California Environmental Protection Agency

Air Resources Board

SOP MLD 066

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF OXYGENATES AND NITRILES IN AMBIENT AIR BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Northern Laboratory Branch
Monitoring and Laboratory Division

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STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF OXYGENATED AND NITRILE HYDROCARBONS IN AMBIENT AIR USING SUMMA CANISTER SAMPLING AND GAS CHROMATOGRAPHIC/MASS SPECTROMETRIC ANALYSIS

1.0 SCOPE

This document describes the procedures followed by Monitoring and Laboratory Division (MLD) staff to analyze oxygenated and nitrile hydrocarbons by Gas Chromatography with Mass Spectrometry detection, (GC/MS), in ambient air samples collected from the California Toxic Monitoring Network. Staff of the Northern Laboratory Branch (NLB), Organic Laboratory Section (OLS), developed the method. This Standard Operating Procedure (SOP) is based on the U.S. Environmental Protection Agency (EPA) Toxic Organic Compounds in Ambient Air 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)", EPA/625/R-96/010b, January 1999. Table 1, page 21, lists the Target Compounds and their Chemical Abstract Service (CAS) numbers.

2.0 SUMMARY OF METHOD

Ambient air is collected in a SUMMA polished stainless steel canister using a Xontech 910A sampler. The sampling procedure for Toxic samples is detailed in the Air Resources Board Quality Assurance Manual, Volume II, Appendix Q. All the operational procedures and sampling conditions for each sample are documented in the field. A record of this information is sent back to the OLS along with the sample. Upon receipt, the sample canister pressure is measured with a calibrated external pressure gauge. This information and particulars of the collection are documented in the laboratory. The sample is then analyzed according to the SOP in the laboratory.

An ambient air sample is introduced into the analytical system from a pressurized canister through stainless steel or Teflon tubing with the aid of a mass flow controller (MFC) and a vacuum system. A digital readout attached to the MFC provides a visual indication of the proper sample flow during sampling. Automated sampling of up to 16 canisters can be accomplished using the system's multiposition stream selector valve.

The sample is trapped on a sorbent trap at 50°C. The sorbent trap consists of carbopack B, carbopack C and carboxen 1000. Moisture in the sample is removed from the sorbent trap by dry purging it with an inert gas. After purging, the

sorbent trap is rapidly heated to 300°C to transfer or desorb the contents onto a cryofocuser which is cooled to -130°. The cryofocuser is rapidly heated to 300°C to inject the sample onto a DB-624 capillary column.

The sample mixture is separated into individual components by their interaction with the capillary column's stationary phase, using temperature programmed gas chromatography. A Mass Selective Detector (MSD) detects the components eluting from the column. The target analytes, as shown in Table 1, page 21, are subsequently identified and quantified. Identification of a component in a sample is based upon both the retention time and mass spectral matching. The response of one mass fragment, the Primary Quantitation Ion, is used for quantitation.

3.0 INTERFERENCES AND LIMITATIONS

3.1 Although studies have shown that the target compounds can be considered stable in stainless steel canisters, every effort must be made to analyze the sample within 30 days of the sampling date. Extreme care must be taken to prevent contamination during sample collection, transportation and subsequent analysis.

3.2 The MSD should be setup and tuned according to the manufacturer's specifications prior to sample analysis. The instrument tuning may be verified with 1-bromo-4-fluorobenzene (BFB). This is not a requirement of this SOP.

3.3 Although the retention time of an analyte is not the only parameter used in identifying a component in GC/MS, the retention times of the GC portion of the system must be reproducible.

3.4 All target compounds are identified by their mass spectrum and retention times. Compounds having similar GC retention times may co-elute. This can lead to misidentification or inaccurate quantitation. The use of a proper compound specific Primary Quantitation Ion, as well as secondary ions, may allow accurate quantitation and identification even under these circumstances. There is no substitute, however, for good chromatographic separation.

3.5 Very low target and non-target analyte concentrations may not produce a good quality spectrum. This may result in either low match quality or misidentification.

3.6 No more than 10 samples should be run consecutively without system recalibration. This is an internal OLS/SOP specific requirement, not a Laboratory Quality Control Manual requirement.

3.7 The analytical system may be contaminated when samples containing high compound concentrations are analyzed. A blank should be analyzed after a high concentration sample to check for possible carryover.

3.8 High boiling compounds being trapped on the column may cause daily baseline shifting, or the appearance of broad, extraneous “ghost” peaks. The column should be baked out prior to each set of analytical runs to remove these contaminants. The bake out temperature should not exceed the column’s maximum operating temperature of 260 °C.

3.8.1 Reference:

“1996/1997 Catalog and Technical Reference”, J & W Scientific, Inc.

3.9 The analytical system is capable of detecting compounds other than the target analytes. Table 1, page 21, lists the compounds addressed by this procedure. Benzene and hexane are being used as stability markers.

4.0 APPARATUS

4.1 A Lotus Consulting/Varian Model 3800 gas chromatograph, configured as a stand-alone Cryogenic Concentration System, with:

4.1.1 An automated sampler, consisting of a multi-position Stream Selector Valve (SSV) and a Mass Flow Controller (MFC) with a Control/Digital Readout module.

4.1.1.1 The MFC is mounted downstream of the SSV, sorbent trap, and cryofocuser to eliminate any contamination and to reduce dead volume in lines from sample trap.

4.1.1.2 The MFC is typically rated at 100 cm^3/min at 100% full scale. The flow rate is set as a percentage of full scale. For example, a flow rate of 50 cm^3/min corresponds to a setting of 50% full scale.

4.1.1.3 The Control/Digital Readout module is set to the side or on top of the GC.

4.1.1.4 A rotometer is mounted on the GC, between the MFC and the vacuum source, to allow visual confirmation of flow.

4.1.1.5 Reference:

"Stream Selector Valve Control Software For Varian Star Workstation Operator's Manual", by Randall Bramston-

4.1.2 A sorbent/cryogenic Concentrator system, containing:

4.1.2.1 A 700 µl, $^1/_8$-inch nickel tubing is packed with 60/80-mesh of carbopack B, carbopack C and carboxen 1000.

4.1.2.2 A 100 µl, $^1/_{16}$ inch cryofocuser constructed of 0.04 inch internal diameter (i.d.) nickel tubing, without packing.

4.1.3 One Electronic Flow Controller (EFC) for automatic control of the cryofocuser/column carrier He flow.

4.1.4 Two manual, digital flow controllers, and two manual pressure regulators for setting He and N_2 purge/sweep flows. Three analog pressure gauges for use in gas monitoring and diagnosing problems with the flow system.

4.1.4.1 The digital flow controllers are calibrated to deliver gas flows from zero to 100 cm^3/min, $\pm$ 3%, with an inlet pressure of 80 psi.

