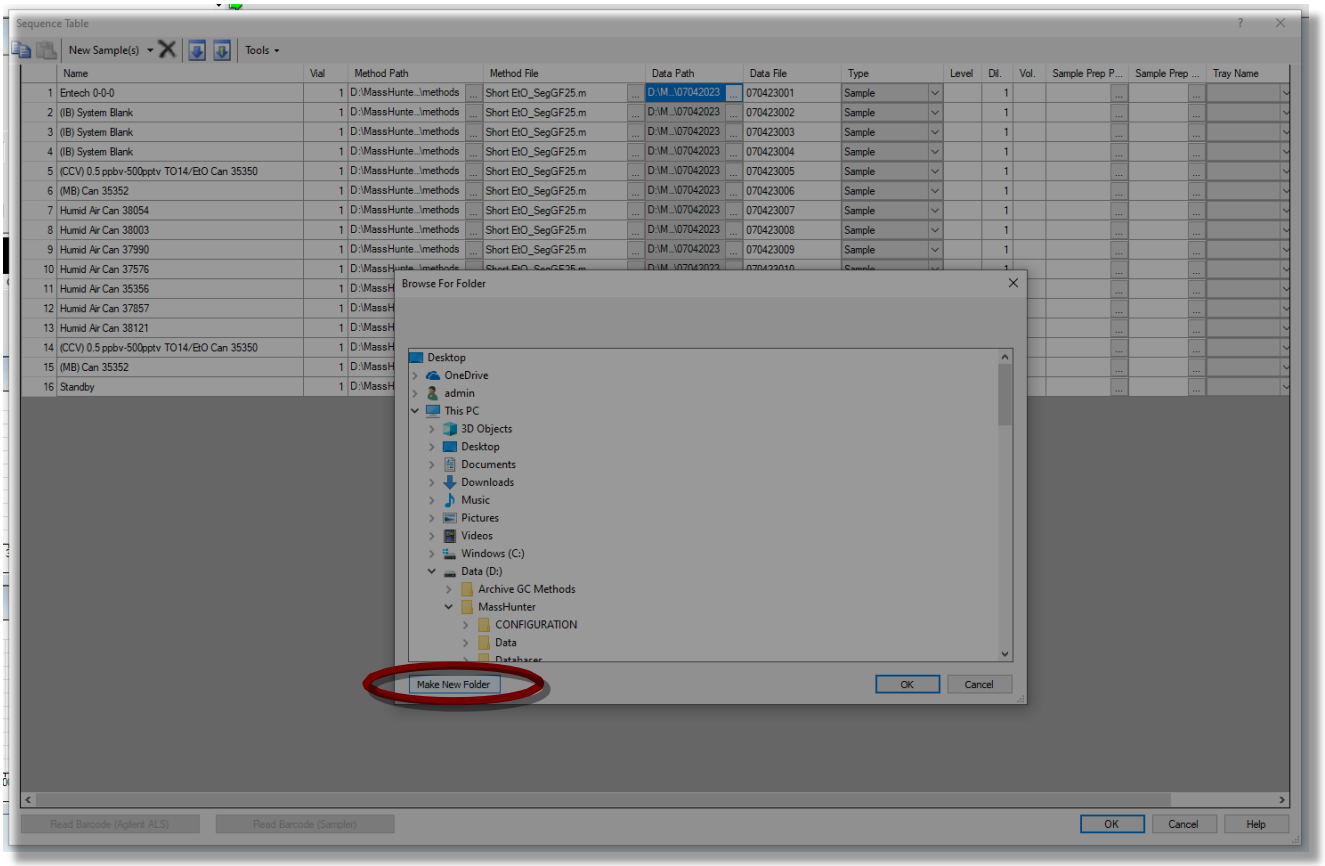
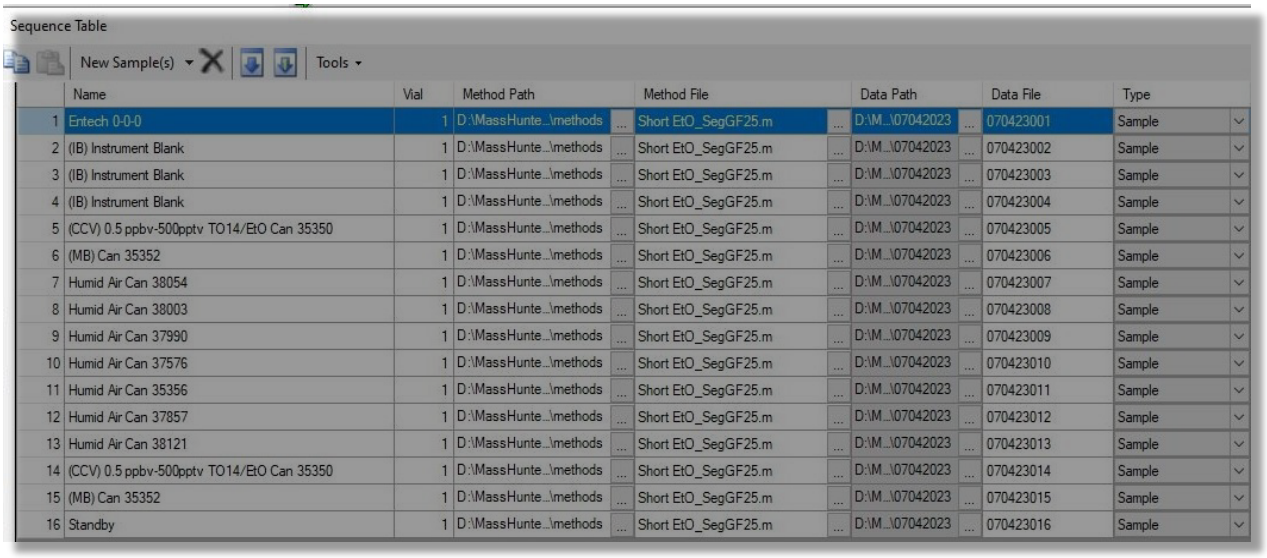


Figure 26. Selecting a year folder and Make New Folder.

12. Click in the **Data File** field in row 1 (Figure 25).
13. Enter the file names in the following format: **MMDDYY###,** where ### in the first file name is 001. The second file name should be MMDDYY002 and so on to increase numerically for each run populated. ***Note:*** To avoid errors when generating file names, it may be helpful to use the fill-down in increments  button.
14. In the **Type** column, select **Sample** for all sample entries (including calibration standards in the ICAL, SSCVs, FSs, FBs, LBs, and LSs).
15. Once the sequence has been edited, click **OK**.

Note: In general, sequence tables should be structured like that shown in Figure 27.

16. Click the **Sequence** tab and select **Save Sequence As** on the drop-down menu (Figure 28).



	Name	Vial	Method Path	Method File	Data Path	Data File	Type
1	Entech 0-0-0	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423001	Sample
2	(IB) Instrument Blank	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423002	Sample
3	(IB) Instrument Blank	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423003	Sample
4	(IB) Instrument Blank	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423004	Sample
5	(CCV) 0.5 ppbv-500pptv TO14/EtO Can 35350	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423005	Sample
6	(MB) Can 35352	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423006	Sample
7	Humid Air Can 38054	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423007	Sample
8	Humid Air Can 38003	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423008	Sample
9	Humid Air Can 37990	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423009	Sample
10	Humid Air Can 37576	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423010	Sample
11	Humid Air Can 35356	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423011	Sample
12	Humid Air Can 37857	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423012	Sample
13	Humid Air Can 38121	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423013	Sample
14	(CCV) 0.5 ppbv-500pptv TO14/EtO Can 35350	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423014	Sample
15	(MB) Can 35352	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423015	Sample
16	Standby	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07042023	070423016	Sample

Figure 27. Edited sequence table.

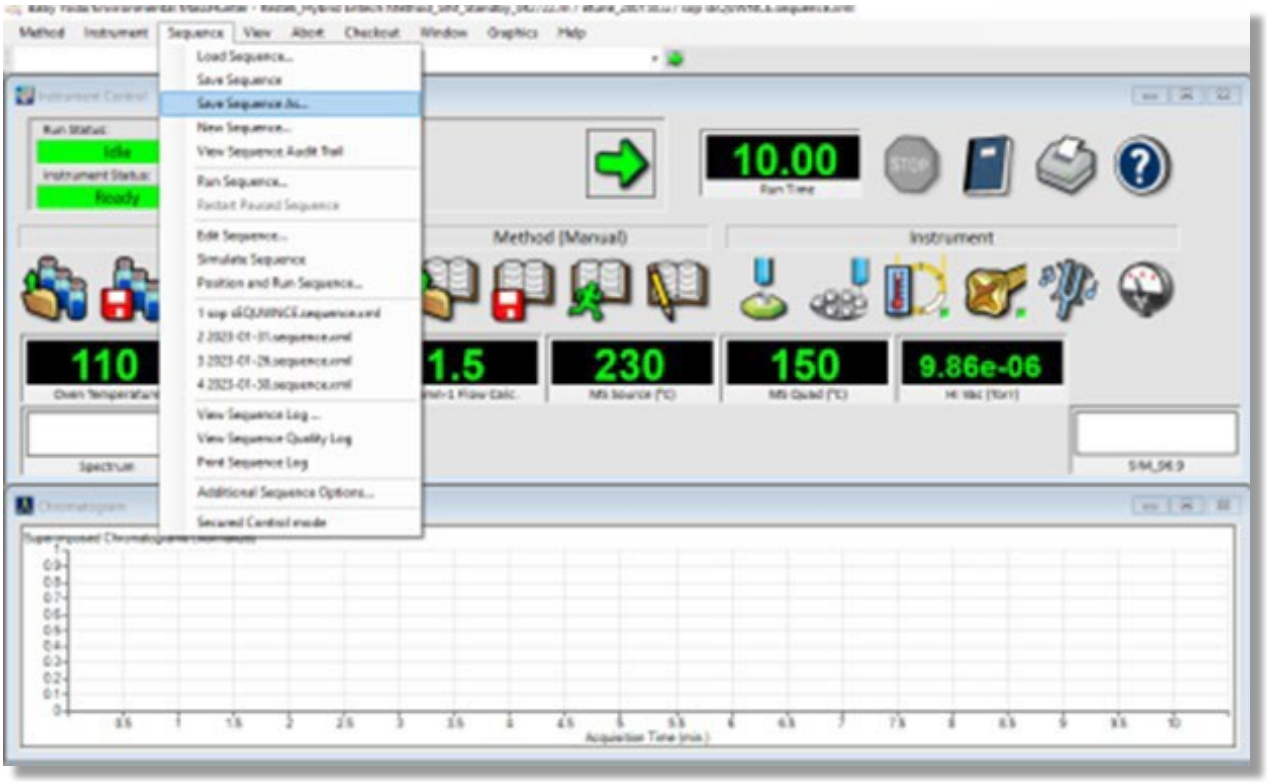


Figure 28. Saving sequence table using Save Sequence As.

17. In the **Save Sequence** dialog box, save the sequence in the format YYYY-MM-DD.sequence, where YYYY-MM-DD reflects the date the sequence was initiated, and click **Save** (Figure 29).

