CALIFORNIA AIR RESOURCES BOARD

Standard Operating Procedure for the Determination of Compounds in Aerosol Coating Consumer Products Using Gas Chromatography

SAS 15
Revision 0.0

Northern Laboratory Branch
Monitoring and Laboratory Division

Approval Signatures	Approval Date
Manisha Singh, Ph.D., Chief Quality Management Branch	8/5/19
Michael Werst, Chief Northern Laboratory Branch	8/5/19

Disclaimer: Mention of any trade name or commercial product in this standard operating procedure does not constitute endorsement or recommendation of this product by the California Air Resources Board. Specific brand names and instrument descriptions listed in the standard operating procedure are for equipment used by the California Air Resources Board's laboratory. Any functionally equivalent instrumentation is acceptable.

Table of Contents

Standard Operating Procedure for the Determination of Compounds in Aerosol Coating Products Using Gas Chromatography

1 Introduction

This standard operating procedure (SOP) is used for the measurement of target compounds in the non-propellant portion of an aerosol coating product and/or a non-aerosol consumer product or the non-propellant portion of an aerosol consumer product. This SOP follows Method 310 as required by the Consumer Products Regulations. This SOP is based on U.S. EPA Method 8260B and ASTM D6730-01.

2 Summary of Method

The samples of aerosol coatings and other consumer products are prepared as a dilution in 1-Methoxy-2-propanol (MPA) or Methanol for Gas Chromatography analysis. Sample dilutions are analyzed on a gas chromatograph equipped with a flame ionization detector for the determination of acetate, ketone, glycol, alcohol compounds. Results are generated in mg/mL, and subsequently converted and reported as weight fraction of the compound in the product. This SOP also describes the process for analyzing hydrocarbons from an undiluted sample aliquot on a GC equipped with a flame ionization detector and mass spectrometer (MS). Hydrocarbon results are generated as a percent fraction of the total liquid sample and converted and reported as weight fraction of the compound in the product.

3 Acronyms and Definitions

Acronym or Term	Definition
ACS Grade	Chemicals meeting standards set by the American Chemical Society.
aliquot	A representative portion of a non-aerosol sample or the non-propellant portion of an aerosol sample.
analytical batch	A set of samples analyzed together as a group for a particular analysis.
CARB	California Air Resources Board
°C	Degrees Celsius
DHA	Detailed Hydrocarbon Analysis
duplicate	A second analysis of a sample submitted for analysis under Method 310.
duplicate aliquot	An additional sample aliquot from the same sample carried through all steps of the sampling and analytical procedures of Method 310 in an identical manner.
EI	Electron Ionization

eV	Electron Volt
FID	Flame Ionization Detector used in gas chromatography
g	Gram
GC	Gas Chromatograph
GC/FID	Gas Chromatograph with Flame Ionization Detector
GC/MS	Gas Chromatograph with Mass Spectrometer
Hz	Hertz
ID	Identification
LIMS	Laboratory Information Management System
LIMS Manual	Consumer Products Database Special Analysis Section (Oracle Database and Applications Manual for LIMS)
µl	Microliter
µm	Micrometer
mg	Milligram
min	Minutes
mL	Milliliter
MPA	1-Methoxy-2-propanol
MS	Mass Spectrometer
NLB	Northern Laboratory Branch
psi	Pounds per square inch
QC	Quality Control
QCM	Quality Control Manual
sample	The sample submitted for analysis under Method 310.
sample aliquot	The sample aliquot is any aliquot used for analysis, and includes the duplicate aliquot, the Batch Sample, or any archive aliquot undergoing a re-test.
sample batch	A set of samples analyzed together under Method 310.
sample dilution	Dilution made from the sample aliquot.
solvent blank	A sample consisting of the reagent used in the sample dilutions without the target compound(s) analyzed to determine interferences or contamination during analysis
SOP	Standard Operating Procedure
VOC	Volatile Organic Compound(s)

4 Interferences

The potential for retention time overlap during analysis occurs as the number of compounds identified increases. The compounds identified are analyzed separately by their functional group to avoid retention time overlap. The identity of compounds are confirmed through GC/MS analysis.

5 Personnel Qualifications

5.1 Prior to performing this method, new personnel must be trained by staff with expert knowledge of this method. Personnel must be trained to understand the program's

requirements per any applicable State and federal regulations and guidance, and this SOP. Personnel will also be trained on how to safely and properly operate the equipment needed to perform the method, the quality assurance components, and LIMS functionality pertaining to the program.

5.2 Personnel should provide an initial demonstration of capability prior to performing this method on real-world samples (i.e., data for record).

5.3 Training will be documented and maintained by the laboratory supervisor.

6 Safety Requirements

6.1 All personnel must follow the general health and safety requirements found in NLB's Chemical Hygiene Plan located in Room 124 in the Safety Data Sheet cabinet.

6.2 Analysts should acknowledge any sample labeling for safety warnings, and take appropriate safety measures.

6.3 Ensure engineering controls are in place and operating (i.e., adequate ventilation).

6.4 Use cryogenic gloves when opening and closing the liquid nitrogen tank valve.

7 Hazardous Waste

7.1 Used GC vials are to be discarded in the satellite hazardous waste accumulation area in the "Consumer Products GC Vial Waste" container, and disposed of in accordance with NLB's Chemical Hygiene Plan.

7.2 Sample aliquots and sample dilutions are to be disposed of in the consumer products waste container in the satellite hazardous waste accumulation area once analysis under Method 310 is complete. (SOP SAS14)

8 Equipment, Supplies, and Chemicals

NOTE: Section 10 details the chemicals used for hydrocarbon analysis

8.1 Gas Chromatograph (GC) configured with a Flame Ionization Detector (FID) and autosampler (Section 9)

8.2 GC configured with a FID, Mass Spectrometer (MS), cryogenic valve, and autosampler (Section 10)

8.3 System Computer for GC and GC/MS equipment

8.4 Software for data acquisition and data analysis (e.g., Agilent ChemStation, Hydrocarbon Expert)

8.5 GC column, Capillary, 30.0 m length, 248 µm diameter, 1.00 µm nominal film thickness, DB-1701 or equivalent (Section 9, analysis of Acetates and ortho-Cresol)

8.6 GC column, Stabilwax Capillary, 30.0 m length, 530 µm diameter, 1.00 µm nominal film thickness, or equivalent (Section 9, analysis of Ketones and Glycols)

8.7 GC column, Custom DHA Capillary, 102 m length, 250 µm diameter, 0.5 µm nominal film thickness, or equivalent (Section 10)

8.8 Top-Loader Balance, capacity of at least 1000g x 0.001g readability

8.9 Software for data collection (e.g., Excel)

8.10 Laboratory Information Management System (LIMS)

8.11 Centrifuge

8.12 Laboratory vented enclosure

8.13 Standards Refrigerator(s)

8.14 Volumetric Flasks, 10mL, 250mL

8.15 Pipettors, ranging 125µL - 5000µL with tips

8.16 Pasteur pipettes, disposable with bulbs

8.17 Transfer pipettes, disposable

8.18 8mL screw top vials with cap

8.19 2 mL autosampler vials with caps

8.20 Autosampler vial cap crimper

8.21 Autosampler vial cap decrimper

8.22 Reagents and Samples

8.22.1 1-Methoxy-2-Propanol (MPA), 99+%

8.22.2 Methanol, ACS grade or better

8.22.3 Helium, ACS grade or better

8.22.4 Air, compressed, ultra-high purity

8.22.5 Nitrogen, compressed, ultra-high purity

8.22.6 Hydrogen Generator, capable of 100 psi output

8.22.7 Nitrogen, Refrigerated Liquid, 99.99+%

8.22.8 Calibration Standards

8.22.8.1 Acetate calibration stock made at an 80 mg/ml concentration containing the following compounds in 1-Methoxy-2-propanol (MPA):

8.22.8.1.1 Methyl Acetate, ACS Grade or better

8.22.8.1.2 Ethyl Acetate, ACS Grade or better

8.22.8.1.3 Isopropyl Acetate, ACS Grade or better

8.22.8.1.4 tert-Butyl Acetate, ACS Grade or better

8.22.8.1.5 Isobutyl Acetate, ACS Grade or better

8.22.8.1.6 Butyl Acetate, ACS Grade or better

8.22.8.1.7 PM Acetate, ACS Grade or better

8.22.8.1.8 Isobutyl Isobutyrate, ACS Grade or better

8.22.8.1.9 Ethyl-3-ethoxypropionate, ACS Grade or better

8.22.8.1.10 Hexyl Acetate, ACS Grade or better

8.22.8.2 Ketone calibration stock made at an 80 mg/ml concentration containing the following compounds in MPA:

8.22.8.2.1 Acetone, ACS Grade or better

8.22.8.2.2 Methyl Ethyl Ketone, ACS Grade or better

8.22.8.2.3 2-Pentanone, ACS Grade or better

8.22.8.2.4 Methyl Isobutyl Ketone, ACS Grade or better

8.22.8.2.5 1-Butanol, ACS Grade or better

8.22.8.2.6 Cyclohexanone, ACS Grade or better

8.22.8.3 Glycol calibration stock made at an 80 mg/ml concentration containing the following compounds in MPA:

8.22.8.3.1 Propylene Glycol n-Propyl Ether, ACS Grade or better

8.22.8.3.2 Ethylene Glycol n-Propyl Ether, ACS Grade or better

8.22.8.3.3 Propylene Glycol n-Butyl Ether, ACS Grade or better

8.22.8.3.4 Dipropylene Glycol Methyl Ether, ACS Grade or better

8.22.8.3.5 Propylene Glycol, ACS Grade or better

8.22.8.3.6 Carbitol, ACS Grade or better

8.22.8.3.7 Ethylene Glycol, ACS Grade or better

8.22.8.3.8 Butyl Carbitol, ACS Grade or better

8.22.8.3.9 Dipropylene Glycol, ACS Grade or better

8.22.8.3.10 Propylene Carbonate, ACS Grade or better

8.22.8.3.11 Diethylene Glycol, ACS Grade or better

8.22.8.4 ortho-Cresol calibration stock made at an 80 mg/ml concentration containing the following in Methanol:

8.22.8.4.1 ortho-Cresol, ACS Grade or better

8.22.8.5 Calibration standards may be prepared from the reagents listed above or purchased as certified solutions.

8.22.8.6 Prepare a sufficient volume of calibration stock for use in multiple analytical batches. For example, weigh 16 grams of each compound in a 200 mL volumetric flask and bring to volume with appropriate solvent as required for the analysis. Mix by inversion. Concentration is in mg/mL.