4.1.5 A canister sampling manifold for connecting canisters to the automated sampler, using appropriate tubing and fittings.

4.1.5.1 Examples of tubing size and material are $^1/_8$-inch teflon tubing, $^1/_{16}$ inch stainless steel tubing, $^1/_{16}$ inch nickel tubing, or $^1/_{16}$ inch glass lined stainless steel tubing.

4.1.5.2 A low-pressure regulator (LPR) with a teflon lined diaphragm.

4.1.5.3 Canisters are connected to the manifold; the manifold is connected to the LPR, and then to the automated sampler's SSV.

4.1.6 Information and instruction on the proper operation of the Varian Model 3800 Gas Chromatograph can be found in the associated Varian manuals.

4.2 A Hewlett-Packard Model 6890 gas chromatograph, with:

4.2.1 Electronic Pneumatic Controllers (EPC) for control of carrier gas, make-up gas, and detector gases.

4.2.1.1 In the current configuration, the Hewlett-Packard carrier gas EPC is not used. Carrier gas control is performed by the Lotus/Varian Cryogenic Pre-Concentrator (Section 4.1.3, page 4).

4.2.1.2 The make-up and detector gases EPCs are not used to perform this analysis. They can be used to control optional GC detectors.

4.2.2 A Hewlett-Packard Model 5973 Mass Selective Detector (MSD) interfaced to the HP 6890 GC. It is a quadrupole mass spectrometer design, capable of scanning from 33 to 550 amu. It is operated in the electron impact mode at 70 electron volts.

4.2.3 Information and instruction on the proper operation of the Hewlett-Packard Model 6890 Gas Chromatograph and the Hewlett-Packard Model 5973 Mass Selective Detector can be found in the associated manuals.

4.3 A J&W DB-624 30 m by 0.32 mm i.d., with 1.80 μm film thickness, fused silica capillary column.

4.3.1 Reference:

"1996/1997 Catalog and Technical Reference", J & W Scientific, Inc.

4.4 A Varian GC Star Workstation that includes an Intel compatible PC, an Ethernet network adapter, Microsoft 9.X or NT 4.0 operating system, and Varian Star Chromatography software.

4.4.1 The Workstation is used for GC system configuration, sample file lists, sequence lists, and method building.

4.4.2 The Ethernet network adapter card provides digital communication with the GC.

4.4.3 Reference:

Manuals, on CD-ROM, "Varian Star Chromatography Workstation", Version 5.5, by Varian, Inc. (P/N 03-910818-01.4)

Manuals, on CD-ROM, "Varian Saturn GC/MS Workstation – System Software", Version 5.51, by Varian, Inc. (P/N 03-910876-01)

"Varian GC Star Workstation Manual", by Randall Bramston-Cook of

Lotus Consulting

4.5 A Hewlett-Packard GC/MS ChemStation that includes an Intel compatible PC, an Ethernet network adapter, a GPIB interface card, Microsoft 9.X or NT 4.0 operating system, and Hewlett-Packard Analytical MSD Productivity ChemStation Software.

4.5.1 The ChemStation is used for storage of raw data files and the subsequent processing of the raw data to produce qualitative/quantitative data.

4.5.2 The Ethernet network adapter card provides digital communication with the GC.

4.5.3 The GPIB interface card provides digital data communication with the MSD.

4.5.4 Reference:

Manuals, on CD-ROM, “HP 5973 MSD Reference Collection”, Revision C.00.00, by Hewlett-Packard

4.6 The Star Chromatography Workstation and the Hewlett-Packard Analytical MSD Productivity ChemStation software can be operated from the same Intel compatible PC.

4.7 Stainless steel SUMMA passivated canisters for sample collection and standard preparation.

5.0 REAGENTS

5.1 A system blank/canister blank, consisting of zero air, ultrapure air, Grade 5 N_2, or ultrapure N_2, in a SUMMA canister that has been humidified with 150 µl of HPLC grade water. Alternatively, Ultrapure or Grade 5 N_2, sampled directly from a gas cylinder, or headspace N_2, sampled directly from a Liquid Nitrogen (LN_2) Dewar can be substituted as the system blank.

5.2 A certified National Institute of Standards (NIST) standard calibration mixture, or mixtures, containing all analytes of interest is being ordered. This standard, or standards, should be slightly higher in concentration than the typical sample and must be within the dynamic range of the GC/MS sytem. Appendix V, page 91, lists the concentrations of the current calibration standards associated with this SOP.

5.3 A control standard mixture, or mixtures, containing all analytes of interest at concentrations within the calibration range of the GC System. Appendix V,

page 91, lists the concentrations of the Control Standards associated with this SOP.

5.4 One high pressure gas cylinder of Grade 5 or better Helium (He) for use as the GC column carrier gas.

5.5 One high pressure gas cylinder of Grade 5 or better Nitrogen (N_2) for use in sample line purging, sorbent trap purging, sample loop purging, and leak testing.

5.6 One Liquid Nitrogen (LN_2) Dewar for cooling the cryofocuser, and the GC column oven.

5.7 Perfluorotributylamine (FC43) for use in MS tuning.

5.8 A 2 part per million (ppm) solution of 1-bromo-4-fluorobenzene (BFB) for MS tuning verification. This optional procedure is not a requirement of this SOP.

6.0 INSTRUMENT CONFIGURATION AND PARAMETERS

6.1 Two separate instruments are used to perform this method. A Lotus Consulting/Varian Model 3800 gas chromatograph, configured as a stand-alone Sorbent Concentration System, handles the concentration of the sample, the introduction of the concentrated sample onto the gas chromatographic column, and the column carrier gas flow (Section 4.1, page 3). A Hewlett-Packard Model 6890 gas chromatograph, equipped with a Hewlett-Packard Model 5973 Mass Selective Detector (MSD), controls the column oven temperature, the interface between the detector and the column, and, through software, the acquisition and processing of data (Section 4.2, page 4).

6.2 Varian 3800 Concentrator

6.2.1 The Varian 3800 Concentrator's gas flow and automation configurations are shown in Figure 1, page 32, through Figure 8, page 39. The nomenclature and function of the Concentrator's thermal zones are shown in Table 2, page 22. A complete listing of the current Varian Star Workstation method, which includes all of the setpoints controlled by the Workstation, is given in Appendix III, page 53. Each major item in the method is described below.

6.2.1.1 Front Valve Oven

This setting controls the isothermal temperature of the in-line Nafion™ sample dryer which is disconnected in this SOP (Section 4.1.6, page 4).

6.2.1.2 Middle Valve Oven

This setting controls the isothermal temperature of the oven in which the SSV (Section 4.1.1, page 3), the Sample Valve (Valve 1), the first Sample Preconcentration Trap (sorbent trap) Valve (Valve 2), and Valve M are installed.