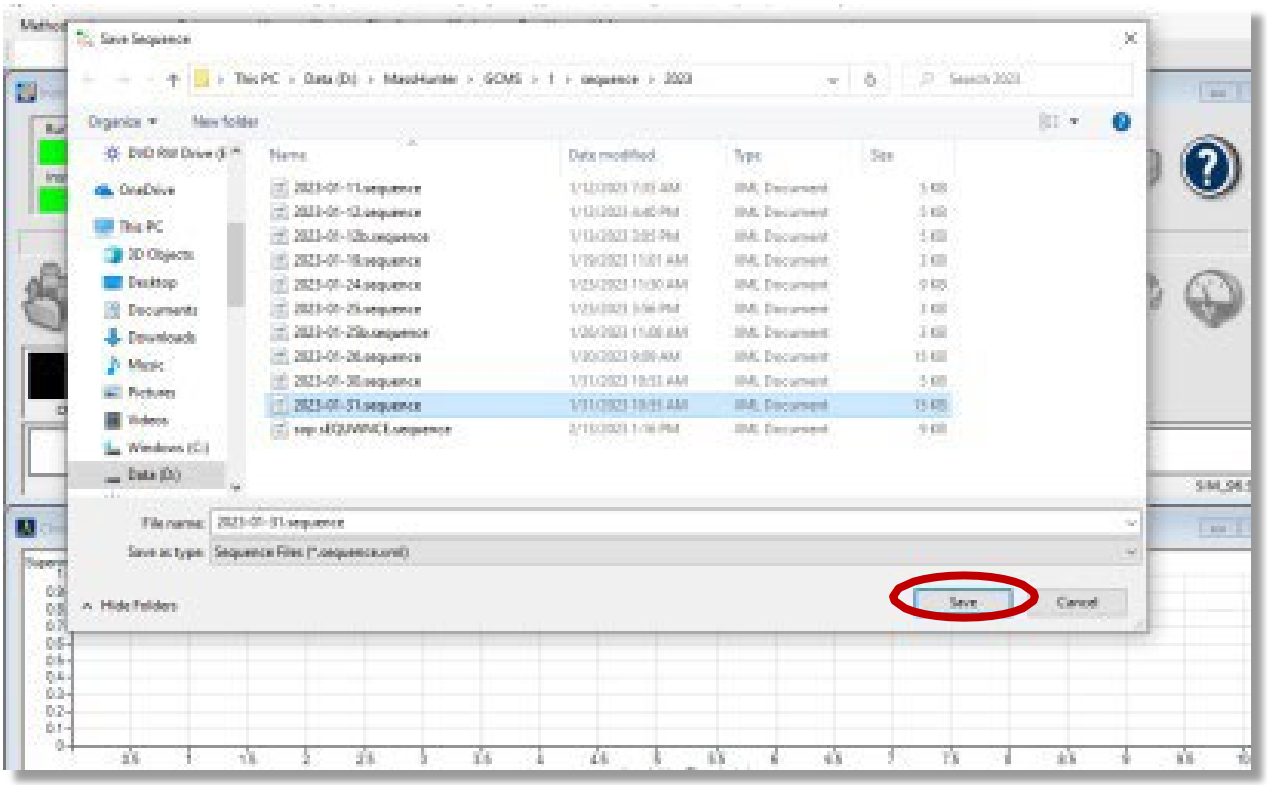


Figure 29. Naming the sequence table in YYYY-MM-DD.sequence format.

18. Record the sequence name on the analysis sheet next to “Agilent Seq”.

19. Copy and paste the sequence into an Excel file, print it out, and tape it and the completed analysis sheet into the laboratory notebook.

20. Verify that the canister numbers, sample information, and port numbers are recorded correctly on the ChemStation sequence table, on the Entech 7200A sequence table, and on the analysis sheet.

21. Inspect the canisters on the autosampler to ensure that the canister valves are open and that the canister numbers, sample information, and port numbers agree with the two sequence tables and analysis sheet.

8.3.3 Running the Analysis Sequence

1. To run the GC-MSD sequence created in the previous section, click the **Run Sequence** button on the toolbar (Figure 30).

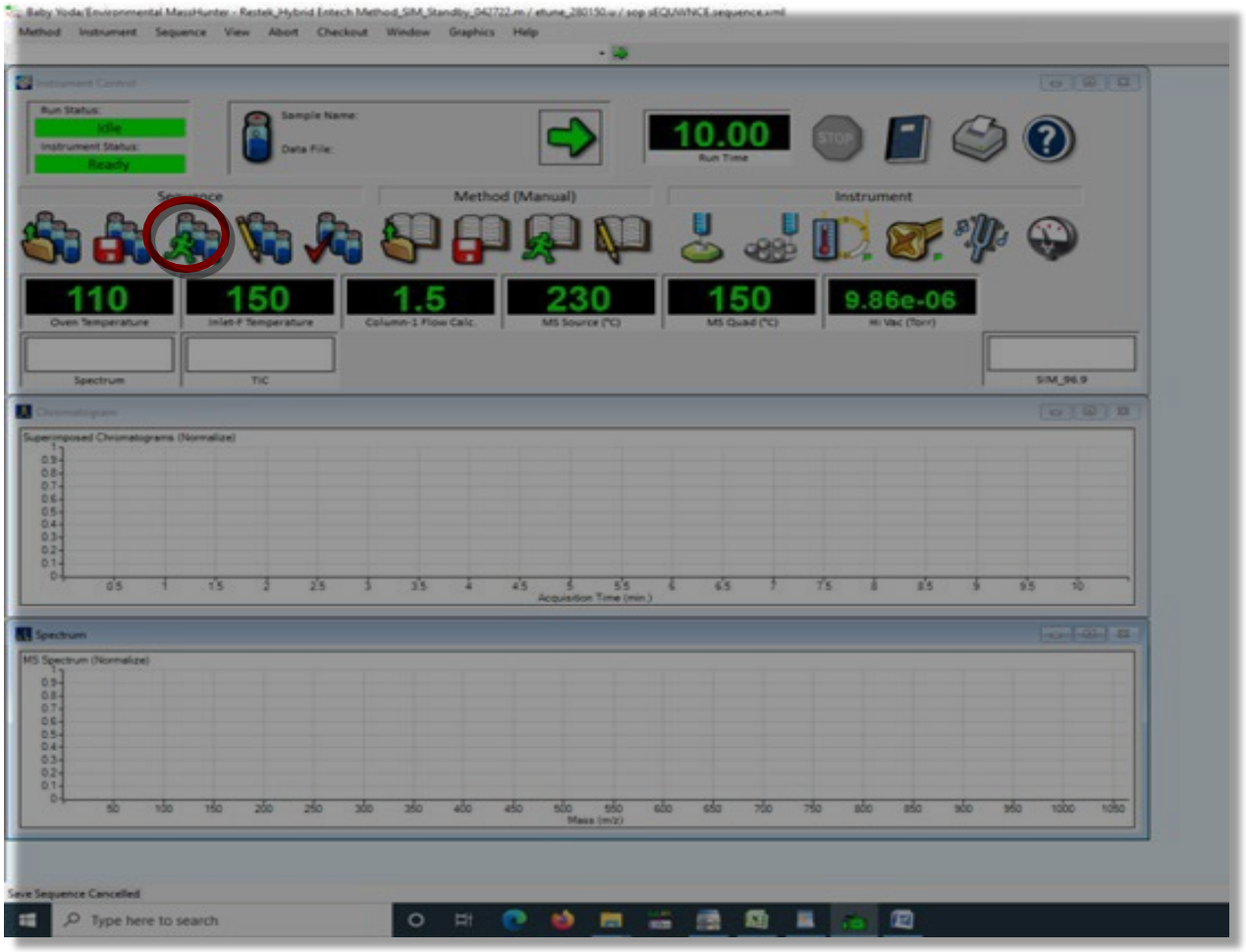


Figure 30. Initiating the analysis sequence on the GC-MSD.

2. In the **Start Sequence** dialog box (Figure 31), edit the **Sequence Comment** field to ensure the comment is relevant to the current analysis sequence and then click **Run Sequence**.
3. **Return to** **section 8.2.8 and complete steps 3–7** to perform the analysis using the Entech 7200A sequence created in section 8.2.4.
4. Review and process the analytical results (chromatograms, peak integrations, and retention times and reports) using the GCMS Environmental Data Analysis software. Details of processing data are discussed in SOP J-AMCD-AAB-SOP-801-2. ***Note:*** Only personnel with extensive Agilent GC and ChemStation knowledge should review and process the data.

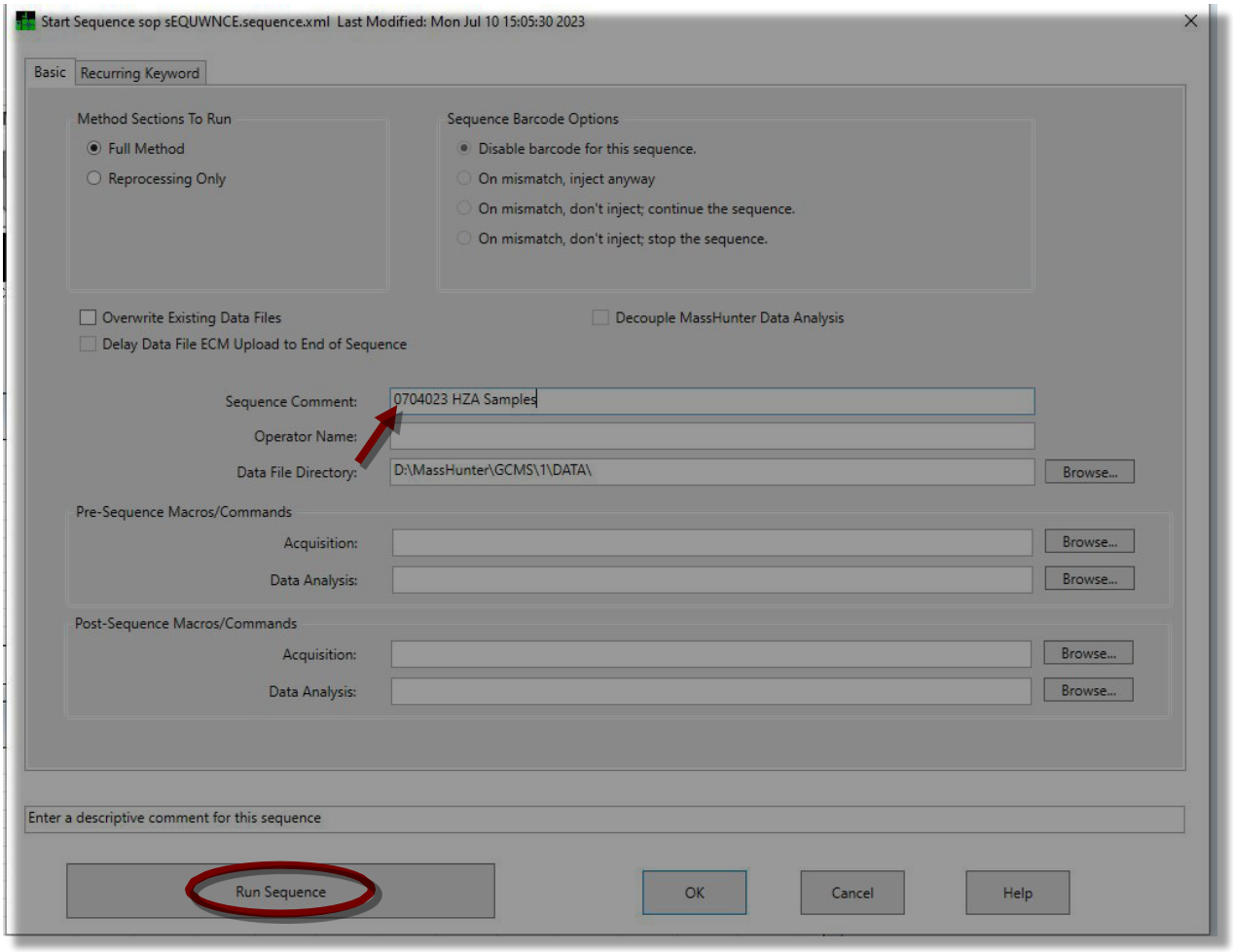


Figure 31. Running the GC-MSD sequence.

9.0 Instrument Calibration

9.1 Refer to J-AMCD-AAB-SOP-3907-1 or J-AMCD-AAB-SOP-3920-1 for standards preparation instructions.

9.2 Before sample analysis, generate an ICAL curve for the Entech/Agilent GC-MSD system. Sample volumes are collected from calibration standard canisters prepared using J-AMCD-AAB-SOP-3907-1 or J-AMCD-AAB-SOP-3920-1.

To generate a **500 pptv calibration curve**, the Entech preconcentrator is set up to collect 25, 32, 38, 50, 63, 125, and 250 cc volumes of a 500 pptv calibration standard to generate 50, 63, 75, 100, 125, 250, and 500 pptv effective sampling concentrations, respectively.