8.22.8.7 Fill 20 mL screw top vials with the calibration stock and cap.

8.22.8.8 Label each vial with “(Analysis Method) Calibration Stock 80 mg/mL”, preparation date, expiration date, and the preparer’s initials. i.e. “Acetate Calibration Stock 80 mg/mL”.

8.22.8.8.1 Store the Calibration Stock aliquots under refrigeration between 0 and 10 °C.

8.22.8.9 Pipette the calibration stock into 10mL volumetric flasks as follows:

Volume of calibration stock	Calibration Standard Concentration
12.5 µL	0.1 mg/ml
125 µL	1 mg/mL
1250 µL	10 mg/mL
2500 µL	20 mg/mL
5000 µL	40 mg/mL

8.22.8.10 Bring to volume with MPA or Methanol as required per analytical method and store the individual calibration standards in an appropriately labeled 2 mL autosampler and 8 mL vials.

8.22.8.11 Fill a 2 mL autosampler vial and an 8 mL vial with the 80 mg/ml calibration stock as the sixth calibration standard.

8.22.9 Control/Check Standard Stock

8.22.9.1 Acetate control/check stock is a 25% solution of Methyl Acetate in MPA

8.22.9.2 Ketone control/check stock is a 25% solution of Acetone in MPA

8.22.9.3 Glycol control/check stock is a 25% solution of Propylene Glycol in MPA

8.22.9.4 ortho-Cresol control/check stock is a 25% solution of ortho-Cresol in Methanol

8.22.9.5 Control/Check standard stock may be prepared from reagents or purchased as certified solutions. Prepare or procure a sufficient volume of control/check standards to use in several analyses. Store control/check standards in the standards refrigerator at a temperature between 0 and 10 °C.

8.22.10 Hydrocarbon Reference Standard (Section 10)

8.22.11 Hydrocarbon Control/Check Standard (Section 10)

8.22.12 Sample aliquots prepared using SOP SAS14

8.22.13 Sample dilutions prepared using SOP SAS14

8.22.14 Solvent blank prepared using SOP SAS14

9 Procedure for the analysis of Acetates, Ketones, Glycols and ortho-Cresol

Note: Section 10 details the procedure of the analysis of hydrocarbons.

9.1 Instrument preparation

9.1.1 Verify Helium and Air cylinder pressures are above 500 psi. Replace cylinder(s) as necessary prior to analysis.

9.1.2 Verify the water in hydrogen generator reservoir is above the refill level. Add more deionized water to the reservoir as necessary prior to analysis.

9.1.3 Prepare the autosampler: Fill solvent rinse vials with appropriate solvent required for the analysis and ensure that the rinse waste vials are empty.

9.1.4 Load the method and verify the conditions in the GC software as specified in for each analytical method:

9.1.4.1 For the ACETATE method:

Initial Oven Temperature	40°C
Initial Time	10.00 min
Ramps	1: 10°/minute to 120° C
	2: 5°/minute to 140° C
	3: 15°/minute to 220° C, hold 1 minute
Final Temperature	220°C
Final Time	6.15 min
Injector Temperature	250°C
Detector Temperature	250°C
Hydrogen Flow	35.0 ml/min
Air Flow	350.0 ml/min
Makeup Flow	25.0 ml/min
Data Rate	20.00 Hz
Peak Width	0.09 min
Column Flow Rate	3.2 mL/min
Column Mode	constant flow

9.1.4.2 For the KETONE method:

Initial Oven Temperature	40°C
Initial Time	15.00 min
Ramps	1: 4°/minute to 60° C
	2: 20°/minute to 220° C, hold 1 minute
Final Temperature	220°C
Injector Temperature	250°C
Detector Temperature	250°C
Hydrogen Flow	30.0 ml/min
Air Flow	400.0 ml/min
Makeup Flow	25.0 ml/min
Data Rate	50.00 Hz
Peak Width	0.09 min
Column Flow Rate	6.0 mL/min
Column Mode	constant flow

9.1.4.3 For the MULTI GLYCOL method:

Initial Oven Temperature	80°C
Initial Time	2.00 min
Ramps	1: 4°/minute to 116° C, hold 3 minutes
	2: 5°/minute to 172° C
	3: 30°/minute to 240° C, hold 2 minutes
Final Temperature	240°C
Injector Temperature	245°C
Detector Temperature	245°C
Hydrogen Flow	35.0 ml/min
Air Flow	400.0 ml/min
Makeup Flow	25.0 ml/min
Data Rate	50.00 Hz
Peak Width	0.09 min
Column Flow Rate	6.9 mL/min
Column Mode	constant flow

9.1.4.4 For the OCRESOL method:

Initial Oven Temperature	40°C
Initial Time	10.00 min
Ramps	1: 10/minute to 120° C
	2: 5°/minute to 140° C
	3: 15°/minute to 220° C, hold 1 minute
Final Temperature	220°C
Injector Temperature	250°C
Detector Temperature	250°C
Hydrogen Flow	35.0 ml/min
Air Flow	350.0 ml/min
Makeup Flow	25.0 ml/min
Data Rate	20.00 Hz
Peak Width	0.09 min
Column Flow Rate	3.2 mL/min
Column Mode	constant flow

9.1.5 To edit an existing sequence, load the sequence you want to use

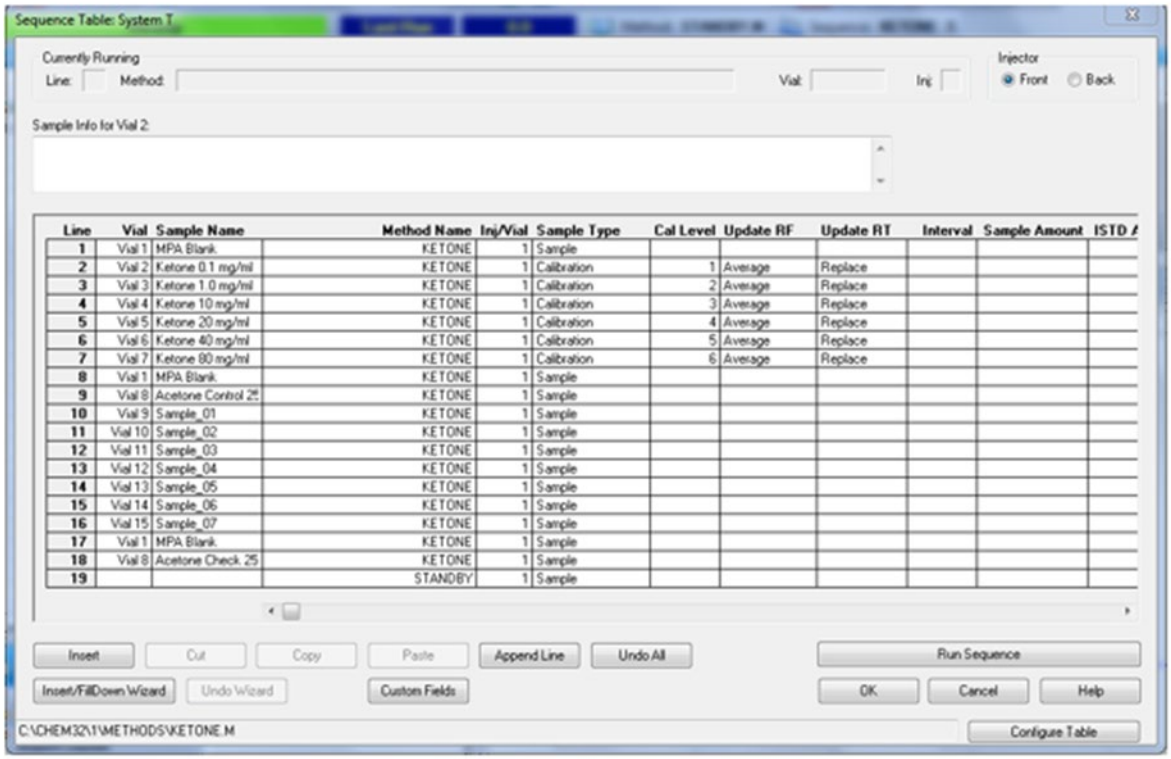
9.1.5.1 Edit Parameters

9.1.5.2 Enter your initials and the subdirectory for the data by editing the Sequence Parameters. The naming convention used for the subdirectory is month, day, year of analysis (e.g., MMDDYY).

9.1.5.3 A message “The directory or Subdirectory does not exist, do you want to create it?” should appear. Click on the Yes button. If the message does not appear, the directory already exists and will need to be modified. A letter or initials can be added to an existing subdirectory to uniquely identify samples analyzed on the same day.

9.1.5.4 Edit the Sequence table. See Figure 1 for representative sequence table.

Figure 1



Line	Vial	Sample Name	Method Name	Inj/Vial	Sample Type	Cal Level	Update RF	Update RT	Interval	Sample Amount	ISTD A
1	Vial 1	MPA Blank	KETONE	1	Sample						
2	Vial 2	Ketone 0.1 mg/ml	KETONE	1	Calibration	1	Average	Replace			
3	Vial 3	Ketone 1.0 mg/ml	KETONE	1	Calibration	2	Average	Replace			
4	Vial 4	Ketone 10 mg/ml	KETONE	1	Calibration	3	Average	Replace			
5	Vial 5	Ketone 20 mg/ml	KETONE	1	Calibration	4	Average	Replace			
6	Vial 6	Ketone 40 mg/ml	KETONE	1	Calibration	5	Average	Replace			
7	Vial 7	Ketone 80 mg/ml	KETONE	1	Calibration	6	Average	Replace			
8	Vial 1	MPA Blank	KETONE	1	Sample						
9	Vial 8	Acetone Control 25	KETONE	1	Sample						
10	Vial 9	Sample_01	KETONE	1	Sample						
11	Vial 10	Sample_02	KETONE	1	Sample						
12	Vial 11	Sample_03	KETONE	1	Sample						
13	Vial 12	Sample_04	KETONE	1	Sample						
14	Vial 13	Sample_05	KETONE	1	Sample						
15	Vial 14	Sample_06	KETONE	1	Sample						
16	Vial 15	Sample_07	KETONE	1	Sample						
17	Vial 1	MPA Blank	KETONE	1	Sample						
18	Vial 8	Acetone Check 25	KETONE	1	Sample						
19			STANDBY	1	Sample						

9.1.5.4.1 The **Vial** column shall have vial numbers corresponding to the position on the autosampler tray. Each vial will have its own vial number. To run the blank and the check multiple times, insert the correct vial number for the location on the autosampler tray (i.e., it is not necessary to prepare a separate vial for each blank and control/check).