6.2.1.3 Rear Valve Oven

This setting controls the isothermal temperature of the sample lines extending from the Sampling Manifold to the SSV (see 4.1.5, page 4).

6.2.1.4 Valve Table

These settings control the action of the seven (7) time programmable valves/events of the Varian 3800 GC. The valve/relay number, the valve/relay name, the relay state, and the function at each state, are given in Table 3, page 8.

6.2.1.5 Front Injector Type 1079

This setting controls the programmed temperature of the multisorbent /Front Trap (Section 4.1.2.1, page 4).

6.2.1.6 Middle Injector Type 1079

This setting controls the programmed temperature of the Cryofocuser/Middle Cold Trap (Section 4.1.2.2, page 4).

6.2.1.7 Rear Injector Type 1041

This setting controls the programmed temperature of the oven in which the Sample Preconcentration Trap Valve (Valve 3) and the Series Bypass Valve (Valve 4) are installed. Under normal conditions, this oven is operated isothermally.

This oven is designed to mount on top of the Hewlett-Packard 6890 gas chromatograph. A heated transfer line connects Valve 3, in this oven, to Valve 2 in the Middle Valve Oven (see 6.2.1.2, page 8).

6.2.1.8 Rear Injector EFC Type 3

This setting controls the programmed H_e capillary column flow rate (Section 4.1.3, page 4).

6.2.1.9 Column Oven

This setting controls the programmed temperature of the GC Column oven. In the current configuration, the GC column is not installed in the Varian Concentrator (Section 6.1, page 7).

6.2.1.10 Since the Varian 3800 Concentrator is not used for data acquisition, method sections dealing with these functions are not used.

6.3 Hewlett-Packard 6890 Gas Chromatograph / 5973 Mass Selective Detector

6.3.1 The Hewlett-Packard 6890/5973 GC/MS System functions normally in this application. The only departure is that the column carrier gas flow is not controlled by this system (Section 4.2.1.1, page 5).

6.3.2 A complete listing of the current Hewlett-Packard GC/MS ChemStation method, which includes all of the setpoints controlled by the ChemStation, is given in Appendix IV, page 70. A description of each major item in the method follows.

6.3.2.1 Oven

This setting controls the gas chromatographic column oven temperature. It includes the column temperature program.

6.3.2.2 Front Inlet (HP PTV) and Back Inlet (Split/Splitless)

This setting controls the temperature and gas flows for both of these injectors. Neither is used in this configuration.

6.3.2.3 Column 1 and Column 2

These are text entries describing the GC column.

6.3.2.4 Front/Back Detector, Signal 1/2, and Column Comp 1/2

These settings are used for GC detectors. They are not used in this configuration.

6.3.2.5 Thermal AUX 2

This controls the temperature of the transfer line connecting the GC column to the MSD.

6.3.2.6 7673 Injector

This injector is not used in this configuration.

6.3.2.7 MS Acquisition Parameters

These values control when the filament is turned on, the electron multiplier voltage, the mass range to be scanned, the MSD temperature, and when the filament is turned off.

6.3.2.8 Data Analysis Parameters

These values include reporting and qualitative/quantitative options for the processing of acquired data. The compound information is updated during the processing cycle.

6.4 The sample volume for the column injection is automated by the Varian GC Star Workstation software. The function of the valves in the Varian 3800 Concentrator are shown in Table 3, page 23. The setpoint for the MFC is shown in Appendix I, page 51.

7.0 DAILY OPERATION

7.1 Instrument Performance Check

7.1.1 The MSD must be tuned with FC43 to meet the tuning and standard mass spectral abundance criteria prior to initiating any data collection. The detector is tuned using the Autotune program once a week, and is checked on a daily basis using the Quick Autotune program. The procedure and criteria for the FC43 tune can be found in the Hewlett-Packard system manuals referenced on page 70.

7.1.2 The tune values, with regard to positions and abundance ratios of the tune m/z's and their corresponding isotope m/z's, are reviewed.

7.1.3 The system leak and electron multiplier voltage are also checked and evaluated.

7.1.4 An example of a tune evaluation report is shown in Table 5, page 29.

7.1.5 BFB Tuning Verification

7.1.5.1 The mass calibration and resolution of the system may be verified by the analysis of the instrument performance check standard, bromofluorobenzene (Section 5.8, page 7).

7.1.5.2 This procedure is not a requirement of this SOP. If performed, the mass spectral ion abundance criteria for BFB analysis are shown in Table 6, page 30.

7.2 Initial Setup

7.2.1 The Varian 3800 Concentrator method (. mth), sample list (. smp), and sequence list (. seq) are set up on the Star GC Workstation. Appendix III, page 53, has further details, including a listing of the method, and examples of the sample and sequence list screens.

7.2.2 The Hewlett-Packard 6890/5973 data acquisition method (. M) and sequence list (. S) are set up on the Hewlett-Packard GC/MS ChemStation. Appendix IV, page 70, has further details, including a listing of the method and an example of the sequence list screen.

The sample flow rate setting is confirmed on the MFC's Control/-Digital Readout module. The sample volume is determined as the product of the trapping time, in minutes, times the flow rate, in cm^3/-min, set on the MFC. Confirmation of the actual flow rate can be done with an external flow meter. For example:

Trapping Time:	3.0 minutes
Flow Rate:	50.0 cm^3/min
Volume:	3.00 min x 50.0 cm^3/min = 150 cm^3

7.2.3 Canister samples are connected to the canister sampling manifold using appropriate tubing and fittings (Section 4.1.5, page 4). The sample canister valves are opened and the canister pressure gauge is monitored to assure a leak-free connection. The initial canister pressure is recorded.

7.3 Sample Concentration and Analysis

7.3.1 Samples are introduced onto the Varian 3800 Concentrator's sorbent trap under control of the Star Chromatography Workstation method. The gas and sample flow and automation configurations for the sorbent trap loading steps are shown Figure 1, page 32, through Figure 5, page 36. The program times, relay # and status, and events are shown in Table 4, page 25.

7.3.2 After the Concentrator's multisorbent trap has finished loading, it is dry purged with nitrogen gas, heated and the contents are transferred to the cyrofocuser. The cryofocuser loading and subsequent direct transfer of the trapped sample onto the GC column steps are shown in Figure 1, page 32, and Figure 6, page 36, through Figure 8, page 39.

7.3.3 A graphical representation of the concentration steps is shown in Figure 9, page 40.

7.4 Samples

7.4.1 A system blank (defined in Section 5.1, page 6) is analyzed prior to calibration standards, controls and samples.

7.4.1.1 A system blank run must be performed at least once every 24 hours.

7.4.1.2 System blanks should also be run after samples which contains high concentrations (>100 times a target compound's LOD) to detect and eliminate possible carry-over.