9.3 Set up a calibration analysis sequence as follows:

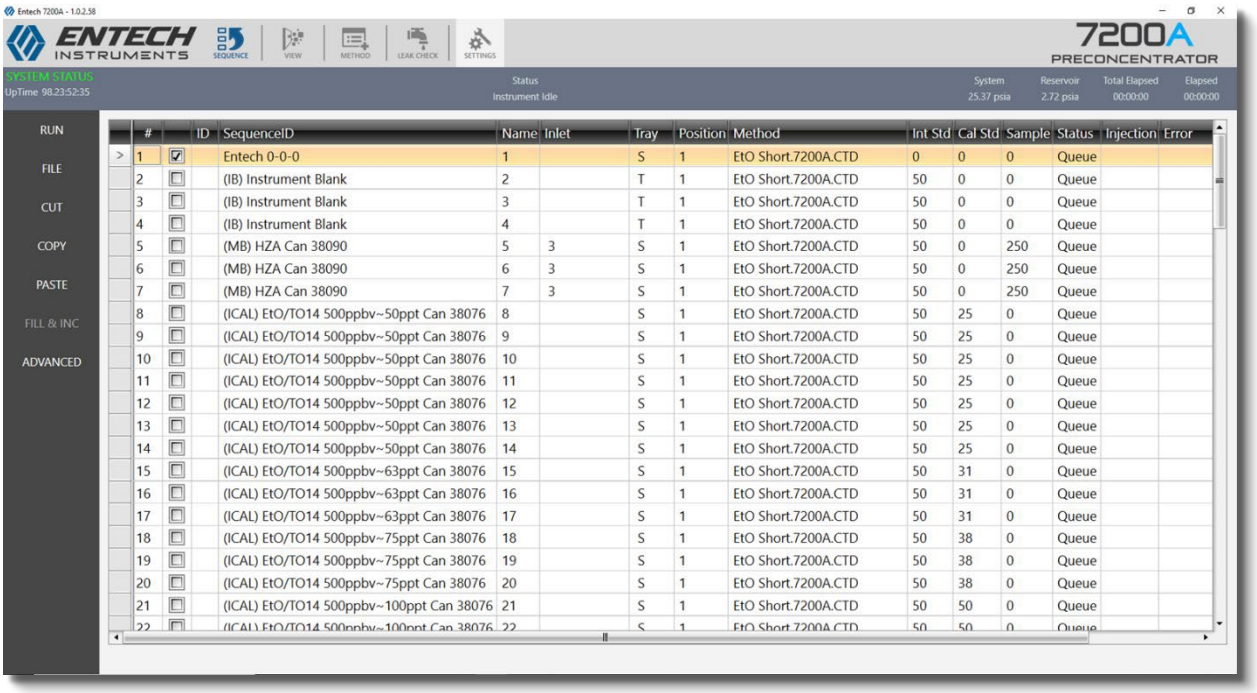
9.3.1 The Entech and Agilent sample sequence table calibration runs are set up in the following order to align with EPA Method TO-15A section 15.2.2:

- **Entech 0-0-0:** Run to demonstrate that background levels in the Entech system meet the system acceptance criteria.
- **IB:** To ready the system by removing any impurities that may still be remaining after the system bakeout, the preconcentration system is cycled through all the preconcentration steps using carrier gas and including internal standards. As mentioned earlier, the IB was previously referred to in this laboratory as the helium blank or system blank. Section 15.3.3.1 of Method TO-15A provides an in-depth description of the IB.
- **MB:** A humidified sample of air is analyzed to demonstrate that the system meets the canister blank acceptance criteria as specified in Method TO-15A Table 10-3 or other QA project documentation. As mentioned earlier, section 15.3.3.2 of EPA Method TO-15A provides further discussion of MBs.

  Note: More than one MB may be needed to clear the system of any contaminants if the system is not being used on a daily basis. Of additional note, if the system has not been used in some time, it is advisable to run a series of HZA canister samples to clean up the system prior to setting up the ICAL sequence.
- **CB:** Section 15.3.3.3 of EPA Method TO-15A provides a description of the CB. In our laboratory, the MB is prepared more stringently than described in Method TO-15A by using the standards dilution system. The previous MB in this case therefore qualifies as a CB and the operator may choose not to run this additional CB.
- **ICAL samples:** Calibration standard runs are performed at various sampling volumes beginning with the smallest concentration and ending with the largest concentration. Method TO-15A section 15.2 provides an in-depth discussion of the ICAL. In this laboratory, each calibration point is generally analyzed in triplicate. In addition, the lowest calibration point is often analyzed seven times to perform a quick TO-15–type method detection limit (MDL) evaluation (as discussed in section 12.1 below) to gauge method performance.
- **MB:** Additional MBs can be run to ensure no carryover from the highest concentration calibration standard.
- **SSCV standard:** An SSCV standard is run at a concentration in the lower third of the calibration curve to verify the ICAL as described in Method TO-15A section 15.3.1.
- **Additional samples:** Immediately following the SSCV, the operator may choose to analyze field samples, CCV standards (every 10 samples), and MBs, ending with a CCV. However, the normal procedure in this laboratory is to end the sequence with the SSCV, create the calibration curve in ChemStation, and evaluate the ICAL and SSCV before analyzing samples.

9.3.2 The Entech 7200A sample sequence table (Figure 32) is set up in the manner listed below when calibrating the system:

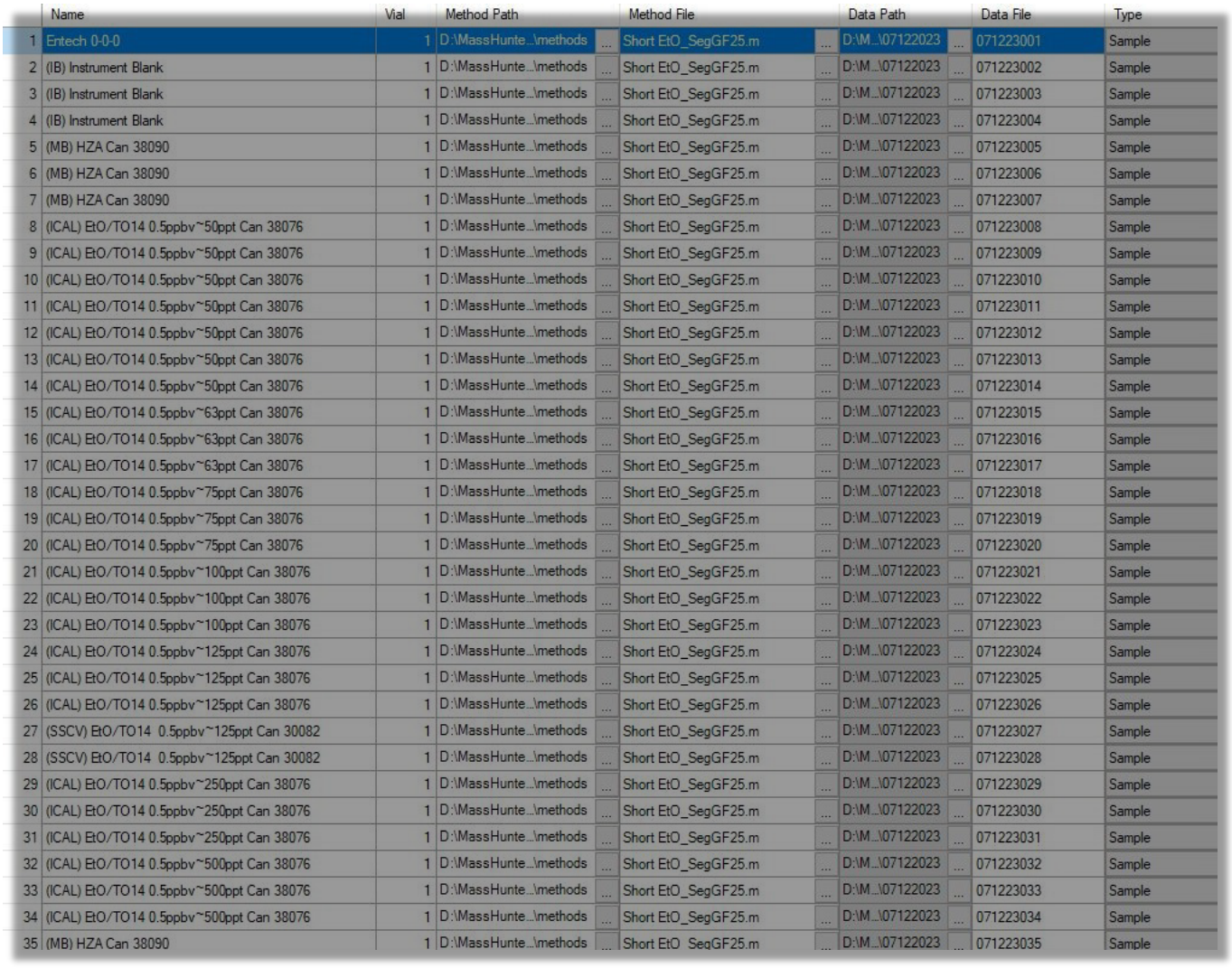
- **Sequence ID:** Enter **Can #####**, where ##### is the canister number stamped on the sampling canister. Enter information on the sample type (for example, ICAL, SSCV, MB, CB, or IB and effective concentration as appropriate).
- **Name:** Do not edit.
- **Inlet:** This value is always blank except for the SSCV, which should be set to 2, and MBs, which should be set to 3.
- **Tray:** Set to S for all calibration and MDL runs.
- **Position:** Do not edit.
- **Method:** Select appropriate method.
- **Int Std:** Enter the volume to be collected from the internal standard canister. For scope and application of the methods mentioned in this SOP, all runs except the Entech 0-0-0 require a 50 cc injection of internal standard.
- **Cal Std:** Alter the sampling volumes by entering a specified volume in this column for the ICAL standards. The entry is 0 for the Entech 0-0-0, IB, MB, and SSCV. ICAL volumes can be found in section 9.2.
- **Sample:** Enter the volume to be collected from the canister. For scope and application of the methods mentioned in this SOP, SSCV and MB canisters are set to a 250 cc collection volume. This entry remains 0 for the Entech 0-0-0, IBs, and ICALs.



#	ID	SequenceID	Name	Inlet	Tray	Position	Method	Int Std	Cal Std	Sample	Status	Injection	Error
1	☑	Entech 0-0-0	1		S	1	EtO Short.7200A.CTD	0	0	0	Queue		
2	☐	(IB) Instrument Blank	2		T	1	EtO Short.7200A.CTD	50	0	0	Queue		
3	☐	(IB) Instrument Blank	3		T	1	EtO Short.7200A.CTD	50	0	0	Queue		
4	☐	(IB) Instrument Blank	4		T	1	EtO Short.7200A.CTD	50	0	0	Queue		
5	☐	(MB) HZA Can 38090	5	3	S	1	EtO Short.7200A.CTD	50	0	250	Queue		
6	☐	(MB) HZA Can 38090	6	3	S	1	EtO Short.7200A.CTD	50	0	250	Queue		
7	☐	(MB) HZA Can 38090	7	3	S	1	EtO Short.7200A.CTD	50	0	250	Queue		
8	☐	(ICAL) EtO/TO14 500ppbv~50ppt Can 38076	8		S	1	EtO Short.7200A.CTD	50	25	0	Queue		
9	☐	(ICAL) EtO/TO14 500ppbv~50ppt Can 38076	9		S	1	EtO Short.7200A.CTD	50	25	0	Queue		
10	☐	(ICAL) EtO/TO14 500ppbv~50ppt Can 38076	10		S	1	EtO Short.7200A.CTD	50	25	0	Queue		
11	☐	(ICAL) EtO/TO14 500ppbv~50ppt Can 38076	11		S	1	EtO Short.7200A.CTD	50	25	0	Queue		
12	☐	(ICAL) EtO/TO14 500ppbv~50ppt Can 38076	12		S	1	EtO Short.7200A.CTD	50	25	0	Queue		
13	☐	(ICAL) EtO/TO14 500ppbv~50ppt Can 38076	13		S	1	EtO Short.7200A.CTD	50	25	0	Queue		
14	☐	(ICAL) EtO/TO14 500ppbv~50ppt Can 38076	14		S	1	EtO Short.7200A.CTD	50	25	0	Queue		
15	☐	(ICAL) EtO/TO14 500ppbv~63ppt Can 38076	15		S	1	EtO Short.7200A.CTD	50	31	0	Queue		
16	☐	(ICAL) EtO/TO14 500ppbv~63ppt Can 38076	16		S	1	EtO Short.7200A.CTD	50	31	0	Queue		
17	☐	(ICAL) EtO/TO14 500ppbv~63ppt Can 38076	17		S	1	EtO Short.7200A.CTD	50	31	0	Queue		
18	☐	(ICAL) EtO/TO14 500ppbv~75ppt Can 38076	18		S	1	EtO Short.7200A.CTD	50	38	0	Queue		
19	☐	(ICAL) EtO/TO14 500ppbv~75ppt Can 38076	19		S	1	EtO Short.7200A.CTD	50	38	0	Queue		
20	☐	(ICAL) EtO/TO14 500ppbv~75ppt Can 38076	20		S	1	EtO Short.7200A.CTD	50	38	0	Queue		
21	☐	(ICAL) EtO/TO14 500ppbv~100ppt Can 38076	21		S	1	EtO Short.7200A.CTD	50	50	0	Queue		
22	☐	(ICAL) EtO/TO14 500ppbv~100ppt Can 38076	22		S	1	EtO Short.7200A.CTD	50	50	0	Queue		

Figure 32. Entech 7200A sample sequence table set up for calibration.