9.1.5.4.2 In the **Sample Name** column, enter the samples to be analyzed. The following sequence should be followed with a maximum of ten samples between control and checks, ending with a check:

Blank
Calibration standards
Blank
Control
Sample dilutions
Blank
Check
Repeat sample dilutions, Blank, Check as necessary

9.1.5.4.3 Ensure that the correct method is listed in the **Method Name** for all

analyses. Add an additional line with the method STANDBY at the end of the sequence.

9.1.5.4.4 The **Inj/Vial** column refers to the number of injections and should be "1" for all analyses.

9.1.5.4.5 **Sample Type** is Calibration for the five calibration standards and Sample for all others.

9.1.5.4.6 For the calibration standards, enter the calibration level in the **Cal Level** column leaving all others blank.

9.1.5.4.7 The **Update RF** column should have Replace for the five calibration standards and all others should be blank.

9.1.5.4.8 The **Update RT** column should have Average selected for the calibration standards and blank for all others. All other columns should be blank.

9.1.5.4.9 Click on OK when done and save the sequence.

9.1.5.4.10 Print the sequence by clicking on Sequence and then Print Sequence.

9.2 Analysis Preparation

9.2.1 Prepare the analytical batch for the analysis either using 2 mL autosampler vials prepared in SOP SAS14 or by transferring sample dilutions prepared in SOP SAS14 to new 2 mL autosampler vials and cap.

9.2.2 Transfer Calibration Standards and Control/Check Standards prepared as described in Section 8 to appropriately labeled 2 mL autosampler vials and cap.

9.3 Sample Analysis

9.3.1 Place the vials in the autosampler, matching the vial location in the sequence.

9.3.2 Run the sequence.

9.3.3 The correlation coefficient for compounds present in the calibration must be greater than 0.98. If the calibration fails, corrective action is implemented and can include reanalyzing the calibration curve or making up a new dilution of standards for the calibration curve. Reanalyze the analytical batch after a successful calibration.

9.3.4 Verify that the control/check recoveries are within the control limits posted at or near the instrument. The control limits are also located in the Consumer

Products Reports LIMS application at the Control Limits link. If any of the control/checks are not within the control limits, reanalyze the affected samples. This may require recalibrating the instrument prior to reanalysis.

9.3.5 Evaluate the solvent blanks. If any blank is above 0.1% wt/volume, refer to section 11.1 for blank subtraction.

9.3.6 Print and review the chromatograms and the calibration curve.

9.3.7 Any anomalies occurring during the analysis that affect the data shall be documented, invalidated, and all affected samples shall be reanalyzed. If anomalies continue, invalidate data. Notify management and proceed under their direction.

9.3.8 Any instrument issues or maintenance shall be documented in the instrument logbook to be kept with the instrumentation at all times.

9.3.9 Upload valid data to LIMS (see LIMS Manual: Aerosol Coatings).

9.3.10 After sequence completion, remove 2 mL autosampler vials from the autosampler, and ensure the instrument has the STANDBY method loaded.

10 Procedure for the analysis of Hydrocarbons (Detailed Hydrocarbon Analysis)

10.1 Chemicals required for Detailed Hydrocarbon Analysis (DHA)

10.1.1 Hydrocarbon Reference Standard composed of the following undiluted compounds:

10.1.1.1 n-Pentane, ACS Grade or better

10.1.1.2 Cyclopentane, ACS Grade or better

10.1.1.3 2,2-Dimethylbutane, ACS Grade or better

10.1.1.4 2,3-Dimethylbutane, ACS Grade or better

10.1.1.5 2-Methylpentane, ACS Grade or better

10.1.1.6 3-Methylpentane, ACS Grade or better

10.1.1.7 n-Hexane, ACS Grade or better

10.1.1.8 Methylcyclopentane, ACS Grade or better

10.1.1.9 Cyclohexane, ACS Grade or better

10.1.1.10 2,2,4-Trimethylpentane, ACS Grade or better

10.1.1.11 n-Heptane, ACS Grade or better

10.1.1.12 Methylcyclohexane, ACS Grade or better

10.1.1.13 Toluene, ACS Grade or better

10.1.1.14 Ethylbenzene, ACS Grade or better

10.1.1.15 m-Xylene, ACS Grade or better

10.1.1.16 p-Xylene, ACS Grade or better

10.1.1.17 o-Xylene, ACS Grade or better

10.1.1.18 1,3,5-Trimethylbenzene, ACS Grade or better

10.1.1.19 1,2,4-Trimethylbenzene, ACS Grade or better

10.1.1.20 1,2,3-Trimethylbenzene, ACS Grade or better

10.1.1.21 1,3-Diethylbenzene, ACS Grade or better

10.1.1.22 1,4-Diethylbenzene, ACS Grade or better

10.1.1.23 1,2-Diethylbenzene, ACS Grade or better

10.1.1.24 Naphthalene, ACS Grade or better

10.1.1.25 Reference standards may be prepared from the reagents listed above or purchased as certified solutions.

10.1.1.25.1 Reference Standard is prepared by pipetting 2 mL of each compound into a 50 mL volumetric flask. Record the weight of each compound added to the flask. Mix by inversion.

10.1.1.25.2 Fill 4 mL screw top vials with 2.5 mL each of the reference standard and cap.

10.1.1.25.3 Label each vial with “DHA Reference Standard” and the concentration level, preparation date, expiration date, and the preparer’s initials.

10.1.1.25.4 Store the Reference Standard aliquots under refrigeration between 0 and 10 °C.

10.1.2 Hydrocarbon control/check containing 25% of each of the following undiluted

compounds:

10.1.2.1 n-Hexane, ACS Grade or better

10.1.2.2 Toluene, ACS Grade or better

10.1.2.3 o-Xylene, ACS Grade or better

10.1.2.4 1,3,5-Trimethylbenzene, ACS Grade or better

10.1.2.5 Hydrocarbon Control/Check standard may be prepared from reagents or purchased as certified solutions.

10.1.2.5.1 Control/Check standard is prepared by pipetting 2.5 mL of each compound into a 10 mL volumetric flask. Record the weight of each compound added to the flask. Mix by inversion.

10.1.2.5.2 Fill GC vials equipped with vial inserts with 250 µL each of the control/check standard. Place vials in a GC vial tray. Label the GC vial tray with “DHA Control/Check” and the compound concentration level, preparation date, expiration date, and the preparer’s initials.

10.1.2.5.3 Store the Control/Check aliquots under refrigeration between 0 and 10 °C.

10.2 Instrument Preparation

10.2.1 Verify the conditions in the GC software as specified in the DHA method:

Initial Oven Temperature	5°C
Initial Time	5.00 min
Ramps	1: 7.6°/minute to 45° C, hold 38 minutes
	2: 2.7°/minute to 200° C, hold 0 minutes
Run time	105.67 minutes
Cryo	On
Cryo Use Temperature	5°C
Cryo Timeout Detection	On 5 minutes
Injector Temperature	250°C
Injection	Split
Injection Volume	0.2 µL
Aux EPC H2	On
Aux EPC Setpoint	2.5 psi
Detector Temperature	250°C
Hydrogen Flow	30.0 ml/min
Air Flow	400.0 ml/min
Makeup Flow	25.0 ml/min
Data Rate	20.00 Hz
Peak Width	0.09 min
Column Flow Rate	5.2 mL/min
Column Mode	constant pressure
MS Ion Source	EI
MS Source Temperature	230°C
MS Quad Temperature	70.3 eV
MS Acquisition Type	Scan
MSD Transfer Line	250°C

10.2.2 Verify Air and Nitrogen cylinder pressures are above 500 psi. Replace cylinder(s) as necessary prior to analysis.

10.2.3 Verify the water in hydrogen generator reservoir is full. Analysis requires high volume of Hydrogen carrier gas. Add more deionized water to the reservoir as necessary prior to analysis.

10.2.4 Inspect the liquid Nitrogen cylinder.

10.2.4.1 Check the indicator at the top of the tank to ensure it is ≥ ¼ full.

10.2.4.2 Check that the hose is connected to the correct treaded valve labeled Liquid.

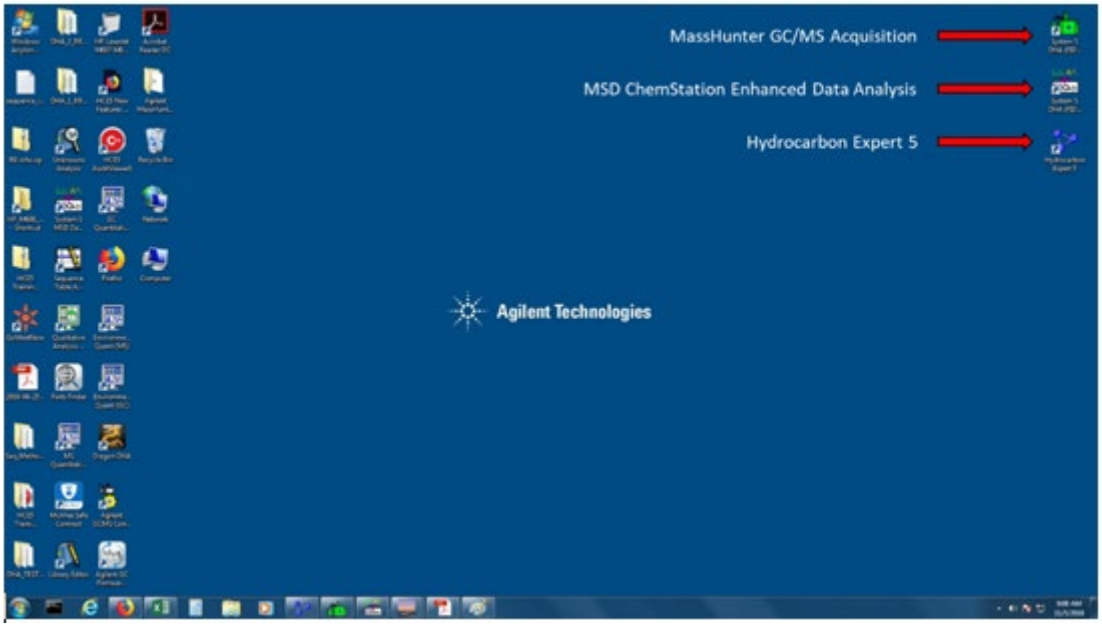
10.2.4.3 Completely open the Liquid valve to allow for cryogenic cooling.