7.4.1.3 Trip blanks, if available, are analyzed like samples and their results are documented and evaluated.

7.4.2 A daily calibration standard, for each standard mixture in use (defined in Section 5.2, page 6), is analyzed after the system blank, prior to controls or samples.

7.4.3 A control standard, for each standard mixture in use (defined in Section 5.3, page 6), is analyzed after the system blank and calibration standards, prior to ambient air samples.

7.4.4 Ambient samples are analyzed using the same sample volume as used for the calibration standard and control standard.

7.4.4.1 A smaller volume is analyzed for samples containing concentrations of target analytes that exceed the linear range of the analysis.

7.4.4.2 Smaller volumes are obtained by reducing the trapping time while keeping the MFC setpoint constant.

7.4.5 Duplicate analyses are performed on 10% of all ambient samples analyzed.

8.0 DATA ANALYSIS

8.1 After data acquisition, the raw data files (data.ms) collected on the Hewlett-Packard GC/MS ChemStation are processed by the software to produce result files (MLD066.res). The result files contain the integrated Primary Quantitation Ion peak areas, retention times, and mass spectra.

8.2 Chromatographic peaks found in the Total Ion Chromatogram (TIC) in the result files for calibration standards are qualitatively identified based on matching the mass spectrum to a reference spectra and the retention time to the reference retention time. Both of these references are stored in the method.

8.3 After analyte identification, the integrated calibration standard areas for the Primary Quantitation Ions are used to calibrate the ChemStation method for both retention time and concentration. The latter is based on the peak areas and the known analyte concentration in the standards.

8.4 After calibration of the method, chromatographic peaks from the TIC in blank, control, and ambient sample result files are qualitatively identified based on matching the mass spectrum to a reference spectra and the retention time to the reference retention time. They are quantified using the Primary Quantitation Ion response factor stored in the method.

8.5 A typical Calibration Standard TIC, Ambient Air TIC, and Mass Spectrum are shown in Figure 10, page 41, through Figure 12, page 42.

9.0 QUALITY CONTROL

9.1 System Blank

9.1.1 A system blank is analyzed before any standard or sample is run to evaluate the system cleanliness.

9.1.2 If the individual concentrations of any target analytes detected in the system blank are less than two (2) times their LOD, no action is taken.

9.1.3 If the concentration of any target analyte detected in the system blank is greater than two (2) times it's LOD, the analytical run associated with the system blank should be invalidated and the cause investigated.

9.1.4 All actions taken in response to system blank results should be approved by the OLS Supervisor.

9.1.5 The actions taken in response to system blank results may be modified by the most current version of the Laboratory Quality Control Manual in effect.

9.2 Daily Calibration

9.2.1 A single point calibration is performed daily by analyzing the calibration standard, or standards.

9.2.2 Retention times, spectra and the Primary Quantitation Ion integration for each target analyte in the calibration standard run should be thoroughly checked prior to calibration.

9.2.2.1 The retention times should fall within ± 0.1 minute of the preceding runs retention times. This difference may be modified if historical data indicates a larger difference is more appropriate (i.e., volatile early eluting compounds, or wider, later eluting compounds).

9.2.2.2 The Primary Quantitation ion response factors should fall within ± 20% of the preceding runs response factors.

9.2.2.3 If either retention times or the response factors are outside these ranges, the analyst must investigate the cause.

9.2.3 The ChemStation method is updated after every run with the new calibration information.

9.2.3.1 The method and response factors can be printed for a hardcopy record.

9.2.3.2 Some typical single point calibration concentrations and instrument responses can be found in the Hewlett-Packard GC/MS ChemStation method listing in Appendix IV, under compound information, page 70.

9.3 Control Standard

9.3.1 In order to evaluate the accuracy of the calibration and the overall performance of the system, a control standard is analyzed daily following the system blank and the calibration standard and prior to sample analysis.

9.3.2 Analysis results of the target analytes in this standard are recorded and used to generate control charts.

9.3.2.1 At least 20 data points are needed for the initial set of control limits, and any subsequent adjustment of these limits. This is a requirement for this SOP.

9.3.2.2 Typical Control Charts for the five target analytes are shown in Figure 18, page 49, through Figure 22, page 50.

9.3.2.3 A typical dataset used for calculating control limits is given in Table 7, page 31.

9.3.3 The control standard results must be within the established Control Limits for sample analyses to be valid. Control standard results are evaluated as follows.

9.3.3.1 Should any analysis of the control standard yield a result that falls outside the established Control Limits, the control standard shall be reanalyzed.

9.3.3.2 If the second result is also outside the Control Limits, the analysis shall be discontinued and the problem investigated.

9.3.3.3 All data generated during the out of control period shall be invalidated, and the samples reanalyzed after the analysis has been reestablished.

9.3.3.4 If reanalysis is not possible, results may be invalidated on a compound by compound basis.

9.3.4 All actions taken in response to control standard analysis results should be approved by the OLS Supervisor.

9.3.5 The actions taken in response to control standard results may be modified by the most current version of the Laboratory Quality Control Manual in effect.

9.4 Method Precision

9.4.1 Sample precision is measured by the analysis of ambient duplicate samples and the analysis of ambient collocated samples.

9.4.2 The percent difference (PD) of the duplicate analyses, for samples with target analyte concentrations greater than five (5) times the Limit of Detection (LOD), are recorded and included in the method quality control report.

9.4.2.1 The control limits for the PD of the duplicate sample analyses are the same as the control limits for the Control Standard. The duplicate criteria limit is three (3) times the per cent relative standard deviation.

9.4.2.2 For this analysis, if the duplicate results do not meet the quality control criteria, the samples associated with the duplicate pair should be reanalyzed, or invalidated if reanalysis is not possible.

9.4.3 The PD for collocated sample analyses is used to evaluate method precision for both sampling and analysis procedures.

9.4.3.1 The PD for collocated sample analyses should be within ± 25%.

9.4.3.2 Collocated sample results that do not meet the criteria are reported to the Air Quality Surveillance Branch for action.

9.4.3.3 Results for collocated samples that do not meet the criteria are not invalidated by the Laboratory.

9.4.4 All actions taken in response to duplicate sample results should be approved by the OLS Supervisor.

9.4.5 The actions taken in response to duplicate sample results may be modified by the most current version of the Laboratory Quality Control Manual in effect.

9.5 Multipoint Analysis Verification

9.5.1 A multipoint verification must be performed every year, as dictated in the most current version of the Laboratory Quality Control Manual, to verify the precision and the calibration working range.

9.5.1.1 A multipoint verification is also required, as dictated in the most current version of the Laboratory Quality Control Manual, whenever a system change occurs that is defined by the analyst as major (i.e., a change in instrument or measurement technique that would likely change the method LOD, linearity, or measured concentrations).