9.3.3 To set up the Agilent sample sequence table for calibration (Figure 33), follow the setup in the Agilent software as described in section 8.3.2. Calibration and SSCV standard runs should be entered in the same format as the CCV standards described in 8.3.2, step 12.



	Name	Vial	Method Path	Method File	Data Path	Data File	Type
1	Entech 0-0-0	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223001	Sample
2	(IB) Instrument Blank	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223002	Sample
3	(IB) Instrument Blank	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223003	Sample
4	(IB) Instrument Blank	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223004	Sample
5	(MB) HZA Can 38090	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223005	Sample
6	(MB) HZA Can 38090	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223006	Sample
7	(MB) HZA Can 38090	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223007	Sample
8	(ICAL) EtO/TO14 0.5ppbv~50ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223008	Sample
9	(ICAL) EtO/TO14 0.5ppbv~50ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223009	Sample
10	(ICAL) EtO/TO14 0.5ppbv~50ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223010	Sample
11	(ICAL) EtO/TO14 0.5ppbv~50ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223011	Sample
12	(ICAL) EtO/TO14 0.5ppbv~50ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223012	Sample
13	(ICAL) EtO/TO14 0.5ppbv~50ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223013	Sample
14	(ICAL) EtO/TO14 0.5ppbv~50ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223014	Sample
15	(ICAL) EtO/TO14 0.5ppbv~63ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223015	Sample
16	(ICAL) EtO/TO14 0.5ppbv~63ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223016	Sample
17	(ICAL) EtO/TO14 0.5ppbv~63ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223017	Sample
18	(ICAL) EtO/TO14 0.5ppbv~75ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223018	Sample
19	(ICAL) EtO/TO14 0.5ppbv~75ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223019	Sample
20	(ICAL) EtO/TO14 0.5ppbv~75ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223020	Sample
21	(ICAL) EtO/TO14 0.5ppbv~100ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223021	Sample
22	(ICAL) EtO/TO14 0.5ppbv~100ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223022	Sample
23	(ICAL) EtO/TO14 0.5ppbv~100ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223023	Sample
24	(ICAL) EtO/TO14 0.5ppbv~125ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223024	Sample
25	(ICAL) EtO/TO14 0.5ppbv~125ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223025	Sample
26	(ICAL) EtO/TO14 0.5ppbv~125ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223026	Sample
27	(SSCV) EtO/TO14 0.5ppbv~125ppt Can 30082	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223027	Sample
28	(SSCV) EtO/TO14 0.5ppbv~125ppt Can 30082	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223028	Sample
29	(ICAL) EtO/TO14 0.5ppbv~250ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223029	Sample
30	(ICAL) EtO/TO14 0.5ppbv~250ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223030	Sample
31	(ICAL) EtO/TO14 0.5ppbv~250ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223031	Sample
32	(ICAL) EtO/TO14 0.5ppbv~500ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223032	Sample
33	(ICAL) EtO/TO14 0.5ppbv~500ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223033	Sample
34	(ICAL) EtO/TO14 0.5ppbv~500ppt Can 38076	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223034	Sample
35	(MB) HZA Can 38090	1	D:\MassHunte...\methods	Short EtO_SegGF25.m	D:\M...\07122023	071223035	Sample

Figure 33. Agilent sample sequence table set up for calibration.

9.4 The analysis of the calibration standards is completed in accordance with this SOP. Once the calibration samples are analyzed, a calibration curve is generated using the Agilent 5975 MSD ChemStation software as discussed in SOP J-AMCD-AAB-SOP-801-2.

10.0 Troubleshooting

See the troubleshooting guide in the user's manuals for guidance on troubleshooting procedures.

11.0 Calculations

11.1 VOC Standard Concentration Calculations

Calculate the concentrations of the VOC standard using the following equation:

$$\frac{Flow_{std}}{Flow_{std} + Flow_{air}} \times Conc_{std} = Conc_{final}$$

where $Flow_{std}$ is the flow rate (cc/min) from the cylinder standard,
$Flow_{air}$ is the flow rate (cc/min) from the dilution air,
$Conc_{std}$ is the concentration of the VOC standard in ppmv or ppbv, and
$Conc_{final}$ is the final concentration in ppbv or pptv.

11.2 Internal Standard Calculation

The internal standard is a four-component standard that is injected into each sample upon analysis (see section 14.8). The internal standard corrects for instrument drift by relating each compound to one of the four components. This relationship generates a response factor (RF) used to correct the drift and is automatically calculated in the ChemStation software using the following equation:

$$\frac{Area_{target} \times Conc_{istd}}{Area_{istd} \times Conc_{target}} = RF$$

where $Area_{target}$ is the integrated area of the target compound,
$Conc_{istd}$ is the concentration of the internal standard,
$Area_{istd}$ is the integrated area of the internal standard, and
$Conc_{target}$ is the concentration of the target compound.

12.0 Method Performance

12.1 The following MDL determination procedure is applicable to samples being analyzed according to EPA Method TO-15. Generally in this laboratory, we use this procedure to quickly gauge method performance when validating and refining the instrument methods.

MDLs are determined at the time of the initial calibration by analyzing replicates at the lowest calibration concentration. The samples are analyzed in accordance with the procedures described in this SOP. The MDL is calculated as follows:

$$MDL = t(n-1, 1-\alpha = 0.99)\ (S),$$

where t(n–1,1–α = 0.99) is the Student's t value appropriate for a 99% confidence level and a standard deviation estimate with n–1 degrees of freedom, and S is the standard deviation of the replicate analyses.

12.2 For samples being analyzed according to EPA Method TO-15A, the operator is referred to the guidance in section 17 of that document. The methodology includes an assessment of both low-level standards and blanks analyzed over a period of time to determine the MDL. The following paragraph from section 17.1 of Method TO-15A briefly summarizes the MDL procedure:

> "To initially determine the MDL, laboratories must prepare a minimum of seven MB canisters and seven spiked canisters in at least three batches on three separate calendar dates. These canisters are analyzed on at least three separate calendar dates. Separate MDLs are calculated for each target VOC based on the results from the spiked canisters and the MBs (MDL_{sp} [section 17.6] and MDL_b [section 17.7], respectively), and the higher of the two concentrations is chosen as the laboratory MDL."

Note: For many of the research projects conducted in this laboratory, the TO-15 MDL determination procedure in 12.1 will be followed since samples are not being analyzed continually in "production mode" for a lengthy period of time.

13.0 Data and Records Management

13.1 All information concerning standards and sample preparation should be recorded in the project laboratory notebook and on the analysis sheet. The operator must maintain the notebook with experimental and sample details.

13.2 Instrument records of use and maintenance are to be kept in the instrument maintenance notebook.

13.3 All data is maintained per specifications outlined in study-specific scientific data management plans.

14.0 Quality Control and Quality Assurance Activities

14.1 All VOC sampling canisters (various vendors) must be tested for cleanliness before use. To assess cleanliness, canisters are cleaned and evacuated (J-AMCD-AAB-SOP-3914-2 or J-AMCD-AAB-SOP-3915-2) and filled with HSA (J-AMCD-AAB-SOP-3907-1 or J-AMCD-AAB-SOP-3920-1). The humidified air mixture must age in the canister for a minimum of 24 hours prior to analyzing an air sample from the canister according to the procedures outlined in this SOP.

14.2 An air/water background check is performed on the Agilent GC-MSD system prior to operation to verify that there are no leaks in the system. The air/water check results are recorded in the laboratory notebook and on analysis sheets (Appendix D).

14.3 The GC-MSD is tuned to optimize instrument sensitivity and analyte response using the tune method included in the ChemStation software (see the Agilent GC-MSD user's manual and SOP J-AMCD-AAB-SOP-801-2) prior to analytical calibration. The tune file

is saved as etune.u. The same tune file is used throughout a study or until an instrument failure (e.g., filament outage, turbopump failure) necessitates a retune and recalibration.

14.4 Although the parameters relating to peak selection and peak integration in the SIM quantitation method have been optimized to ensure correct data capture, integration of each target analyte peak in every sample is checked and peaks are manually integrated if necessary (see the Agilent GC-MSD user's manual and J-AMCD-AAB-SOP-801-2).

14.5 By using the Entech 7200A preconcentrator software, the operator initiates a leak check for the canisters prior to starting a sampling sequence (section 8.2.5). This leak check verifies that the canister connections are leak free in order to prevent sample loss or ingress of contaminants from ambient air. When a leak is reported by the software, the operator may be able to tighten the fitting slightly to correct the leak. If the canister connection still leaks after retightening the connection, the canister must be removed and repaired and the sample contained in the canister will be lost.

14.6 An Entech 0-0-0, an IB (consisting of helium gas and internal standard), and a minimum of one MB should be analyzed at the beginning of every sample sequence to check the cleanliness of the analytical system.

14.7 CCV standards are run at the beginning of a sample batch and are used to monitor filament wear and system drift.

14.8 Internal standards are injected in each sample to account for instrument drift. The responses of the internal standards are used by the MSD software for calculation of compound concentrations and by the operator to monitor changes in the sensitivity of the analytical system. The responses of internal standard compounds should be monitored daily to ensure their response remains steady. Decreased response for these compounds indicates the system might need to be retuned and calibrated. See the Agilent GC-MSD user's manual for more information.

14.9 Depending on the DQOs of a particular study, LBs, LSs, FBs, and/or FSs may be loaded on the 7016D autosampler for inclusion in the sample sequence.

14.10 During sampling, samples can be collected alone or in pairs depending on the DQOs of the study. The criterion for acceptable results for duplicate analytical precision, as specified in EPA Method TO-15A, section 18, Table 18-1 "Quality Control Parameters and Performance Specifications for EPA Method TO-15A," is "Precision ≤ 25% RPD [relative percent difference] of target VOCs in the compared samples when both measurements are ≥ fivefold MDL."

14.11 Depending on the DQOs of a particular study, audit standards might be included in the sample sequence. The criterion for acceptable results for audit accuracy as defined in Method TO-15A, section 18, Table 18-1 "Quality Control Parameters and Performance Specifications for EPA Method TO-15A," is "Within ±30% of accepted reference value."

14.12 For studies that are conducted according to Method TO-15 procedures rather than Method TO-15A procedures, the method performance requirements are stated in section 11, "Requirements for Demonstrating Method Acceptability for VOC Analysis from Canisters," of that document and are essentially the same as the analytical precision and audit accuracy requirements of Method TO-15A.

15.0 Standard Operating Procedures, References, and Supporting Documentation

15.1 Standard Operating Procedures

J-AMCD-AAB-SOP-801-2. 2010. Standard Operating Procedure for Operation, Maintenance, and Sample Analysis Using the Agilent 6890 GC and 5973/75 MSD Systems. U.S. Environmental Protection Agency, Center for Environmental Measurement and Modeling.

J-AMCD-AAB-SOP-3907-1. 2022. Standard Operating Procedure for Preparation of Volatile Organic Compound Standards in Canisters Using the Entech 4700 Static Diluter. U.S. Environmental Protection Agency, Center for Environmental Measurement and Modeling.

J-AMCD-AAB-SOP-3914-2. 2022. Standard Operating Procedure for Cleaning Canisters Used for Collection of Whole Air Samples. U.S. Environmental Protection Agency, Center for Environmental Measurement and Modeling.