10.2.4.4 Check that the Vent valve is closed.

10.2.5 Prepare the autosampler: Fill two solvent rinse vials each with Acetone and Dichloromethane and ensure that the rinse waste vials are empty.

10.2.6 Open the MassHunter GC/MS Acquisition software as shown in Figure 2.

Figure 2



10.2.7 Load the BAKEOUT method in the GC software to perform an instrument blank.

10.2.7.1 Verify that the oven temperature reaches 300 °C.

10.2.7.2 Run the BAKEOUT method for one hour.

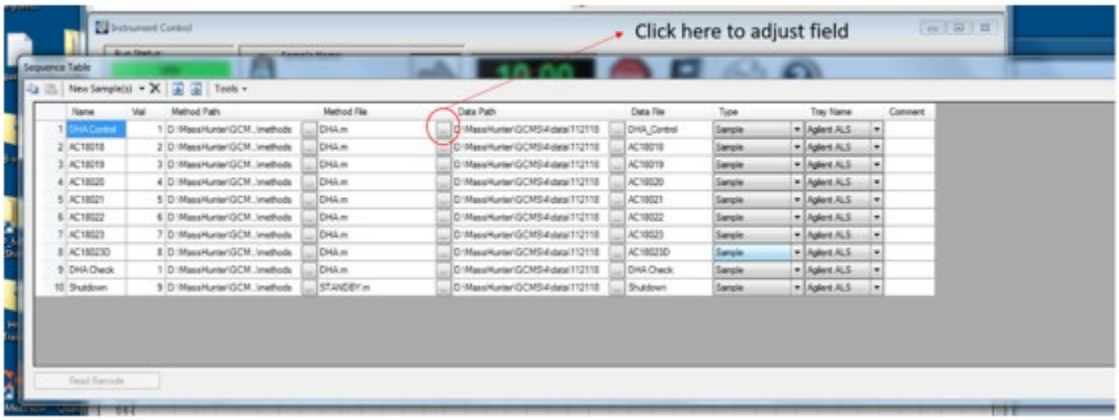
10.2.8 Load the STANDBY method.

10.2.9 Edit a sequence

10.2.9.1 Load the DHA Sequence.

10.2.9.2 Select Edit Sequence from the Sequence menu. The Sequence Table opens as shown in Figure 3.

Figure 3



10.2.9.3 In the **Name** column, enter the samples to be analyzed. The following sequence should be followed with a maximum of ten samples between control and checks, ending with a check:

Reference Sample (only when updating reference file)
DHA Control
Sample aliquots
DHA Check
Repeat sample aliquots and DHA Check as necessary
Shutdown

10.2.9.4 In the **Vial** column, enter the vial number corresponding to the position on the autosampler tray. Each vial will have its own vial number. To run a check multiple times, insert the correct vial number for the location on the autosampler tray.

10.2.9.5 Verify that the correct Method Path and Method File is selected in the **Method Path** column.

10.2.9.6 Ensure DHA is listed in the **Method File** column for all analyses. Verify that the last line in the sequence has the STANDBY method listed.

10.2.9.7 In the **Data Path** column, update the subdirectory. The naming convention for the subdirectory is month, day, year (MMDDYY).

10.2.9.8 Update the names in the **Data File** column to correspond to the sample names in the Name column. Additional DHA Check samples can be distinguished with an “A” after the file name for distinction.

10.2.9.9 Verify that Sample is listed in the **Type** column.

10.2.9.10 Verify that Agilent ALS is listed in the **Tray Name** column.

10.2.9.11 Print sequence by clicking on Tools, then Print.

10.2.9.11.1 Print in landscape orientation to ensure that all columns in the sample table appear on one page.

10.2.9.12 Click OK.

10.2.10 Save sequence by selecting Save Sequence from the Sequence menu.

10.3 Analysis Preparation

10.3.1 Prepare the analytical batch for analysis by transferring sample aliquots prepared in SOP SAS14 into 2 mL autosampler vials and cap.

10.3.1.1 Any pigment present in the sample aliquot must be separated prior to analysis by either allowing the pigments/solids to settle over a period of 3 to 5 days or by placing the aliquots in a centrifuge set to 18,000 revolutions per minute for 20 minutes.

10.3.2 If creating a new Reference Standard file, transfer Reference Standard prepared in section 10.1.1.25 to appropriately labeled 2 mL autosampler vials and cap.

10.3.3 Obtain a DHA Control/Check standard in a 2 mL autosampler vial prepared in section 10.1.2.5.

10.4 Detailed Hydrocarbon Analysis

10.4.1 Place vials in the autosampler, matching the vial location in the sequence.

10.4.2 Verify that the STANDBY method is loaded.

10.4.2.1 The sequence is started with the STANDBY method loaded to ensure the instrument loads the STANDBY method upon sequence completion.

10.4.3 Run the sequence.

10.4.4 Any anomalies occurring during the analysis that affect the data shall be documented and all affected samples shall be reanalyzed.

10.4.5 Any instrument issues or maintenance shall be documented in the instrument logbook.

10.4.6 Review data and print reports using the DHA software Hydrocarbon Expert.

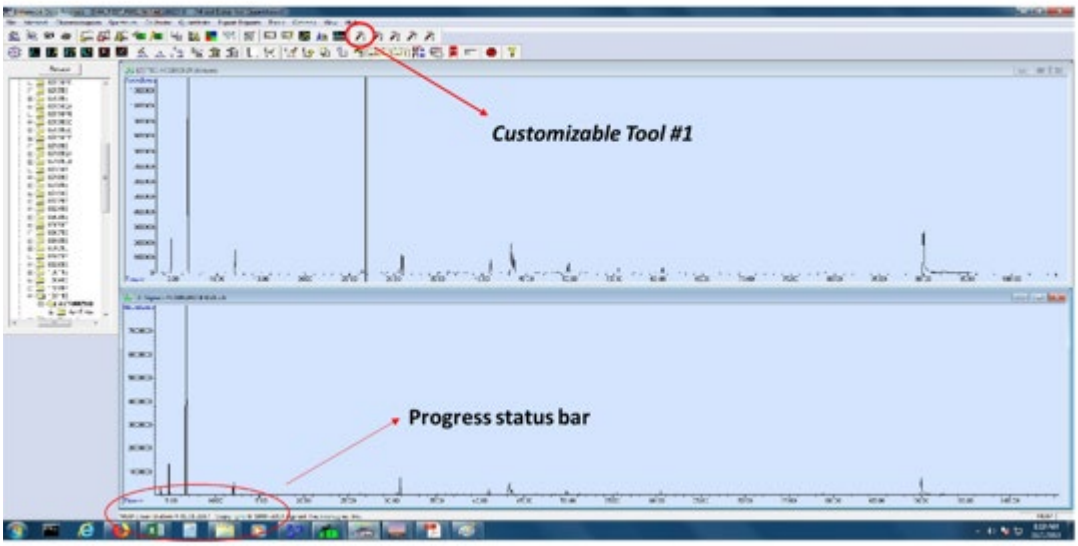
10.4.6.1 Open MSD ChemStation Enhanced Data Analysis Software by double clicking on the System S DHA (FID + MS) icon as shown in Figure 2.

10.4.6.2 Locate the subdirectory folder that contains the data at the following location: **D:\MassHunter\GCMS\4\data**.

10.4.6.3 Load the data file from the appropriate subdirectory.

10.4.6.4 Click once on the Custom Tool #1 as shown in Figure 4.

Figure 4



10.4.6.4.1 The Custom Tool generates a FID.CDF and a MS.CDF files for the Hydrocarbon Expert software to process.

10.4.6.5 Check the progress/status at the bottom left corner of the display window.

10.4.6.5.1 The status will indicate when the sample is ready to be analyzed by the Hydrocarbon Expert software.

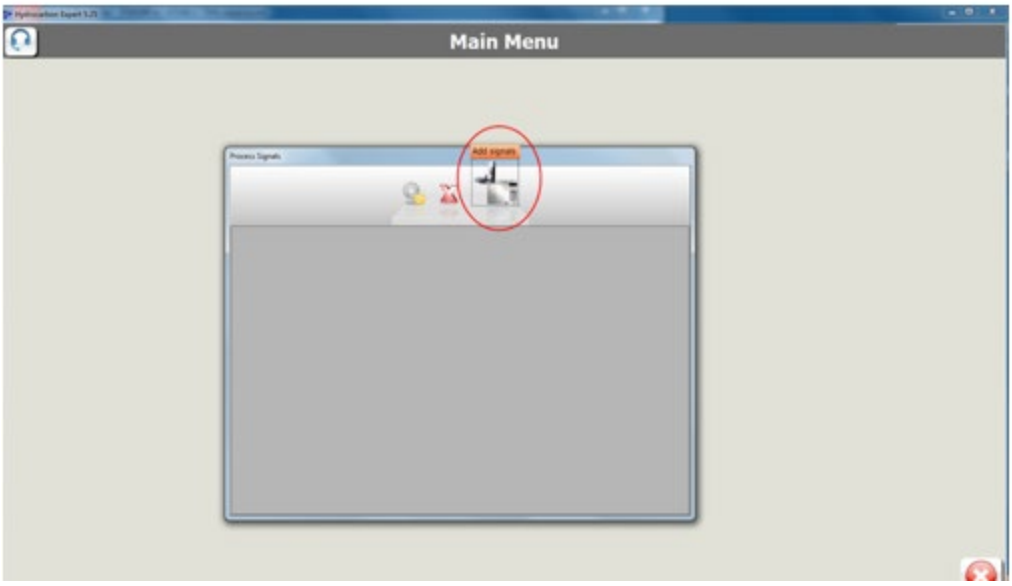
10.4.6.6 Open the Hydrocarbon Expert software from the computer desktop by double clicking on the Hydrocarbon Expert icon (Figure 2).