9.5.1.2 This is done by analyzing at least three (3) concentration levels of the NIST standard, using at least three (3) replicates at each level.

9.5.1.3 One of the multipoint verification points must be at the same concentration level as the daily calibration standard level.

9.5.1.4 One of the points should be near the LOD concentration of the target analytes.

9.5.1.5 The highest concentration point determines the upper limit of the analytical concentration range.

9.5.2 In order to verify that the system is linear:

9.5.2.1 The plot of response vs. concentration must appear linear;

and

9.5.2.2 The correlation coefficient, r, calculated from a least square fit of the response/concentration data must be 0.98 or greater. This corresponds to a coefficient of determination, r^2, of 0.96 or greater.

9.5.3 Typical multipoint data and graphs for target analytes are presented in Figure 13, page 44 through Figure 17, page 48. Correlation coefficient and highest calibrated concentration values for each target analyte are shown in Appendix II, page 52.

9.5.4 If the verification is considered substantially different from an initial or immediately preceding check, by either the analyst or the OLS Supervisor, the analytical system should be evaluated for problems and the procedure repeated.

9.5.5 All actions taken in response to the multipoint verification should be approved by the OLS Supervisor.

9.5.6 The actions taken in response to the multipoint verification may be modified by the most current version of the Laboratory Quality Control Manual in effect.

9.6 Limit of Detection (LOD) Verification

9.6.1 The LOD verification must be performed every year, as dictated in the most current version of the Laboratory Quality Control Manual,

9.6.1.1 It must also be verified when the conditions as listed under multipoint calibration verification occur (Section 9.5.1.1, page 17).

9.6.1.2 This is done by analyzing at least seven (7) replicates of the NIST standard.

9.6.1.3 The concentration must be no more than five (5) times the published LOD.

9.6.1.4 The calculated LODs must be equal to or less than the published LOD values.

9.6.2 The LOD is calculated using the following equation, as specified in most current version of the Laboratory Quality Control Manual in use.

$$\mathbf{MDL} = \mathbf{T}_{(n-1,\ 1-\alpha=0.99)} \times \mathbf{s}$$

where

n = the number of replicates

T = the Students' t-value at the 99% confidence level ($1 - \alpha$) for n -1 degrees of freedom

s = the Standard Deviation of the sample Mean

9.6.3 The published LODs for most target analytes analyzed by this method and example verification values are presented in Appendix II, page 52.

9.6.4 If the verification is considered substantially different from an initial or immediately preceding check, by either the analyst or the OLS Supervisor, the analytical system should be evaluated for problems and the procedure repeated.

9.6.5 All actions taken in response to the LOD verification should be approved by the OLS Supervisor.

9.6.6 The actions taken in response to the LOD verification may be modified by the most current version of the Laboratory Quality Control Manual in effect.

9.7 Method Accuracy

9.7.1 Providing performance audits to the NLB, in order to assess the accuracy of the generated data, is the responsibility of the Quality Assurance Section (QAS) of the Quality Management Branch (QMB).

9.7.1.1 The analysis of performance audit materials shall follow the same procedures as the analysis of regular samples, where possible.

9.7.1.2 Several replicate analyses of the performance audit material should be performed to provide an estimate of precision (i.e., the sample standard deviation).

9.7.1.3 The concentration results of audit sample analyses, including the sample standard deviation and the number of replicate analyses, shall be provided as quickly as possible to the QAS staff, and shall be included in the quarterly QC reports.

9.7.1.4 If after receiving the QAS Audit Report any results are considered substantially different from the preceding audit results, the OLS Supervisor in conjunction with the QAS Supervisor shall formulate an appropriate course of action.

9.7.1.5 All actions taken in response to the performance audit should be approved by the OLS Supervisor.

9.7.1.6 The actions taken in response to the performance audit may be modified by the most current version of the Laboratory Quality Control Manual in effect.

9.7.2 Providing blind Through the Probe audit samples to the NLB, in order to assess the accuracy of the entire sampling and analysis system, is the responsibility of the Quality Assurance Section (QAS) of the Quality Management Branch (QMB).

9.7.2.1 Through the Probe audit samples shall be treated as regular ambient air samples.

9.7.2.2 Replicate analyses of Through the Probe audit samples, unless the sample is picked as the analytical duplicate, should not be performed.

9.7.2.3 The concentration results of Through the Probe audit sample analysis shall be provided as quickly as possible to the QAS staff, and shall be included in the quarterly QC reports.

9.7.2.4 If after receiving the QAS Through the Probe Audit Report any results are considered substantially different from the preceding audit results, the OLS Supervisor in conjunction with the QAS Supervisor shall formulate an appropriate course of action.

9.7.2.5 All actions taken in response to Through the Probe audit should be approved by the OLS Supervisor.

9.7.2.6 The actions taken in response to the Through the Probe may be modified by the most current version of the Laboratory Quality Control Manual in effect.

9.7.3 The analysis of any audit samples provided by other sources should be performed as directed by the OLS Supervisor.

9.7.4 Method accuracy may also be assessed by periodically analyzing other standard reference materials (i.e., other NIST Standards). The results of replicate analysis of these materials should be consistent with the estimated uncertainty of the sample, the standard, and the analytical replicates.

Table 1: Target Compounds and Characteristic Masses (m/z) for Quantification

Compound Name	Type	Abbr. [1]	Chemical Formula	CAS No.	Primary Ion	Secondary Ion(s)
Acrolein	T		C3H4O	000107-02-8	56	55,44
Ethanol	T	EtOH	C2H6O	000115-10-6	45	46,43
Acetone	T		C3H6O	000067-64-1	43	58,42
Acetonitrile	T	ACN	C2H3N	000075-05-8	41	40,39
Acrylonitrile	T	AcryN	C3H3N	0001071-13-1	53	52,51
Benzene			C6H6	71-43-2	78	77
Hexane			C6H14	000110-54-3	57	56,86

[1] Abbr. = Abbreviation – sometimes used in lieu of the full name in the analytical software.
T = Target compound

Table 2: Thermal Zones for the Varian 3800 Concentrator

Thermal Zone #	Status Label	GC Control Label	Function
1	Front: 1079	Front 1079	Multisorbent trap Temperature (Front Cold Trap)
2	Middle: 1079	Middle 1079	Cryofocuser Temperature (Middle Cold Trap)
3	Rear Valve Oven	Large Valve Oven	Sampling Manifold to SSV Line Heater Temperature
4	Front Valve Oven	Small Valve Oven	Nafion Dryer Heater Temperature (not used in this SOP)
5	Middle Valve Oven	Large Valve Oven	SSV, Valve 1, Valve 2, and Valve M Heated Valve Oven Temperature
6	Rear: 1041	Rear 1041	Valve 3 and Valve 4 Heated Valve Oven Temperature