J-AMCD-AAB-SOP-3915-2. 2022. Standard Operating Procedure for Cleaning Canisters Used for Collection of Whole Air Samples Using the Xonteck Model 960 Canister Cleaning System. U.S. Environmental Protection Agency, Center for Environmental Measurement and Modeling.

J-AMCD-AAB-SOP-3920-1. 2020. Standard Operating Procedure for Preparation of Calibration Samples of Volatile Organic Compounds in Air Using Dynamic Dilution Techniques. U.S. Environmental Protection Agency, Center for Environmental Measurement and Modeling.

15.2 References

Agilent Technologies, Inc. 2022. How to Check the Air and Water Background in the Agilent 5975 and 5977 GC/MSD. Agilent Community Blog. Retrieved from: https://community.agilent.com/knowledge/gcms-portal/kmp/gcms-articles/kp373.how-to-check-the-air-and-water-background-in-the-agilent-5975-and-5977-gc-msd (last accessed July 17, 2023).

Entech. Instruments, Inc. 2019. 7200A - Fast US EPA TO15 Analysis Providing Higher Productivity Using the New Entech 7200A and Agilent 7890B/5977 GCMS. Application Note A-3742-01. Entech Instruments Inc., Simi Valley, CA.

U.S. EPA. 2019. Method TO-15A: Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography–Mass Spectrometry (GC-MS). Research Triangle Park, NC: Office of Research and Development, National Exposure Research Laboratory, and Office of Air Quality Planning and Standards, Air Quality Assessment Division. https://www.epa.gov/sites/production/files/2019-12/documents/to-15a_vocs.pdf (last accessed June 29, 2023).

U.S. EPA. 1999a. Compendium Method TO-14A: Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography. In *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, 2nd ed., EPA/625/R-96/010b. Cincinnati, OH: Office of Research and Development.

U.S. EPA. 1999b. Compendium Method TO-15: Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/ Mass Spectrometry (GC/MS). In *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, 2nd ed., EPA/625/R-96/010b. Cincinnati, OH: Office of Research and Development.

15.3 Supporting Documentation

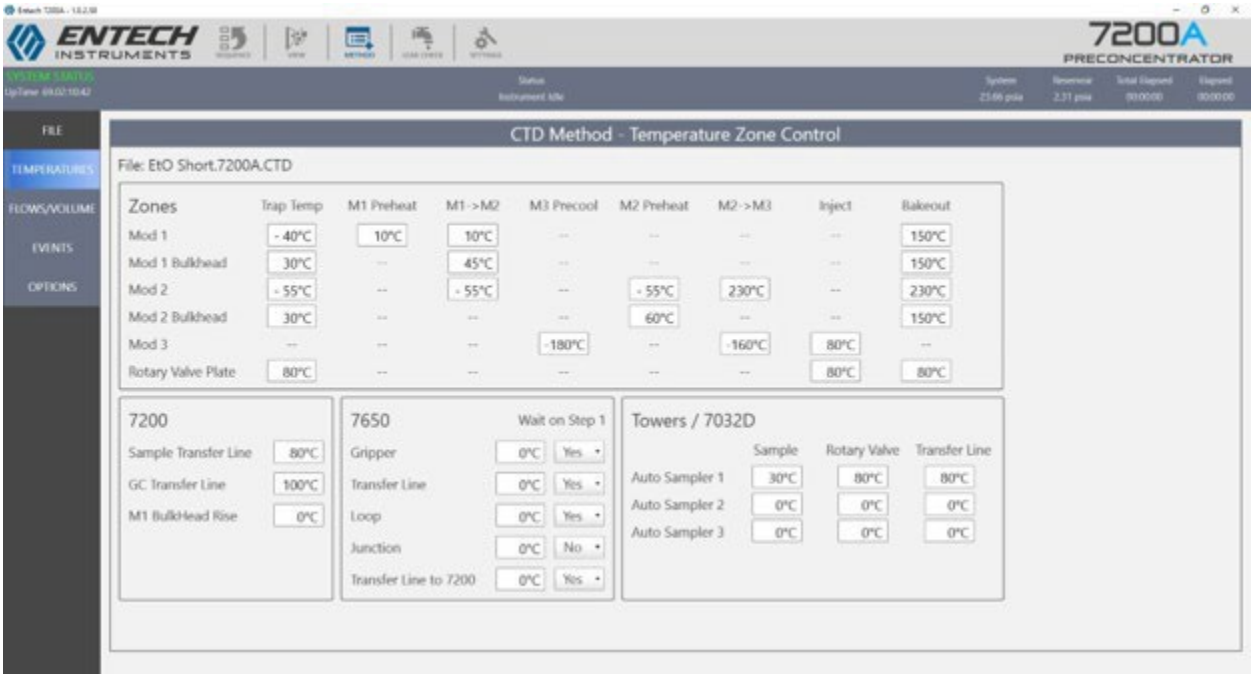
Agilent 8890 Gas Chromatograph Operation Manual, Fourth Edition, part number G3540-90015. November 2020. Agilent Technologies, Inc., 2850 Centerville Road Wilmington, DE 19808.

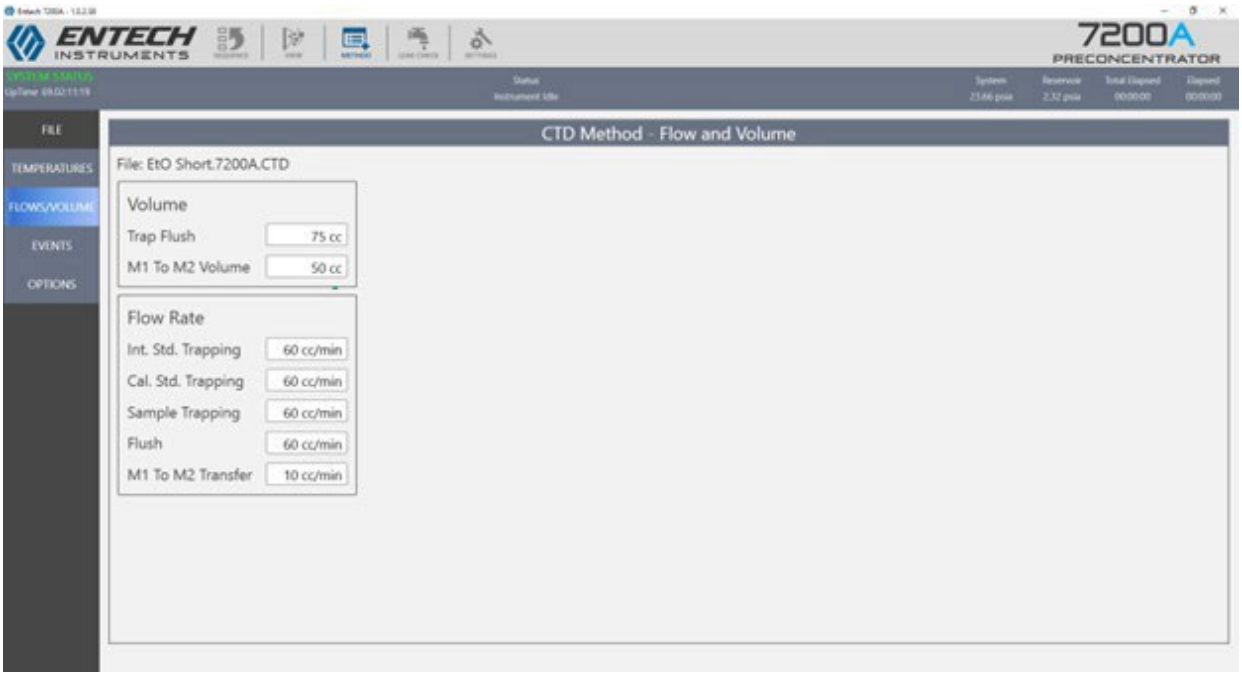
Agilent 5977B Series MSD Operating Manual, First Edition, part number G7077-90034. January 2019. Agilent Technologies, Inc., 5301 Stevens Creek Boulevard, Santa Clara, CA 95051.

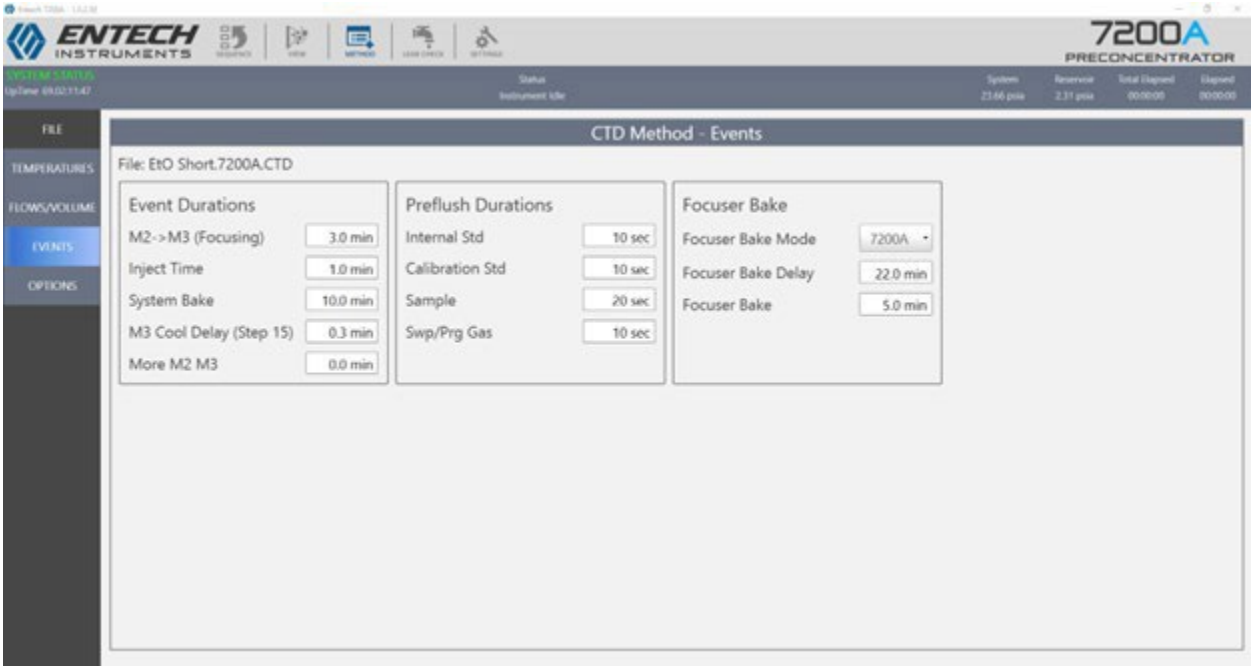
Entech Model 7200A Accelerated Preconcentrator User Manual, version 1.0. June 2021. Entech Instruments Inc., Simi Valley, CA.

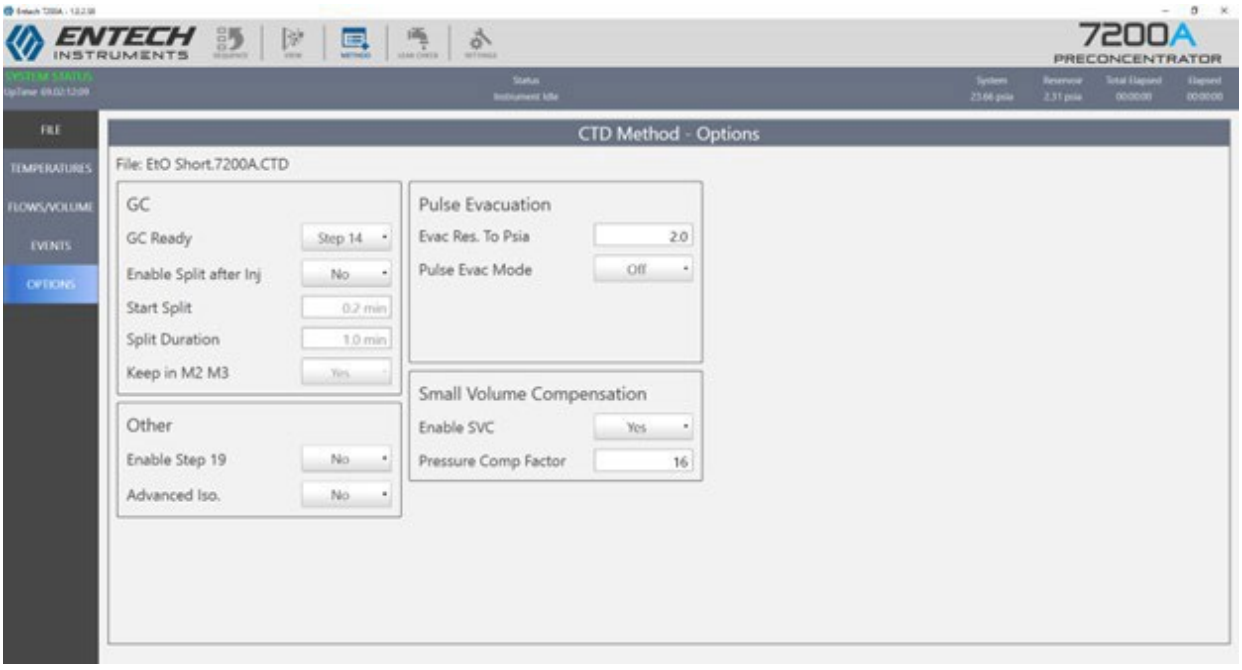
Entech Model 7200A Preconcentrator User Service Manual, version 1.0. June 2021. Entech Instruments Inc., Simi Valley, CA.