10.4.6.7 From the Main Menu, click the Analyze Samples window as shown in Figure 5.

Figure 5

10.4.6.8 Within the Process Signals window, click on the Add Signals icon as shown in Figure 6.

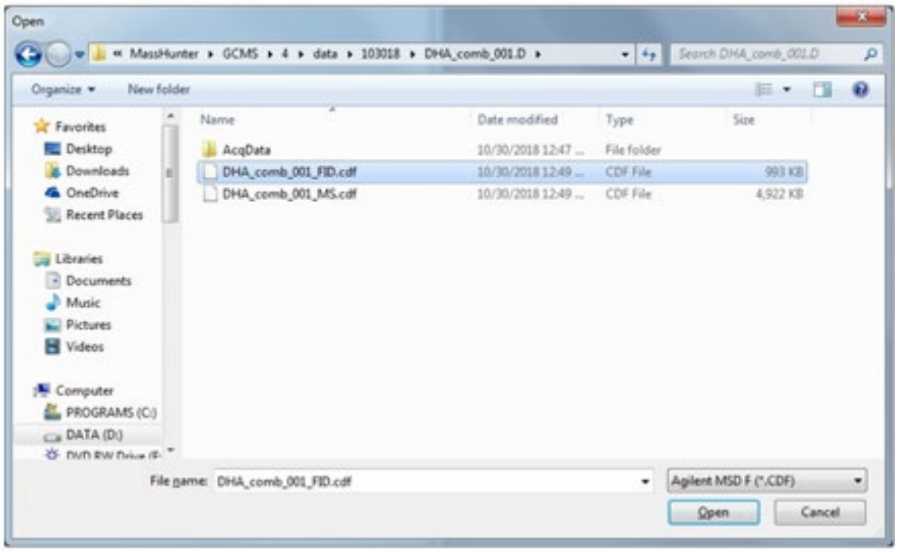
Figure 6



10.4.6.9 The file directory opens. Locate the FID.CDF file(s) created in 10.4.6.4 in the subdirectory sample folder. The directory file path is **D:\MassHunter\GCMS\4\data\MMDDYY**.

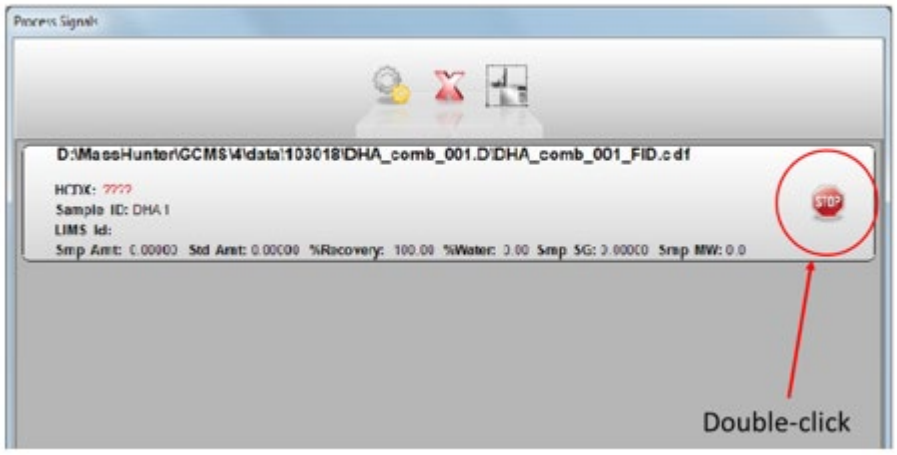
10.4.6.10 Select the appropriate “sample name_FID.CDF” file and click Open as shown in Figure 7.

Figure 7



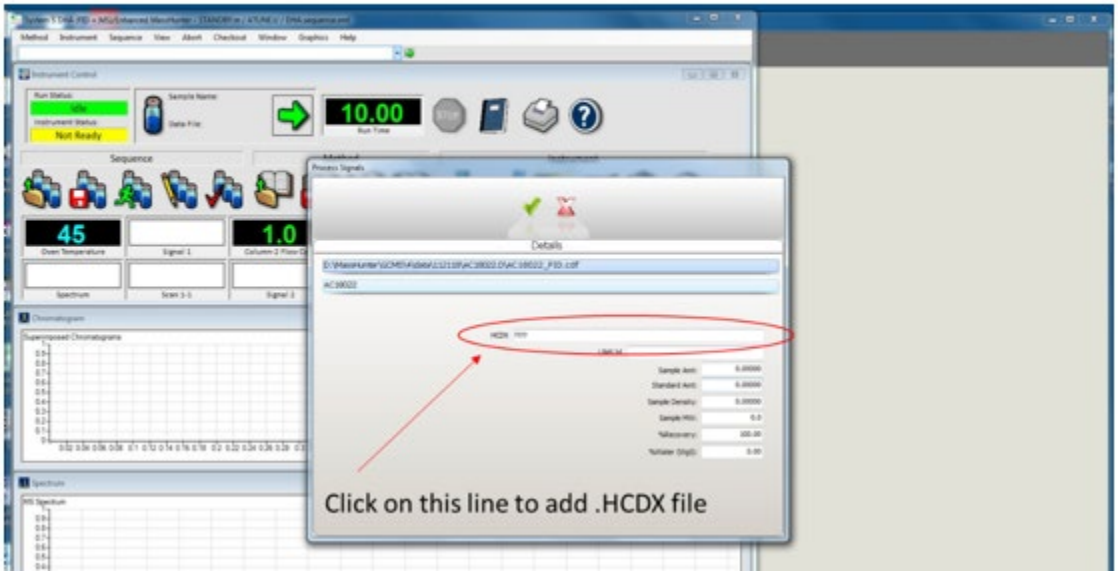
10.4.6.11 Within the Process Signals window, double-click on the added signal box to add the reference chromatogram file for data analysis. See Figure 8.

Figure 8



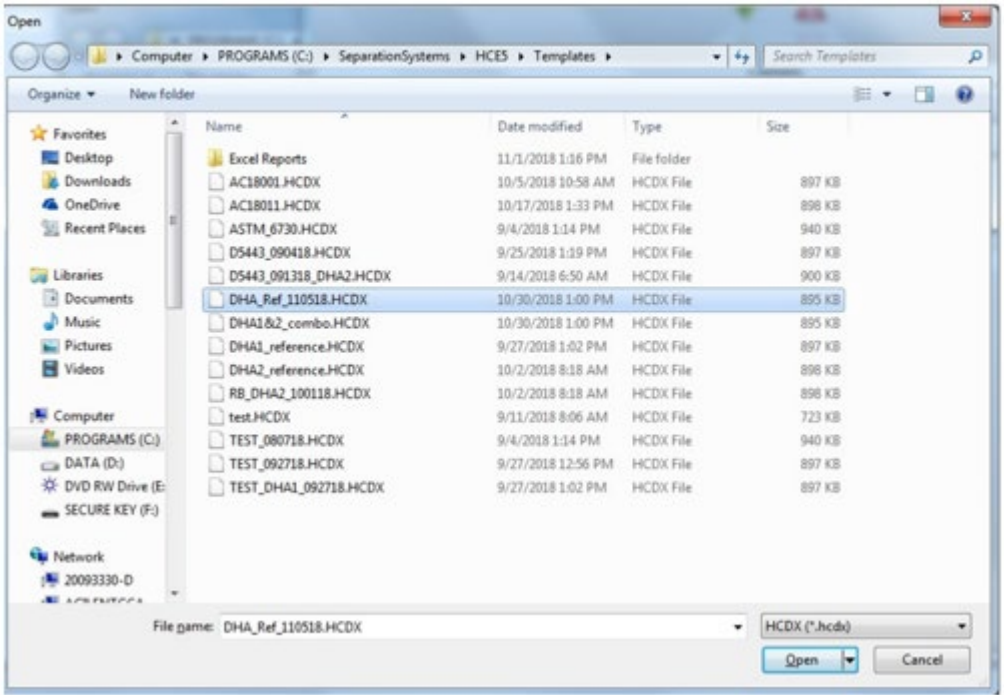
10.4.6.12 The Process Signals Details window opens. Single click on the box that contains the HCDX line followed by "????" as shown in Figure 9.

Figure 9



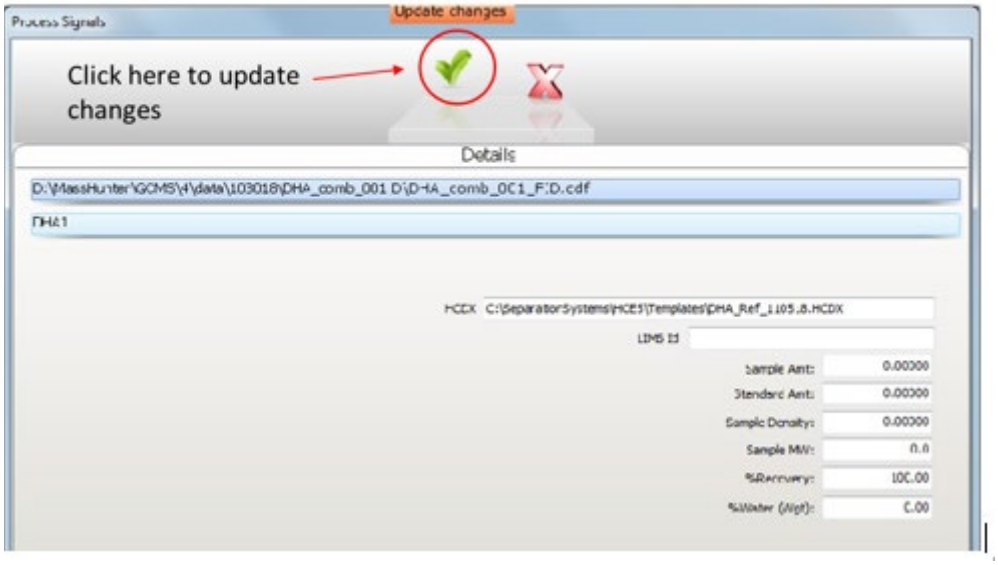
10.4.6.13 Select the appropriate Reference Chromatogram and click Open as shown in Figure 10.