Table 3: Function of Valves for the Varian 3800 Concentrator			
Valve/ Relay #	**Name**	**Relay Event and Description**	**Function**
1	Sample Valve	– Off	Sample Flow Blocked Internal Standard Inlet to Vent Purge N2 Flow through Loop to Valve 2 – Purge Lines or Transfer Internal Standard from Loop to Valve 2
		+ On	Sample Flow to Valve 2 Internal Standard Flow through Loop to Vent Purge N2 Flow to Vent
2	Sample Preconcentration Trap Valve	– SPT Desorb	Flow from Valve 1 to Vacuum Purge He Flow through Multisorbent trap to Valve 3
		+ SPT Trap	Flow from Valve 1 through Multisorbent trap to Vacuum Purge He Flow to Valve 3
3	Sample Preconcentration Trap Valve	– SPT Desorb	Flow from Valve 2 to Valve 4 Column Carrier He Flow to Column
		+ SPT Trap	Flow from Valve 2 to Vent Column Carrier He Flow to Valve 4 then Column
4	Series Bypass Valve	– Series	Cryofocuser in Series with Flow from Valve 3
		+ Bypass	Cryofocuser Isolated
5	Event A Valve	– Off	No Action

Table 3: Function of Valves for the Varian 3800 Concentrator			
		+ On	Start Hewlett-Packard GC and MS Data Acquisition
6	Event B Valve	– Off	Sample Line to Vent
		+ On	Enable Leak test
7	Event C Valve	– Off	N2 Pressurization Gas Off
		+ On	N2 Pressurization Gas On

Table 4: Program Times, Relay #'s, and Status for the Concentrator		
Time (minutes)	**Relay # & Status**	**Events**
0.00	-1-2-3-4-5-6-7	All Valves are off (-): The sample flow is blocked and N_2 purge gas flows through the loop to Valve 2 and then through the MFC to vacuum. He purge gas flows through Valve 2, through the Multisorbent trap (Front Cold Trap), through Valve 3, through the cryofocuser (Middle Cold Trap), back through Valve 3 to vent. He carrier gas flows through Valve 3 to the column.
0.01	**+1**-2-3-4-5-6-7	Valve 1 is turned on (**+1**): This allows the sample to flow through Valve 1 then through the MFC to vacuum, purging the lines with new sample. The N_2 purge gas flow is blocked. He purge gas flows through Valve 2, through the Multisorbent trap, through Valve 3, through the cryofocuser, back through Valve 3 to vent. He carrier gas flows through Valve 3 to the column.
2.00	+1+2-3-4-5-6-7	Valve 2 is turned on (**+2**) and Valve 1 remains on (**+1**): This allows the sample to flow through Valve 1, through Valve 2, through the multisorbent trap and then through the MFC to vacuum. The N_2 purge gas flow remains blocked. ***This starts sample loading of the multisorbent trap.*** He purge gas flows through Valve 2, through Valve 3, through the cryofocuser, back through Valve 3 to vent. He carrier gas flows through Valve 3 to the column.

Table 4: Program Times, Relay #'s, and Status for the Concentrator		
Time (minutes)	**Relay # & Status**	**Events**
3.00	+1+2-3-4+5-6-7	Sample loading of the multisorbent trap continues. Valve 5 is turned on (+5) and starts the HP GC/MS data acquisition.*.* He purge gas flows through Valve 2, through Valve 3, through the cryofocuser, back through Valve 3 to vent. He carrier gas flows through Valve 3 to the column. ***Note: The sample volume is varied by controlling the actions of Valve 1.***
4.00	+1+2-3-4-5-6-7	Same as at 3.0 min. except that Valve 5 is turned off(-5). HP GC/MS data acquisition continues. He carrier gas flows through Valve 3 to the column.
5.00	-1-2-3-4-5-6-7	All Valves but Valve 2 are off. ***This terminates sample loading of the multisorbent trap***. The sample flow is blocked and N2 purge gas flows through the loop to Valve 2, through the multisorbent trap, then through the MFC to vacuum. This purges the multisorbent trap of possible contaminants and moisture for six minutes. He purge gas flows through Valve 2 to Valve 3 then to Valve 4, through the cryofocuser, back to Valve 3 and to vent. He carrier gas flows through Valve 3 to the column.

Table 4: Program Times, Relay #'s, and Status for the Concentrator		
Time (minutes)	**Relay # & Status**	**Events**
11.00	-1-2-3-4-5-6-7	All Valves are off. Stops N2 purging of multisorbent trap. He purge gas flows through Valve 2, through the multisorbent trap, through Valve 3, to Valve 4, through the cryofocuser and to Vent. He carrier gas flows through Valve 3 and to the column. ***This starts transfer and loading of sorbent trap contents to the cryofocuser.***
14.00	-1-2-3+4-5-6-7	Valve 4 is turned on(+). He purge gas flows through Valve 2, through the multisorbent trap, through Valve 3 to Valve 4 and to Vent. He carrier gas flows through Valve 3 to column. ***Transfer of analytes to cryofocuser stops, and cryofocuser is isolated***.
14.90	-1-2+3+4-5-6-7	Valve 3 is turned on(+) and Valve 4 remains on. All other valves are off. He purge gas flows through Valve 2, through the multisorbent trap (Front Cold Trap), through Valve 3, and to Vent. He carrier gas flows through Valve 3 to Valve 4 and back to Valve 3 to Column.
15.0	-1-2+3-4-5-6-7	Valve 3 remains on (+3) and Valve 4 is off (-4). All other Valves are off. He purga gas flows through Valve 2, through the multisorbent trap, to Valve 3 and to Vent. He carrier gas flows through Valve 3 to Valve 4, through the cryofocuser, back to Valve 3 and to Column. ***This backflushes the contents of the cryofocuser to GC column.***

Table 4: Program Times, Relay #'s, and Status for the Concentrator		
Time (minutes)	**Relay # & Status**	**Events**
20.0	-1-2-3-4-5-6-7	All Valves are off. Sample flow is blocked, N2 purge gas flows through sample loop through MFC to Vacuum. He purge gas flushes the multisorbent trap and cryofocuser to Vent.