Appendix A: Primary Entech and GC-MS Method Parameters






ENTECH INSTRUMENTS
7200A
PRECONCENTRATOR
FILE
TEMPERATURES
FLOWS/VOLUME
EVENTS
OPTIONS
CTD Method - Events
File: EtO Short.7200A.CTD
Event Durations
M2->M3 (Focusing) 3.0 min
Inject Time 1.0 min
System Bake 10.0 min
M3 Cool Delay (Step 15) 0.3 min
More M2 M3 0.0 min
Preflush Durations
Internal Std 10 sec
Calibration Std 10 sec
Sample 20 sec
Swp/Prg Gas 10 sec
Focuser Bake
Focuser Bake Mode 7200A
Focuser Bake Delay 22.0 min
Focuser Bake 5.0 min


ENTECH INSTRUMENTS
7200A
PRECONCENTRATOR
FILE
TEMPERATURES
FLOWS/VOLUME
EVENTS
OPTIONS
CTD Method - Options
File: EtO Short.7200A.CTD
GC
GC Ready Step 14
Enable Split after Inj No
Start Split 0.2 min
Split Duration 1.0 min
Keep in M2 M3 Yes
Other
Enable Step 19 No
Advanced Iso. No
Pulse Evacuation
Evac Res. To Psia 2.0
Pulse Evac Mode Off
Small Volume Compensation
Enable SVC Yes
Pressure Comp Factor 16

METHOD CONTROL PARAMETERS

Method Information for: D:\MassHunter\GCMS\3\methods\Short EtO_SegGF25.m

Method Sections To Run:

( ) Save Copy of Method With Data
( ) Instrument Control Pre-Run Cmd/Macro -
( ) Data Analysis Pre-Run Cmd/Macro -
(X) Data Acquisition
(X) Data Analysis
( ) Instrument Control Post-Run Cmd/Macro -
( ) Data Analysis Post-Run Cmd/Macro -

Method Comments:
TO15A method

END OF METHOD CONTROL PARAMETERS

Single Quadrupole Acquisition Method - MS Parameters Report

Method file	D:\MassHunter\GCMS\3\methods\Short EtO_SegGF25.m
Tune file	etune.u
Ion source	EI
Source temperature (°C)	300
Quad temperature (°C)	180
Fixed Electron energy (eV)	70.0
Acquisition Type	SIM
Stop time (min)	10.00
Solvent delay (min)	5.00
Trace Ion Detection	False
Gain Factor	25
EM Saver	False
EM Saver Limit	N/A

Scan Time Segments

Time	Start Mass	End Mass	Threshold	Scan Speed

Timed Events

Time	Type of Event	Parameter

Real-Time Plots

Type of Plot	Label	Low Mass	High Mass
Total Ion	N/A	N/A	N/A
Spectrum	N/A	N/A	N/A

Self-Cleaning Ion Source Parameters

Mode	No Cleaning

Single Quadrupole Acquisition Method - MS Parameters Report

SIM Time Segment 1

Group Name	Auto_1		
Start Time	5.00		
Resolution	Low		
Detector EMV Override			

Ion mass-to-charge	Dwell time (ms)	Plot This Ion?	Label
39	25	NO	
50	25	NO	
52	25	NO	
53.1	25	NO	
54.1	25	YES	
62	25	NO	
64	25	NO	
85	25	NO	
87	25	NO	
134.9	25	NO	

Single Quadrupole Acquisition Method - MS Parameters Report

SIM Time Segment 2

Group Name	Auto_2		
Start Time	14.00		
Resolution	Low		
Detector EMV Override			

Ion mass-to-charge	Dwell time (ms)	Plot This Ion?	Label
15	25	NO	
29	25	NO	
30	25	NO	
31	25	NO	
32	25	NO	
41	25	NO	
43	25	NO	
43.9	25	NO	
56	25	NO	
57	25	NO	
60	25	NO	
64	25	NO	
66	25	YES	
93.9	25	NO	
95.9	25	NO	

SIM Time Segment 3

Group Name	Auto_3		
Start Time	18.00		
Resolution	Low		
Detector EMV Override			

Ion mass-to-charge	Dwell time (ms)	Plot This Ion?	Label
61	25	NO	
96	25	NO	
100.9	25	YES	
102.9	25	NO	
150.9	25	NO	

Single Quadrupole Acquisition Method - MS Parameters Report

SIM Time Segment 4

Group Name	Auto_4		
Start Time	22.00		
Resolution	Low		
Detector EMV Override			

Ion mass-to-charge	Dwell time (ms)	Plot This Ion?	Label
41.1	25	YES	
52	25	NO	
53	25	NO	
63	25	NO	
65	25	NO	
76	25	NO	
83.9	25	NO	
85.9	25	YES	

SIM Time Segment 5

Group Name	Auto_5		
Start Time	24.10		
Resolution	Low		
Detector EMV Override			

Ion mass-to-charge	Dwell time (ms)	Plot This Ion?	Label
49	25	NO	
61	25	NO	
62	25	NO	
64	25	NO	
78.1	25	NO	
79.1	25	NO	
83	25	NO	
85	25	NO	
95.9	25	NO	
96.9	25	NO	
98.9	25	NO	
116.9	25	NO	
118.9	25	NO	
129.9	25	NO	

Single Quadrupole Acquisition Method - MS Parameters Report

SIM Time Segment 6

Group Name	Auto_6		
Start Time	25.50		
Resolution	Low		
Detector EMV Override			

Ion mass-to-charge	Dwell time (ms)	Plot This Ion?	Label
63	25	NO	
76	25	NO	
114	25	YES	
115	25	NO	
129.9	25	NO	
131.9	25	YES	

SIM Time Segment 7

Group Name	Auto_7		
Start Time	26.50		
Resolution	Low		
Detector EMV Override			

Ion mass-to-charge	Dwell time (ms)	Plot This Ion?	Label
75	25	NO	
82.9	25	NO	
91.1	25	NO	
92.1	25	NO	
96.9	25	YES	
107	25	NO	
109	25	NO	
109.9	25	NO	
128.9	25	NO	
165.9	25	NO	

Single Quadrupole Acquisition Method - MS Parameters Report

SIM Time Segment 8

Group Name	Auto_8		
Start Time	28.20		
Resolution	Low		
Detector EMV Override			

Ion mass-to-charge	Dwell time (ms)	Plot This Ion?	Label
77	25	NO	
78.1	25	NO	
82.1	25	NO	
91.1	25	NO	
104.1	25	NO	
105.1	25	NO	
106.1	25	NO	
112	25	NO	
117	25	NO	

SIM Time Segment 9

Group Name	Auto_9		
Start Time	29.30		
Resolution	Low		
Detector EMV Override			

Ion mass-to-charge	Dwell time (ms)	Plot This Ion?	Label
82.9	25	NO	
84.9	25	NO	
95	25	NO	
105.1	25	NO	
120.1	25	YES	
173.9	25	NO	

Single Quadrupole Acquisition Method - MS Parameters Report

SIM Time Segment 10

Group Name	Auto_10		
Start Time	30.50		
Resolution	Low		
Detector EMV Override			

Ion mass-to-charge	Dwell time (ms)	Plot This Ion?	Label
146	25	NO	
148	25	NO	
179.9	25	NO	
181.9	25	NO	
224.9	25	NO	
226.9	25	NO	

INSTRUMENT CONTROL PARAMETERS: Baby Yoda 2

D:\MassHunter\GCMS\3\methods\Short EtO_SegGF25.m
Fri Jun 30 12:06:46 2023

Control Information

Sample Inlet	: GC
Injection Source	: Manual
Mass Spectrometer	: Enabled

No Sample Prep method has been assigned to this method.

GC

GC Summary

Run Time	35.778 min
Post Run Time	5 min

Oven

Temperature	
Setpoint	On
(Initial)	-20 °C
Hold Time	3 min
Post Run	180 °C
Program	
#1 Rate	1.5 °C/min
#1 Value	1 °C
#1 Hold Time	0 min
#2 Rate	18 °C/min
#2 Value	150 °C
#2 Hold Time	0 min
#3 Rate	12 °C/min
#3 Value	240 °C
#3 Hold Time	3 min

Equilibration Time	2 min
Max Temperature	320 °C
Maximum Temperature Override	Disabled
Slow Fan	Disabled
Cryo	On
Cryo Type	N2
Quick Cool	Off
Ambient Temperature	50 °C
Timeout Detection	On 60 min
Fault Detection	Off

Front SS Inlet He

Mode	Splitless
Heater	On 150 °C
Pressure	On 17.425 psi
Total Flow	On 34.5 mL/min
Septum Purge Flow	On 3 mL/min
Septum Purge Flow Mode	Standard
Pre-Run Flow Test	Off
Gas Saver	Off
Purge Flow to Split Vent	30 mL/min at 999 min
Liner	A Liner has not been selected.