Figure 10



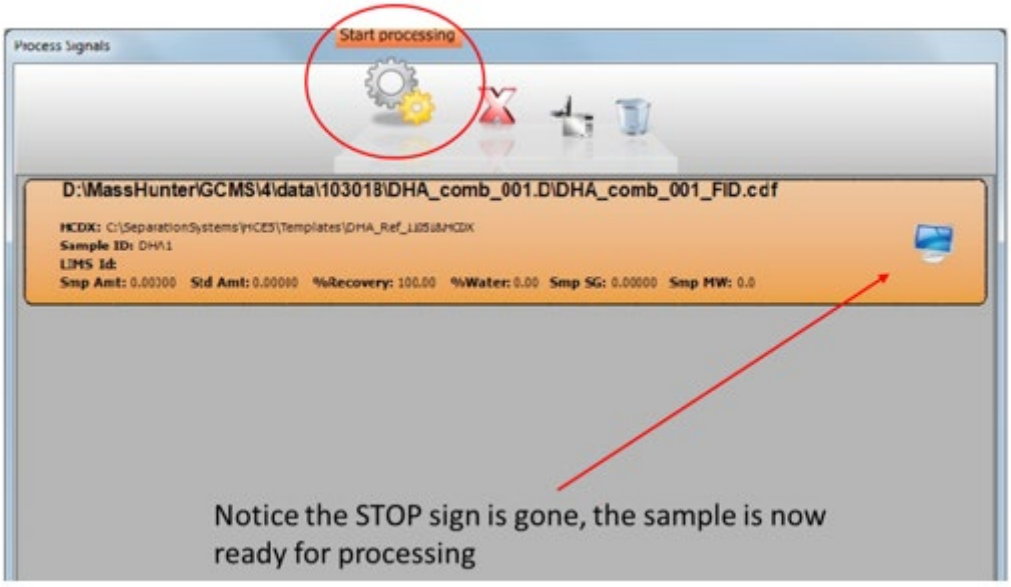
10.4.6.14 Click on the green check mark to update changes as shown in Figure 11.

Figure 11



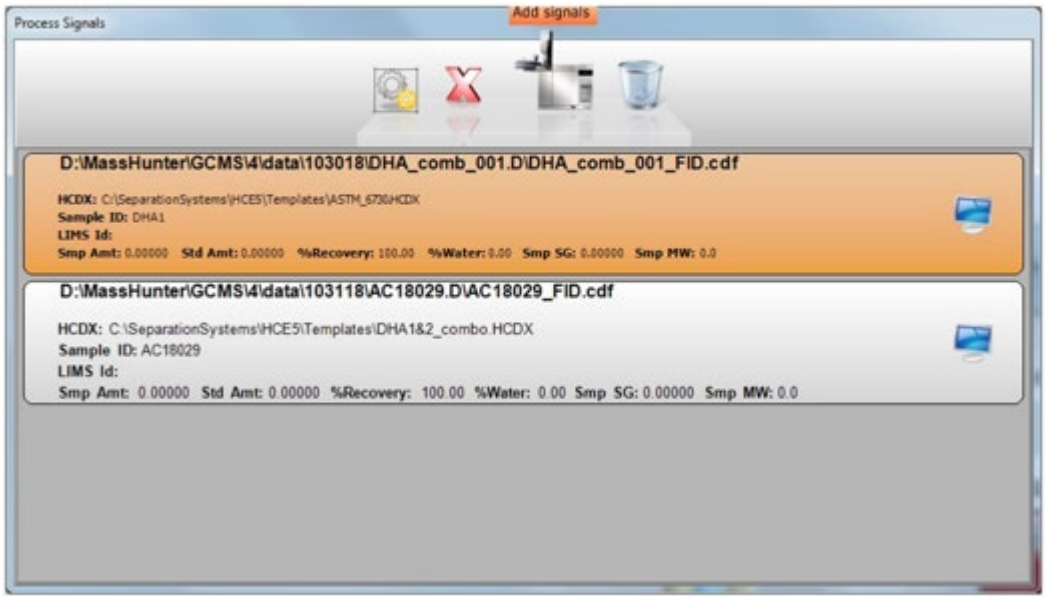
10.4.6.15 Click the gear icon to start processing the sample. See Figure 12.

Figure 12



10.4.6.16 Multiple sample signals can be loaded simultaneously and will be evaluated in the order selected or highlighted orange (See Figure 13).

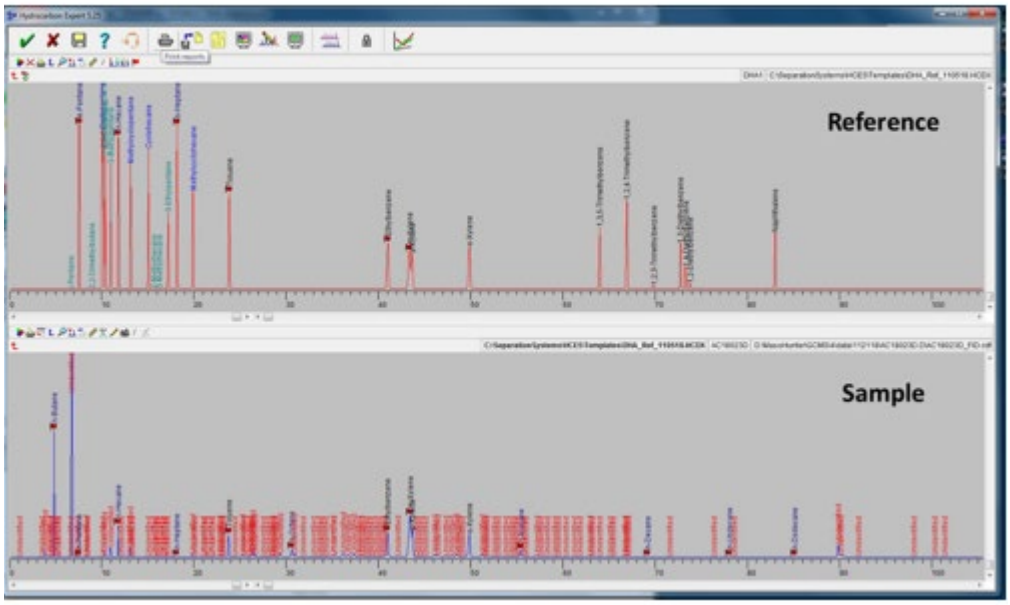
Figure 13



10.4.6.16.1 To remove a sample signal, highlight the sample signal and click on the trash can icon shown in Figure 13 above.

10.4.6.17 After processing, the reference chromatogram and sample chromatogram are displayed as shown in Figure 14.

Figure 14



10.4.6.18 Confirm peak identification using MSD ChemStation Enhanced Data Analysis Software. Open System S DHA (FID + MS) software on computer desktop (See Figure 2).

10.4.6.19 Locate the MSD data file from the appropriate subdirectory (MMDDYY).

10.4.6.20 Load the data file.

10.4.6.21 Use the NIST library to identify unknown peaks of interest or confirm peaks identified by Hydrocarbon Expert pattern recognition.

10.4.6.22 Return to Hydrocarbon Expert software to assign peak names.

10.4.6.22.1 Avoid re-assigning peak names for any flagged peaks. Flagged peaks have a red flag at the top of the peak.

10.4.6.22.2 If a flagged peak name is re-assigned the following prompt window appears, “Adding or removing a reference component will affect the identification, continue?” –click YES.

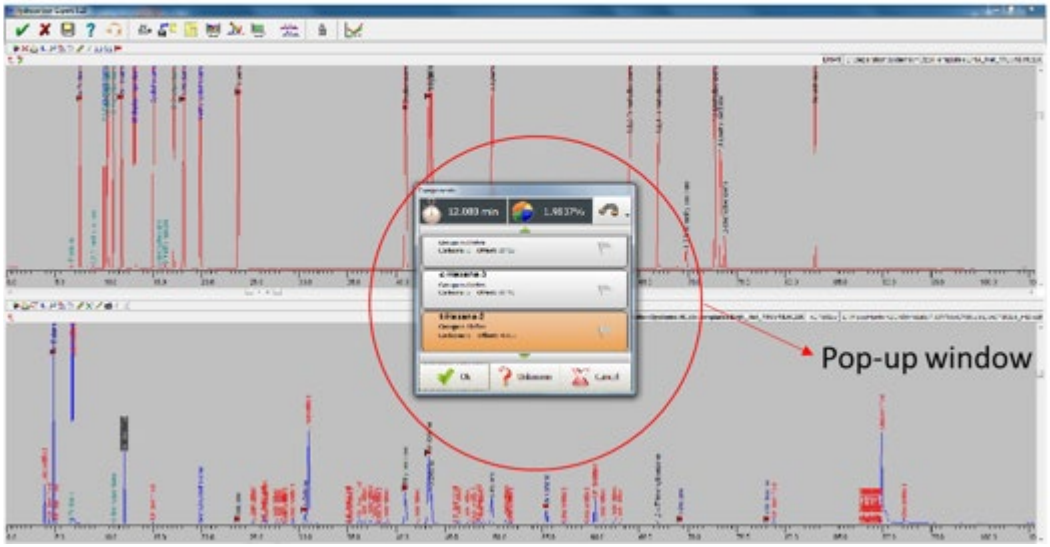
10.4.6.22.3 Peaks between that flag and the next closest flag downfield may need to be re-assigned.

10.4.6.23 Double-click on a peak in the sample chromatogram labeled Unidentified

or Component Name.

10.4.6.24 Toggle through the list of component names from the pop-up window to assign the peak name as shown in Figure 15.

Figure 15



10.4.6.24.1 The pop-up list is ordered based on retention time.

10.4.6.25 Select the peak name from the component list and click OK or click Unknown if peak name is not known.

10.4.6.26 If the peak name is not found, be sure the peak name was not previously assigned. If the peak name was previously assigned, assign that peak Unknown and repeat steps 10.4.6.23 through 10.4.6.25. Unknown peaks are labeled Unidentified in the sample chromatogram.

10.4.6.26.1 Two peaks cannot be assigned the same name in Hydrocarbon Expert.

10.4.6.26.2 Alternatively, assign peak name by right-clicking on the Unidentified or peak name in the sample chromatogram and select from a shortened list and assign the new peak name.