Table 5: Autotune Evaluation Report

Instrument Name:	GC/MS Instrument #3 (HP6890/HP5973)	
DC Polarity:	Positive	
Filament:	1	
Basepeak should be 69 or 219		OK
Position of mass 69	69.00	OK
Position of mass 219	219.00	OK
Position of isotope mass 70	70.00	OK
Position of isotope mass 220	219.99	OK
Position of isotope mass 503	502.91	OK
Ratio of mass 70 to mass 69 (0.5 – 1.6%)	1.11	OK
Ratio of mass 220 to mass 219 (3.2 – 5.4%)	4.30	OK
Ratio of mass 503 to mass 502 (7.9 – 12.3%)	9.98	OK
Ratio of 219 to 69 should be >40% and is	66.88	OK
Ratio of 502 to 69 should be >2.4% and is	5.69	OK
Mass 69 Precursor (<= 3%)	0.08	OK
Mass 219 Precursor (<= 6%)	0.33	OK
Mass 502 Precursor (<= 12%)	3.32	OK
Testing for a leak in the system		
Ratio of 18 to 69 (<20%)	2.12	OK
Ratio of 28 to 69 (<10%)	2.67	OK
Electron Multiplier Voltage	1341	OK
Tune portion of system verification passed		

Table 6: BFB Ion Abundance Criteria

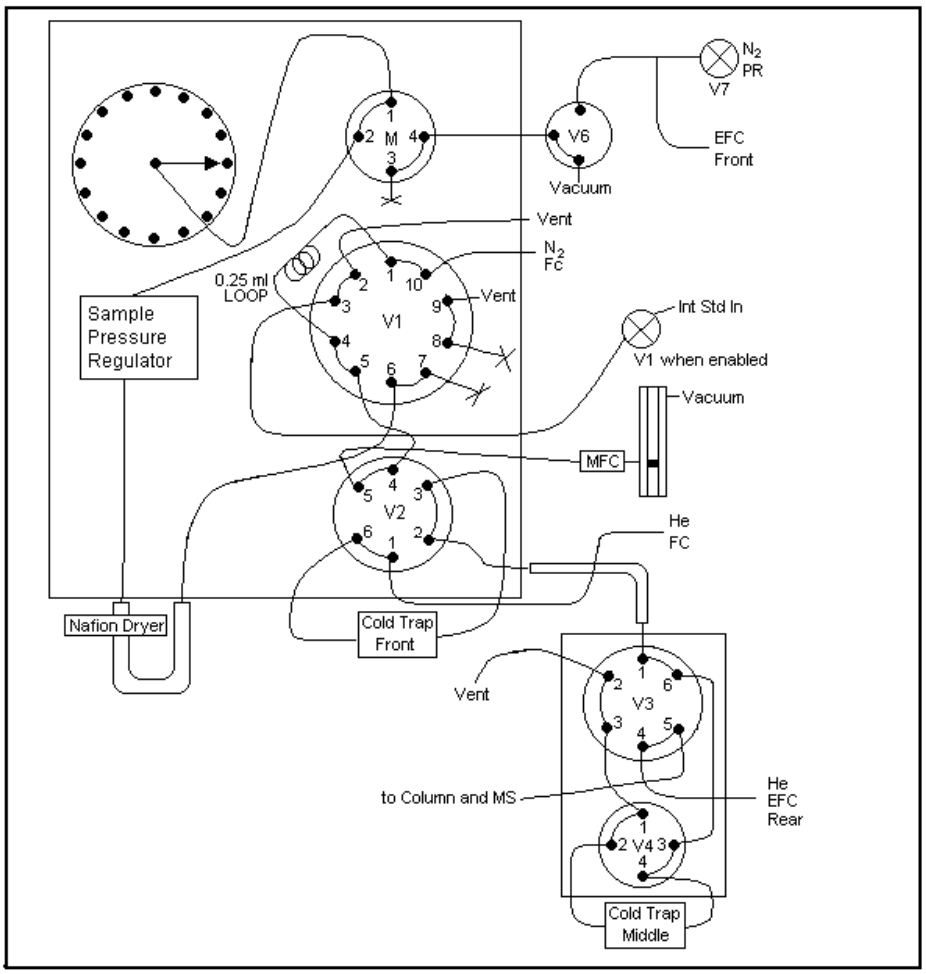
m/z	Ion Abundance Criteria
50	8.0 to 4.0 Per cent of m/z 95
75	30.0 to 66.0 Percent of m/z 95
95	Base peak, 100 Percent Relative Abundance
96	5.0 to 9.0 Percent of m/z 95 (see note)
173	Less than 2.0 Percent of m/z 174
174	50.0 to 120 Percent of m/z 95
175	4.0 to 9.0 Percent of m/z 174
176	93.0 to 101.0 Percent of m/z 174
177	5.0 to 9.0 Percent of m/z 176

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

Table 7: Precision Measurements and Control Limits for MLD066
ALM069798

Compound	Acrolein	Ethanol	Acetone	Acetonitrile	Acrylonitrile
File Name	ppb	ppb	ppb	ppb	ppb
SE1911.D	3.08	20.81	19.14	8.54	4.37
SE1912.D	3.14	21.02	18.91	8.51	4.25
SE1913.D	3.11	19.20	18.76	8.40	4.15
SE1914.D	2.99	19.33	19.18	8.46	4.20
SE1915.D	3.04	18.39	18.81	8.43	4.16
SE1917.D	3.08	17.37	19.85	7.90	3.95
SE1918.D	2.96	17.06	19.85	7.86	3.94
SE1919.D	2.94	16.66	19.89	7.92	4.03
SE1920.D	3.03	16.94	19.85	7.89	4.04
SE1921.D	2.91	18.29	19.93	7.90	3.93
SE1922.D	3.04	18.72	19.48	8.32	4.08
SE1923.D	3.07	20.82	19.58	8.11	4.15
SE1924.D	3.06	20.83	19.60	8.40	4.16
SE1925.D	2.94	20.29	20.76	8.31	4.11
SE1926.D	2.96	18.82	19.73	8.12	3.88
SE2210.D	3.12	18.98	19.69	8.50	4.19
SE2211.D	3.00	20.14	19.28	8.51	4.43
SE2223.D	2.92	19.41	19.01	8.27	4.17
SE2224.D	3.05	20.01	18.73	8.38	4.07
SE2225.D	2.77	19.42	18.80	8.26	4.16
Ave.	3.01	19.13	19.44	8.25	4.12
Std. Dev.	0.089	1.363	0.527	0.241	0.140
%RSD	2.95	7.12	2.71	2.93	3.40
UCL	3.28	23.21	21.02	8.97	4.54
UWL	3.19	21.85	20.50	8.73	4.40
LWL	2.83	16.40	18.39	7.77	3.84
LCL	2.74	15.04	17.86	7.53	3.70

Figure 1: All Valves OFF
Time: Idle state at 0.00 min, Transfer of Trap Contents to Cryofocuser at 11.00 min, and flushes sampling system at 20.00 min