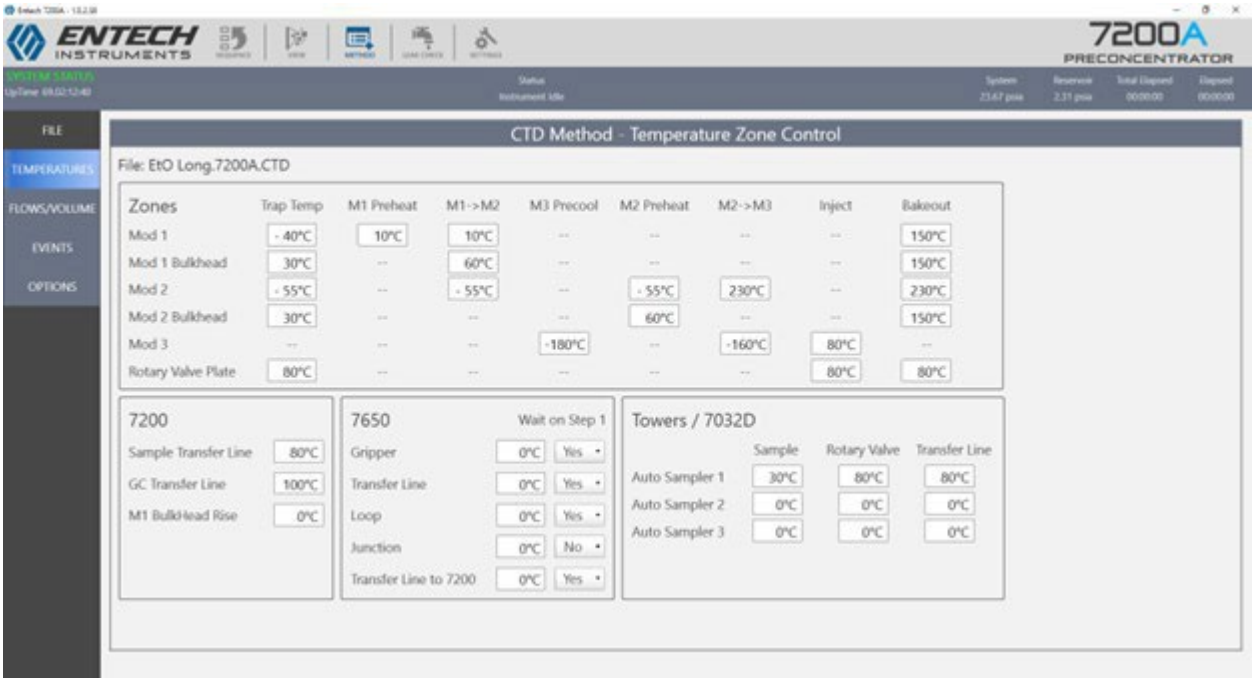
Column

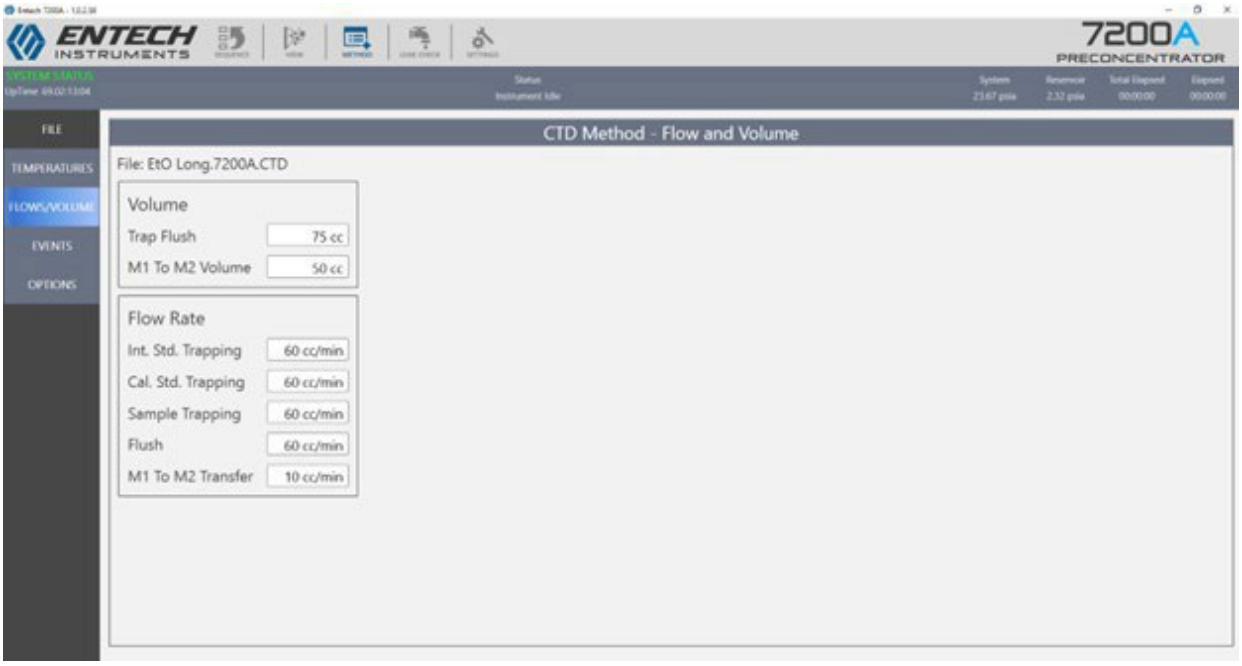
Column #1	
Flow	
Setpoint	On
(Initial)	1.5 mL/min
Post Run	1.5 mL/min
Column Information	Agilent 13869: 1649780
Description	DB-624
Temperature Range	-60 °C-320 °C (320 °C)
Dimensions	60 m x 250 µm x 1.4 µm (Uncalibrated)
Column lock	Locked
In	Front SS Inlet He
Out	MSD
(Initial)	-20 °C
Pressure	17.425 psi
Flow	1.5 mL/min
Average Velocity	30.353 cm/sec
Holdup Time	3.2946 min
Control Mode	Constant Flow
Column Outlet Pressure	0 psi
Detector Evaluation	
Perform Detector Evaluation Test	Off
Signal Selected	No Signal Selected
Checkout Sample	None
MSD Transfer Line	
Temperature	
Setpoint	On
(Initial)	250 °C
Signals	
Signal #1:	
Description	None
Signal #2:	
Description	None
Signal #3:	
Description	None
Signal #4:	
Description	None
Signal #5:	
Description	None
Signal #6:	
Description	None
Signal #7:	
Description	None
Signal #8:	
Description	None

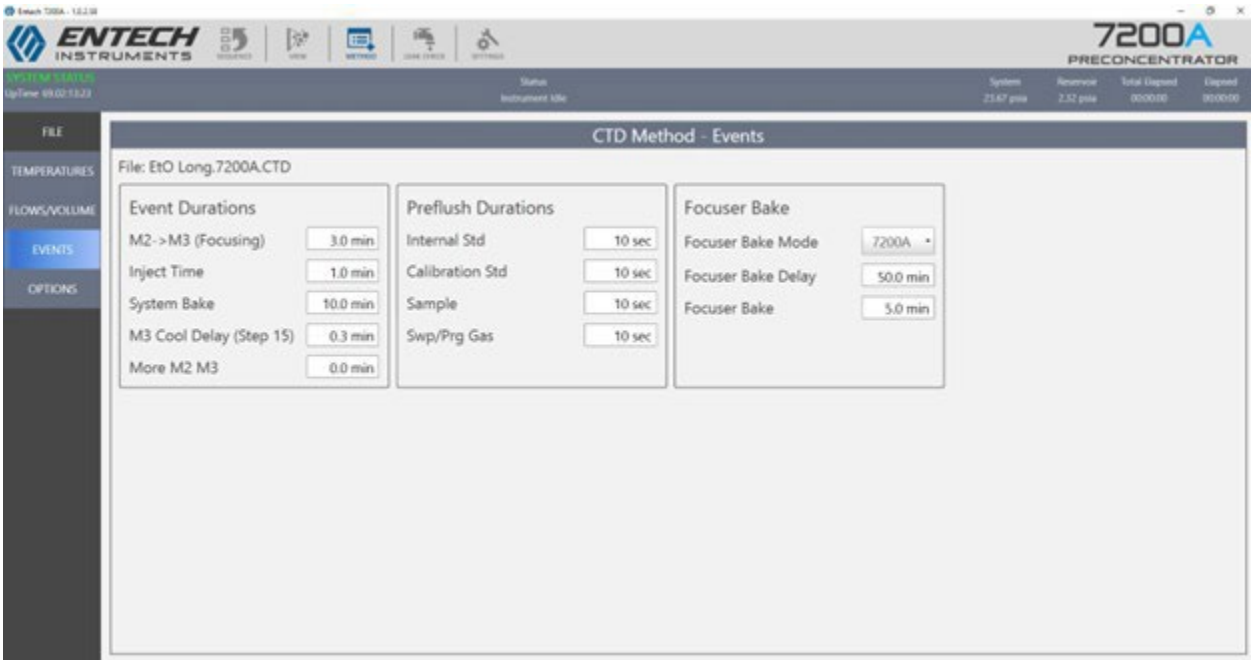
TUNE PARAMETERS for SN: US2124M004

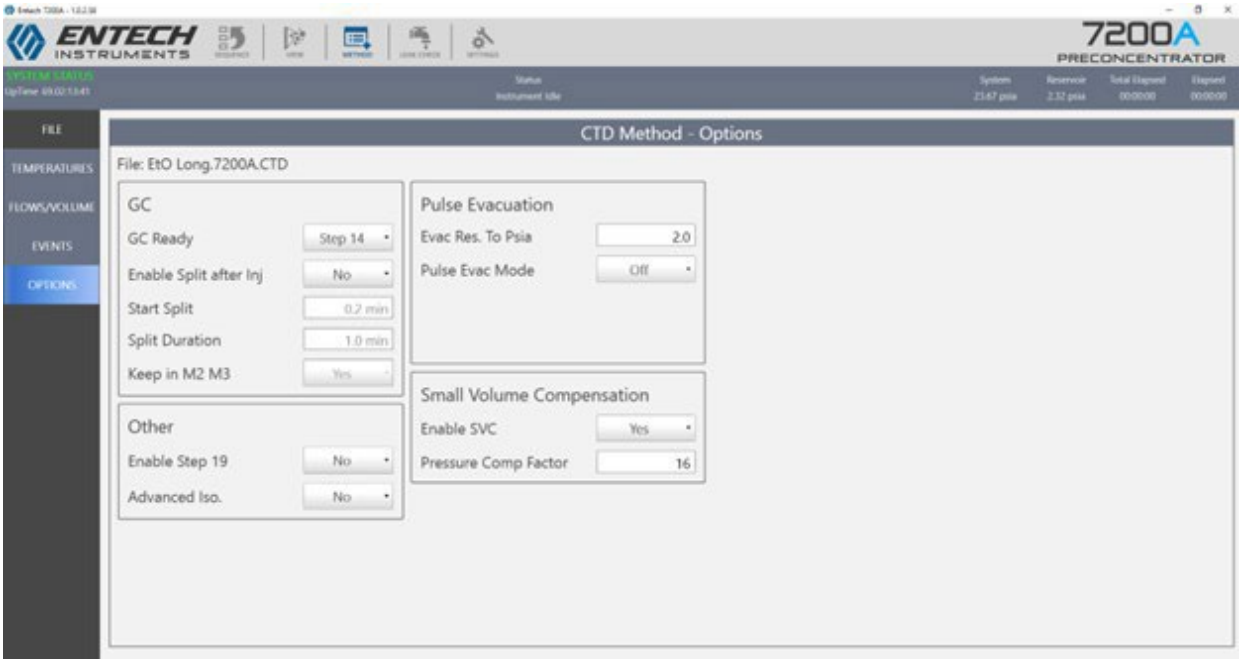
```
Trace Ion Detection is OFF.

   34.593   :   EMISSION
   70.007   :   ENERGY
    1.399   :   REPELLER
   89.822   :   IONFOCUS
   12.582   :   ENTRANCE_LENS
 1557.956   :   EMVOLTS
                          1558   : Actual EMV
                          0.77   : GAIN FACTOR
 2526.000   :   AMUGAIN
  140.250   :   AMUOFFSET
    1.000   :   FILAMENT
    1.000   :   DCPOLARITY
   11.650   :   ENTLENSOFFSET
   10.002   :   Ion_Body
    2.104   :   EXTLENS
   85.000   :  MASSGAIN
  -22.000   :  MASSOFFSET

                END OF TUNE PARAMETERS


            END OF INSTRUMENT CONTROL PARAMETERS
```

Appendix B: Secondary Entech and GC-MS Method Parameters






ENTECH INSTRUMENTS
7200A
PRECONCENTRATOR
FILE
TEMPERATURES
FLOWS/VOLUME
EVENTS
OPTIONS
CTD Method - Events
File: EtO Long.7200A.CTD
Event Durations
M2->M3 (Focusing) 3.0 min
Inject Time 1.0 min
System Bake 10.0 min
M3 Cool Delay (Step 15) 0.3 min
More M2 M3 0.0 min
Preflush Durations
Internal Std 10 sec
Calibration Std 10 sec
Sample 10 sec
Swp/Prg Gas 10 sec
Focuser Bake
Focuser Bake Mode 7200A
Focuser Bake Delay 50.0 min
Focuser Bake 5.0 min


ENTECH INSTRUMENTS
7200A
PRECONCENTRATOR
FILE
TEMPERATURES
FLOWS/VOLUME
EVENTS
OPTIONS
CTD Method - Options
File: EtO Long.7200A.CTD
GC
GC Ready Step 14
Enable Split after Inj No
Start Split 0.2 min
Split Duration 1.0 min
Keep in M2 M3 Yes
Other
Enable Step 19 No
Advanced Iso. No
Pulse Evacuation
Evac Res. To Psia 2.0
Pulse Evac Mode Off
Small Volume Compensation
Enable SVC Yes
Pressure Comp Factor 16

METHOD CONTROL PARAMETERS

Method Information for: D:\MassHunter\GCMS\3\methods\Long EtO.m

Method Sections To Run:

( ) Save Copy of Method With Data
( ) Instrument Control Pre-Run Cmd/Macro =
( ) Data Analysis Pre-Run Cmd/Macro =
(X) Data Acquisition
(X) Data Analysis
( ) Instrument Control Post-Run Cmd/Macro =
( ) Data Analysis Post-Run Cmd/Macro =

Method Comments:
TO15A method

END OF METHOD CONTROL PARAMETERS

Single Quadrupole Acquisition Method - MS Parameters Report

Method file	D:\MassHunter\GCMS\3\methods\Long EtO.m
Tune file	etune.u
Ion source	EI
Source temperature (°C)	300
Quad temperature (°C)	180
Fixed Electron energy (eV)	70.0
Acquisition Type	SIM
Stop time (min)	10.00
Solvent delay (min)	5.00
Trace Ion Detection	False
Gain Factor	10
EM Saver	False
EM Saver Limit	N/A

Scan Time Segments

Time	Start Mass	End Mass	Threshold	Scan Speed

Timed Events

Time	Type of Event	Parameter

Real-Time Plots

Type of Plot	Label	Low Mass	High Mass
Total Ion	N/A	N/A	N/A
Spectrum	N/A	N/A	N/A

Self-Cleaning Ion Source Parameters

Mode	No Cleaning

Single Quadrupole Acquisition Method - MS Parameters Report

SIM Time Segment 1

Group Name	Auto_1		
Start Time	5.00		
Resolution	Low		
Detector EMV Override			

Ion mass-to-charge	Dwell time (ms)	Plot This Ion?	Label
39	25	NO	
50	25	NO	
52	25	NO	
53.1	25	NO	
54.1	25	YES	
62	25	NO	
64	25	NO	
85	25	NO	
87	25	NO	
134.9	25	NO	

Single Quadrupole Acquisition Method - MS Parameters Report

SIM Time Segment 2

Group Name	Auto_2		
Start Time	11.00		
Resolution	Low		
Detector EMV Override			

Ion mass-to-charge	Dwell time (ms)	Plot This Ion?	Label
15	25	YES	
29	25	NO	
30	25	NO	
31	25	NO	
32	25	NO	
41	25	NO	
43	25	NO	
43.9	25	NO	
56	25	NO	
57	25	NO	
60	25	NO	
64	25	NO	
66	25	NO	
93.9	25	NO	
95.9	25	NO	

SIM Time Segment 3

Group Name	Auto_3		
Start Time	15.00		
Resolution	Low		
Detector EMV Override			

Ion mass-to-charge	Dwell time (ms)	Plot This Ion?	Label
61	25	NO	
96	25	NO	
100.9	25	NO	
102.9	25	NO	
150.9	25	NO	

Single Quadrupole Acquisition Method - MS Parameters Report

SIM Time Segment 4

Group Name	Auto_4		
Start Time	21.00		
Resolution	Low		
Detector EMV Override			

Ion mass-to-charge	Dwell time (ms)	Plot This Ion?	Label
41.1	25	NO	
52	25	NO	
53	25	NO	
63	25	NO	
65	25	NO	
76	25	NO	
83.9	25	NO	
85.9	25	NO	

SIM Time Segment 5

Group Name	Auto_5		
Start Time	27.00		
Resolution	Low		
Detector EMV Override			

Ion mass-to-charge	Dwell time (ms)	Plot This Ion?	Label
49	25	NO	
61	25	YES	
62	25	NO	
64	25	NO	
78.1	25	NO	
79.1	25	NO	
83	25	NO	
85	25	NO	
95.9	25	NO	
96.9	25	NO	
98.9	25	NO	
116.9	25	NO	
118.9	25	NO	
129.9	25	NO	

Single Quadrupole Acquisition Method - MS Parameters Report

SIM Time Segment 6

Group Name	Auto_6		
Start Time	33.00		
Resolution	Low		
Detector EMV Override			

Ion mass-to-charge	Dwell time (ms)	Plot This Ion?	Label
63	25	NO	
76	25	NO	
114	25	YES	
115	25	NO	
129.9	25	NO	
131.9	25	NO	

SIM Time Segment 7

Group Name	Auto_7		
Start Time	37.00		
Resolution	Low		
Detector EMV Override			

Ion mass-to-charge	Dwell time (ms)	Plot This Ion?	Label
75	25	NO	
82.9	25	NO	
91.1	25	NO	
92.1	25	NO	
96.9	25	YES	
109.9	25	NO	
128.9	25	YES	
165.9	25	YES	

Single Quadrupole Acquisition Method - MS Parameters Report

SIM Time Segment 8

Group Name	Auto_8		
Start Time	42.00		
Resolution	Low		
Detector EMV Override			

Ion mass-to-charge	Dwell time (ms)	Plot This Ion?	Label
77	25	NO	
82.1	25	NO	
91.1	25	NO	
106.1	25	NO	
106.9	25	NO	
108.9	25	NO	
112	25	NO	
117	25	NO	

SIM Time Segment 9

Group Name	Auto_9		
Start Time	46.00		
Resolution	Low		
Detector EMV Override			

Ion mass-to-charge	Dwell time (ms)	Plot This Ion?	Label
78.1	25	NO	
82.9	25	NO	
84.9	25	NO	
91.1	25	NO	
95	25	NO	
104.1	25	NO	
105.1	25	NO	
106.1	25	NO	
120.1	25	NO	
173.9	25	NO	

Single Quadrupole Acquisition Method - MS Parameters Report

SIM Time Segment 10

Group Name	Auto_10		
Start Time	50.50		
Resolution	Low		
Detector EMV Override			

Ion mass-to-charge	Dwell time (ms)	Plot This Ion?	Label
105.1	25	NO	
120.1	25	NO	
146	25	NO	
148	25	NO	

SIM Time Segment 11

Group Name	Auto_11		
Start Time	53.00		
Resolution	Low		
Detector EMV Override			

Ion mass-to-charge	Dwell time (ms)	Plot This Ion?	Label
179.9	25	NO	
181.9	25	NO	
224.9	25	NO	
226.9	25	NO	

INSTRUMENT CONTROL PARAMETERS: Baby Yoda 2

D:\MassHunter\GCMS\3\methods\Long EtO.m
Fri Jun 30 12:06:11 2023

Control Information

Sample Inlet	: GC
Injection Source	: Manual
Mass Spectrometer	: Enabled

No Sample Prep method has been assigned to this method.

GC
GC Summary

Run Time	55.662 min
Post Run Time	6 min

Oven

Temperature	
Setpoint	On
(Initial)	-20 °C
Hold Time	2 min
Post Run	180 °C
Program	
#1 Rate	3 °C/min
#1 Value	69 °C
#1 Hold Time	0 min
#2 Rate	4 °C/min
#2 Value	141 °C
#2 Hold Time	0 min
#3 Rate	40 °C/min
#3 Value	240 °C
#3 Hold Time	3.52 min
Equilibration Time	2 min
Max Temperature	320 °C
Maximum Temperature Override	Disabled
Slow Fan	Disabled
Cryo	On
Cryo Type	N2
Quick Cool	Off
Ambient Temperature	50 °C
Timeout Detection	On 60 min
Fault Detection	Off

Front SS Inlet He

Mode	Splitless
Heater	On 150 °C
Pressure	On 17.425 psi
Total Flow	On 34.5 mL/min
Septum Purge Flow	On 3 mL/min
Septum Purge Flow Mode	Standard
Pre-Run Flow Test	Off
Gas Saver	Off
Purge Flow to Split Vent	30 mL/min at 999 min
Liner	A Liner has not been selected.

Column

Column #1	
Flow	
Setpoint	On
(Initial)	1.5 mL/min
Post Run	1.5 mL/min
Column Information	Agilent 13869: 1649780
Description	DB-624
Temperature Range	-60 °C-320 °C (320 °C)
Dimensions	60 m x 250 µm x 1.4 µm (Uncalibrated)
Column lock	Locked
In	Front SS Inlet He
Out	MSD
(Initial)	-20 °C
Pressure	17.425 psi
Flow	1.5 mL/min
Average Velocity	30.353 cm/sec
Holdup Time	3.2946 min
Control Mode	Constant Flow
Column Outlet Pressure	0 psi
Detector Evaluation	
Perform Detector Evaluation Test	Off
Signal Selected	No Signal Selected
Checkout Sample	None
MSD Transfer Line	
Temperature	
Setpoint	On
(Initial)	250 °C
Signals	
Signal #1:	
Description	None
Signal #2:	
Description	None
Signal #3:	
Description	None
Signal #4:	
Description	None
Signal #5:	
Description	None
Signal #6:	
Description	None
Signal #7:	
Description	None
Signal #8:	
Description	None

TUNE PARAMETERS for SN: US2124M004

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Trace Ion Detection is OFF.

   34.593   :   EMISSION
   70.007   :   ENERGY
    1.399   :   REPELLER
   89.822   :   IONFOCUS
   12.582   :   ENTRANCE_LENS
 1557.956   :   EMVOLTS
                          1558   : Actual EMV
                          0.77   : GAIN FACTOR
 2526.000   :   AMUGAIN
  140.250   :   AMUOFFSET
    1.000   :   FILAMENT
    1.000   :   DCPOLARITY
   11.650   :   ENTLENSOFFSET
   10.002   :   Ion_Body
    2.104   :   EXTLENS
   85.000   :  MASSGAIN
  -22.000   :  MASSOFFSET

                    END OF TUNE PARAMETERS
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                  END OF INSTRUMENT CONTROL PARAMETERS
                  ------------------------------------
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Appendix C: Suggested GC Column Conditioning Parameters

1. Conduct initial column flush for 40 min with a constant flow of helium (1–2 ml/min) and an oven temperature of 35 °C. Check outlet of column in small beaker of methanol to ensure bubbles of helium are observed.
2. Follow the column conditioning method below ("pulsing" methodology, courtesy of Lee Marotta of PerkinElmer) for two cycles:

	˚C/min	˚C	Hold (min)
Initial	--	70.00	0.00
Ramp 1	5.00	320*	17.5
Ramp 2	50.00	100	0.0
Ramp 3	5.00	320	17.5
Ramp 4	50.00	100	0.00
Ramp 5	5.00	320	17.5
Ramp 6	50.00	100	0.00
Post			209

*Do not exceed column maximum operating temperature; a general rule of thumb is to set at 10–20 ˚C above highest oven program temperature that will be used or to the column maximum – whichever is lower. Currently, we are setting the highest temperature in the above table to 280 ˚C since the oven temperature program high temperature is 240 ˚C.

Note: The column conditioning procedure and associated notes are documented in laboratory notebook number 318 on pages 80–81 and 84–90.

Helpful references:

Agilent 5977B Series MSD Operating Manual, part number G7077-90034, p. 41. 2019. Agilent Technologies, Inc., 5301 Stevens Creek Boulevard, Santa Clara, CA 95051.

https://www.restek.com/en/technical-literature-library/articles/restek-capillary-column-installation-guide/ (accessed July 5, 2023)

https://www.restek.com/en/technical-literature-library/articles/how-to-condition-a-new-capillary-GC-column/ (accessed July 5, 2023)

Appendix D: Entech 7200A Preconcentrator and Agilent 8890/5977B GC-MSD Canister Analysis Setup Sheet

Date: _____ Operator: _____ Calibration: _____
Entech Seq: _____ Entech Method: _____
Agilent Seq: _____ Agilent Method: _____

Entech 7200A Inlet Setup				
Name/Type	Inlet	Canister No.	Date	Initial Pressure
	2			
	3			

Int Std: _____ Int Std Can # _____ Int Std Date: _____ Int Std Pressure: _____
Cal Std: _____ Cal Std Can # _____ Cal Std Date: _____ Cal Std Pressure: _____

7016D Canister Autosampler					
Can No.	Port	Sample ID	Ambient Air Pressure (psia)	Canister Pressure (psia)	Psid
	1				
	2				
	3				
	4				
	5				
	6				
	7				
	8				
	9				
	10				
	11				
	12				
	13				
	14				
	15				
	16				

Flush Complete: _____ Yes _____ No
Gases (LN_2, Helium [Research Grade] and UHP N_2): _____ Yes _____ No
Entech Bakeout: _____ Yes _____ No
Air/H_20 Check (GC-MS Oven 110 °C):
69 amu: ____
28 amu: ____
18 amu: ____
Comments: _____