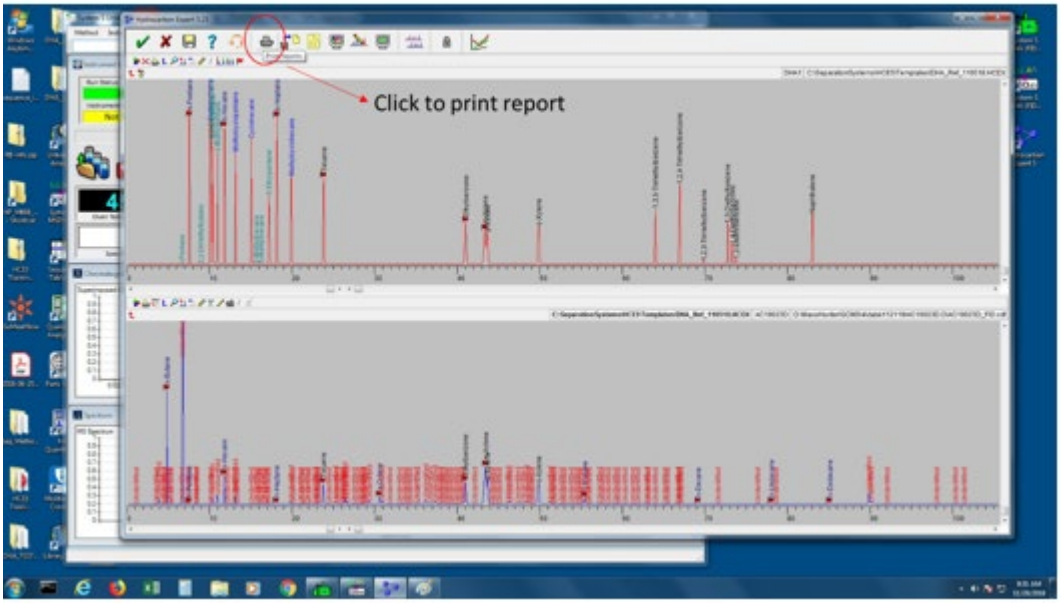
10.4.6.27 Peaks labeled Unidentified are not reported or labeled in the report print out but accounted for in the weight percent calculation performed by the Hydrocarbon Expert software.

10.4.6.28 Peak assignments are at the analyst's discretion

10.4.6.29 Export / Print Report

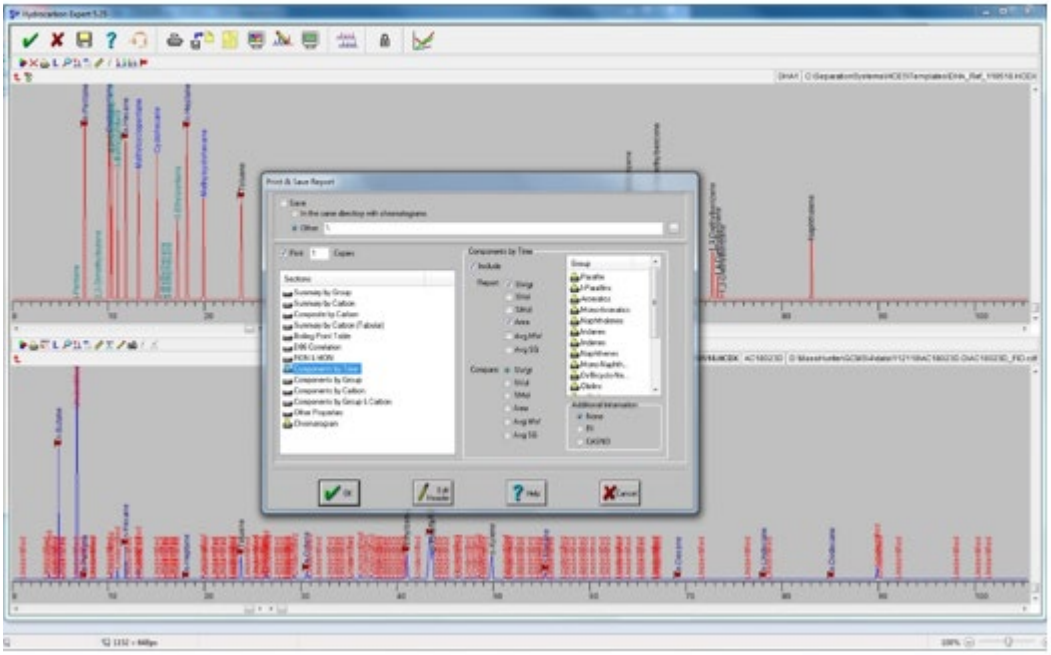
10.4.6.29.1 Single-click the Printer icon to bring up Print & Save Report window as shown in Figure 16.

Figure 16



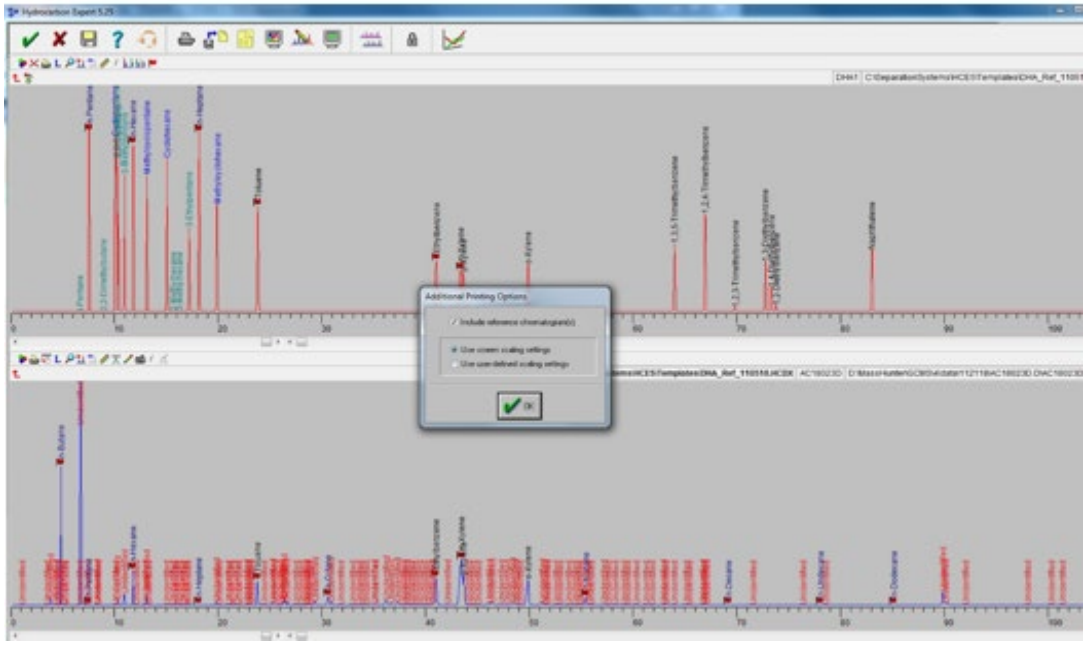
10.4.6.29.2 Select “Components by Time” from the list of reporting options in the Print & Save Report window and click OK (Figure 17).

Figure 17



10.4.6.29.3 Select “Use screen scaling settings” and Click OK as shown in Figure 18. The printer window opens. Click OK to print report.

Figure 18

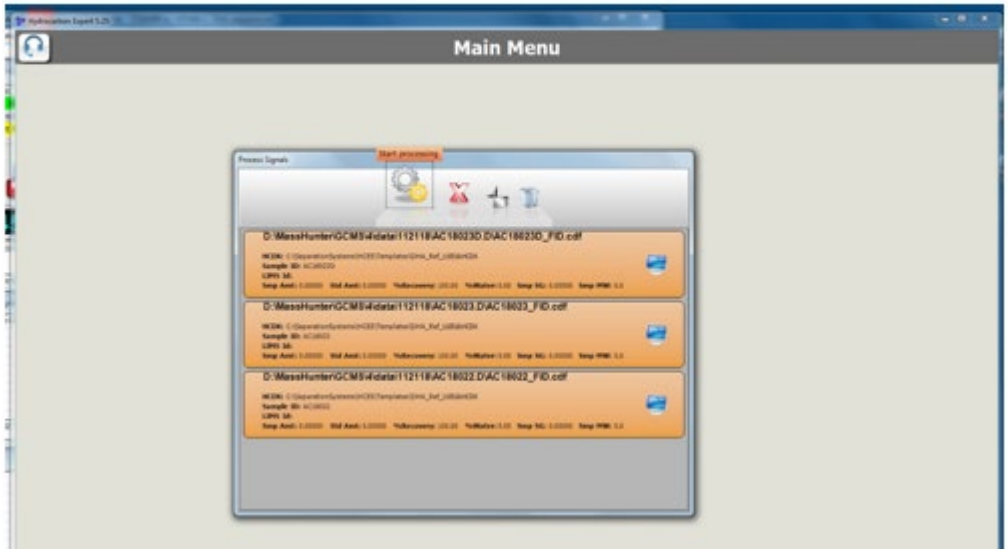


10.4.6.30 Verify that the control/check recoveries are within the control limits posted at or near the instrument. The control limits are also located in the Consumer Products Reports LIMS application at the Control Limits link. If any of the control/checks are not within the control limits, reanalyze the affected samples.

10.4.6.31 For continuous processing of sample files do the following:

10.4.6.31.1 From the Process Signals window, load multiple sample signals (Figure 19).

Figure 19



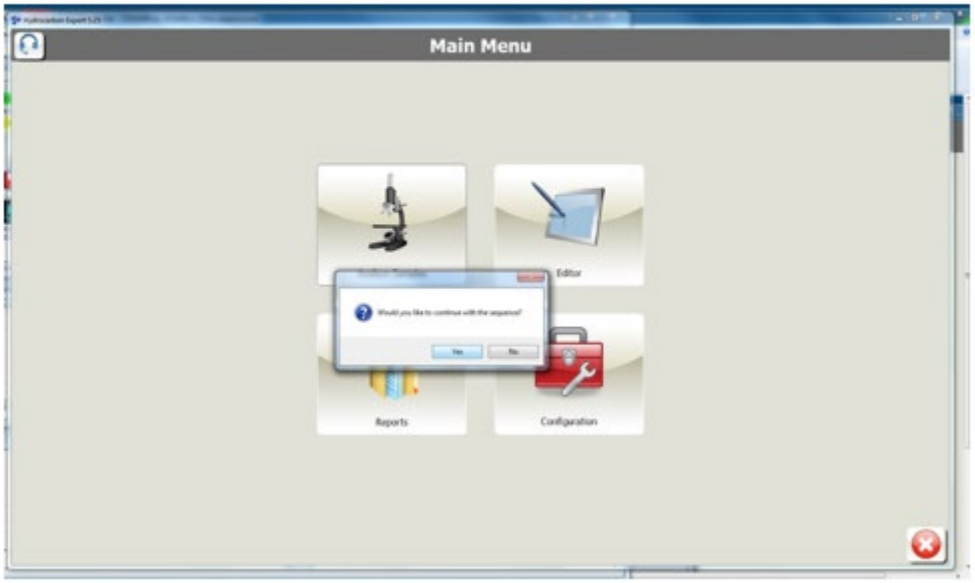
10.4.6.31.2 Click the gear icon to start processing and the sequence can be processed in the order the samples were added.

10.4.6.31.3 If no peak names are re-assigned, click on the green check mark as shown in Figure 20.

Figure 20

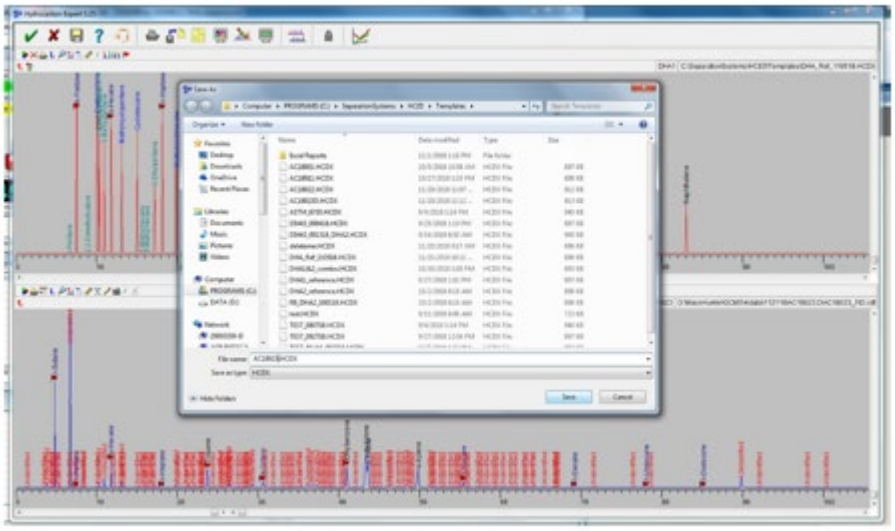
10.4.6.31.4 The following window prompt appears: “Would you like to continue with the sequence?” Click Yes (Figure 21).

Figure 21



10.4.6.31.5 If peak names are re-assigned, click on the green check mark to load as shown in Figure 20. The Save As window appears as shown in Figure 22.

Figure 22

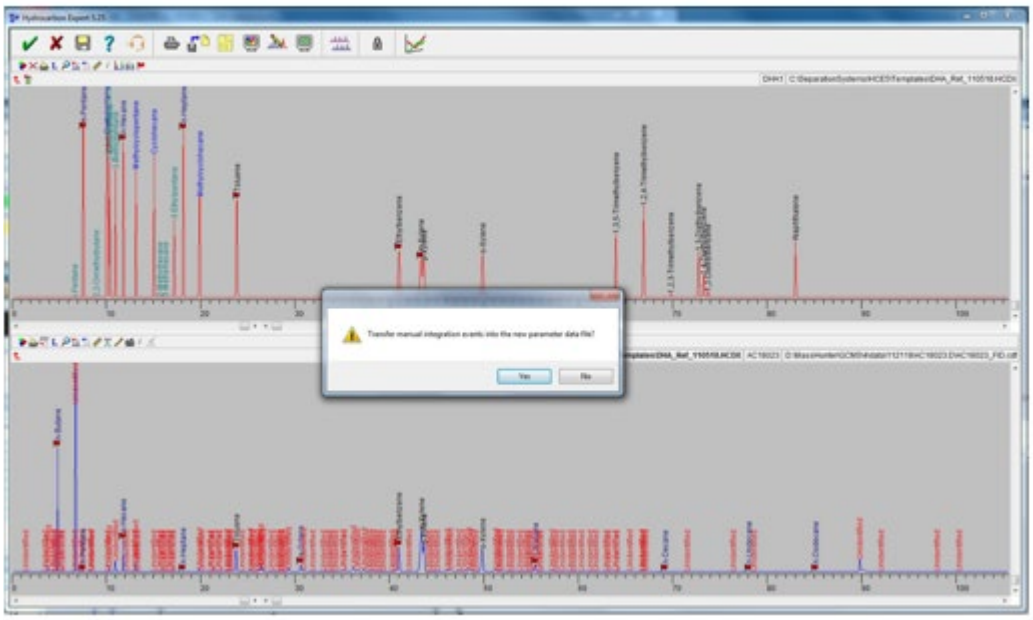


10.4.6.31.6 Do not overwrite the in use .HCDX reference file. Give the file a new name; sample name_.HCDX. If creating a new reference file, name

the file DHAreference_mmddyy.HCDX.

10.4.6.31.7 The following prompt window appears, “Transfer manual integration events into the new parameter data file” –click No (Figure 23).

Figure 23



10.4.6.32 When data analysis and report printing are complete, delete sample signals from Hydrocarbon Expert Process Signals window (See Figure 13).

10.4.6.32.1 Select/highlight the sample signal and click on the Trash Can icon shown in Figure 13 or Figure 19.

10.4.6.33 Upload the data to LIMS (see LIMS Manual: Detailed Hydrocarbon Analysis).

11 Quality Control

11.1 Table of Quality Controls

QC TYPE	FREQUENCY	CRITERIA	CORRECTIVE ACTION
Solvent Blank	At minimum before the control and each check	The target compound concentration in the solvent blank should be less than 0.1% wt./volume	If a target compound or interference is identified at the expected retention time in any of the blanks run after the calibration, the values for the blanks are averaged and subtracted from the value of the target compound for any samples. This is known as “blank subtraction”.
Calibration	Each analytical batch	Must have a correlation coefficient greater than 0.98.	If criteria is not met, reanalyze the calibration curve or make up a new dilution of the calibration curve. Reanalyze the analytical batch after a successful calibration.
Control/Check	The control is analyzed after the calibration, and the checks after every ten or less samples and at the end of the analytical sequence.	Upper and lower control limits set at ± 10 percent of the target value	If an analysis is out of the control limits, the conditions are evaluated and the control/check and any samples not bracketed by successful control/checks will be reanalyzed.
Duplicate	One of ten or fewer samples in the sample batch	The relative percent difference of the duplicate results are set at 25%.	Any duplicate pair with a relative percent difference exceeding 25% shall be flagged to track method precision.

11.2 Equipment Requirements

11.2.1 The balances require calibration by an outside source annually.

11.2.2 Pipettors require certification by an outside source annually.

11.2.3 The MDL for the compound groups should be determined annually following procedures outlined in the NLB Laboratory Quality Control Manual.

12 Sample and Data Management

12.1 Data management consists of samples logged into the LIMS, documentation of unusual occurrences and their resolutions, creation of data packages (monthly, amendments, and special projects) for peer review and management approval, submittal of data to clients, and archival procedures for sample media and respective chains of custody. Program and maintenance notebooks and/or logbooks are to be kept with the instrumentation at all times.

12.2 Information that has been designated as confidential, proprietary, or trade secrets must be maintained in a locked file cabinet in a secure area. Access to this file cabinet is subject to management approval.

13 Calculations

13.1 Acetate, Ketone, Glycol, and ortho-Cresol Method Calculation:

LIMS will automatically calculate the weight fraction of each compound found in each sample as follows:

$$\text{Weight Fraction Compound} = \frac{\text{mg/ml Compound}}{\text{dilution weight (g)}} \times 10^{-2}$$

13.2 Hydrocarbon Method Calculation:

LIMS will automatically calculate the weight fraction of each compound found in each sample as follows:

$$\text{Weight Fraction Compound} = \left(\text{HC Result}/100 \times \frac{\text{LP (g)}}{\text{TW (g)}} \times \text{TV}/100 \times (1\text{-avg } H_2O/100) \right)$$

13.2.1 Where HC = Percent hydrocarbon from Detailed Hydrocarbon Analysis

13.2.2 Where LP = Liquid Product Weight as determined by SOP SAS05

13.2.3 Where TW = The sum of the propellant weight and liquid product weight as determined by SOP SAS05

13.2.4 Where TV = Percent total volatile material in the non-propellant portion of an aerosol coating product as determined by SOP SAS01

13.2.5 Where avg H_2O = Average of the percent water determined by SOP SAS03 and SOP SAS04

14 References

14.1 Method 310 Determination of Volatile Organic Compounds (VOC) in Consumer Products and Reactive Organic Compounds (ROC) in Aerosol Coating Products, May 25, 2018 https://www.arb.ca.gov/regact/2018/cp2018/method310.pdf

14.2 U.S. EPA Method 8260B Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS) (capillary column), Revision 2, December 1, 1996

14.3 ASTM D6730-01 Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100–Metre Capillary (with Precolumn) High-Resolution Gas Chromatography, 2016

14.4 NLB Laboratory Quality Control Manual, Revision 4.0, September 17, 2018

14.5 SOP MLD076 Standard Operating Procedure Preparation of Northern Laboratory Branch's Standard Operating Procedures, Revision 0.0, July 18, 2017

14.6 NLB Chemical Hygiene Plan, June 2019

14.7 Consumer Products Database Special Analysis Section (Oracle Database and Applications Manual for LIMS), February 6, 2019

14.8 SOP SAS01 Standard Operating Procedure for the Total Volatile Measurement of Consumer Products, Revision 1.7, October 24, 2018

14.9 SOP SAS03 Standard Operating Procedure for Water Determination in Consumer Products Using Karl Fischer (KF) Drying Oven, Revision 3.0, September 19, 2012

14.10 SOP SAS04 Standard Operating Procedure for Water Determination in Consumer Products Using Gas Chromatography, Revision 1.5, August 19, 2010

14.11 SOP SAS05 Standard Operating Procedure for the Determination of Compounds in Aerosol Consumer Product Propellant by Gas Chromatography, Revision 3.2, August 18, 2010

14.12 SOP SAS13 Standard Operating Procedure for Consumer Product Sample Batch Management and Reporting

14.13 SOP SAS14 Standard Operating Procedure for Consumer Product Sample Preparation

15 SOP Revision History

	Date	Updated Revision	Original Procedure
1	**Description:** New SOP for the analysis of Aerosol Coatings, Revision 0.0		
	August 5, 2019	Procedure for the determination of compounds in Aerosol Coating Consumer Products under Method 310.	None