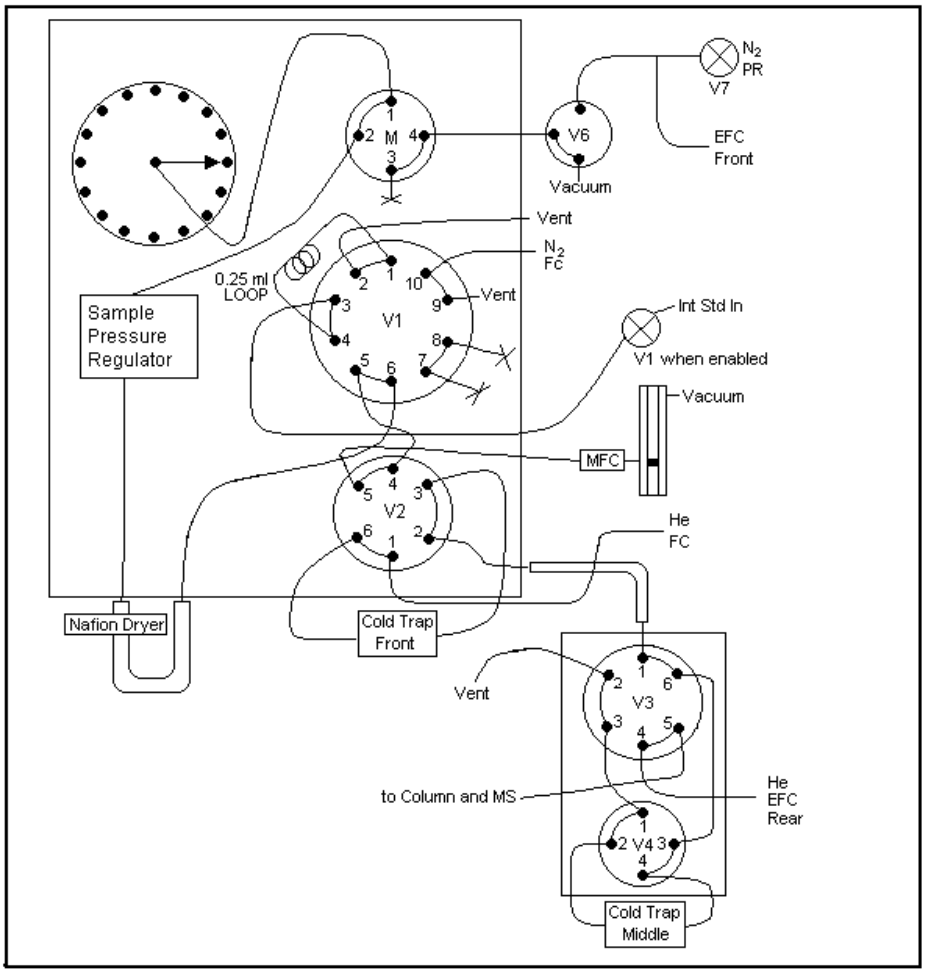


Sample Delivery Program

	Time	V1	V2	V3	V4	V5	V6	V7
*	0.00	-	-	-	-	-	-	-
	0.01	+	-	-	-	-	-	-
	2.00	+	+	-	-	-	-	-
	3.00	+	+	-	-	+	-	-
	4.00	+	+	-	-	-	-	-
	5.00	-	+	-	-	-	-	-
*	11.00	-	-	-	-	-	-	-
	14.00	-	-	-	+	-	-	-
	14.90	-	-	+	+	-	-	-
	15.00	-	-	+	-	-	-	-
*	20.00	-	-	-	-	-	-	-

V1 Sample Valve
V2 Sample Preconcentration Trap Valve
V3 Sample Preconcentration Trap Valve
V4 Series Bypass Valve
V5 Event A Valve
V6 Event B Valve
V7 Event C Valve

Figure 2: Purges Sample Line
Time: 0.01

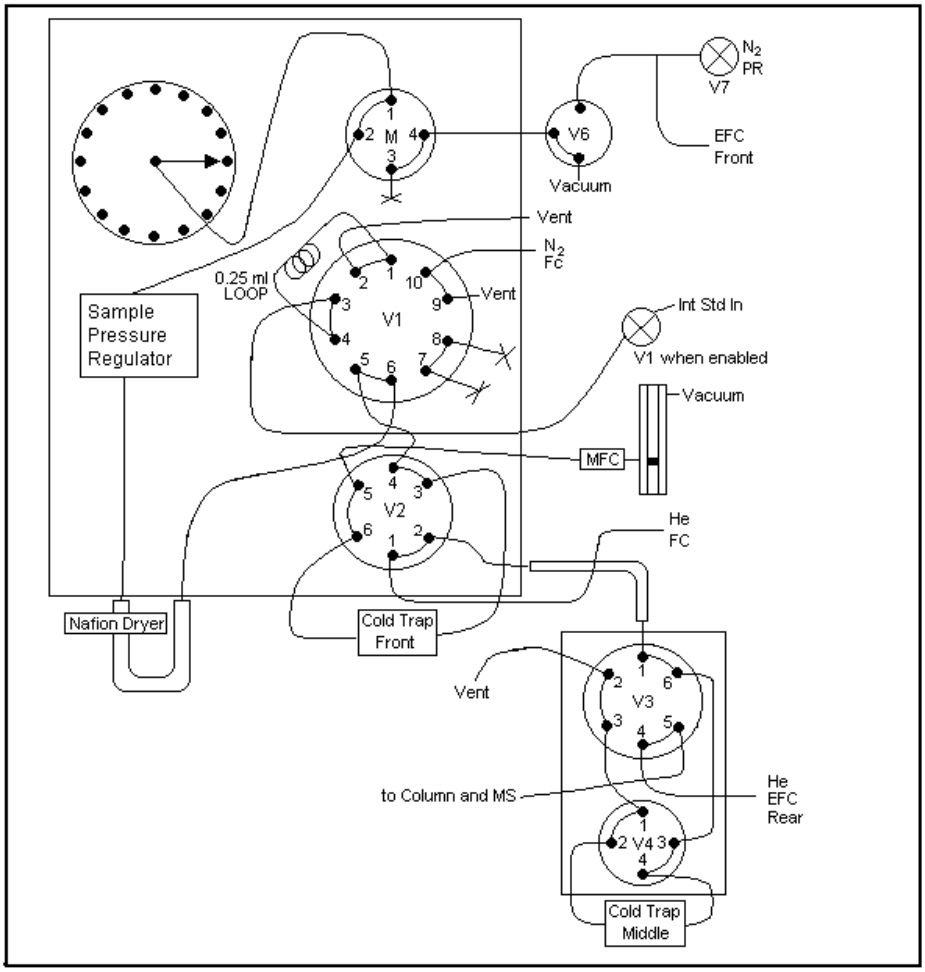


Sample Delivery Program

Time	V1	V2	V3	V4	V5	V6	V7
0.00	-	-	-	-	-	-	-
0.01	+	-	-	-	-	-	-
2.00	+	+	-	-	-	-	-
3.00	+	+	-	-	+	-	-
4.00	+	+	-	-	-	-	-
5.00	-	+	-	-	-	-	-
11.00	-	-	-	-	-	-	-
14.00	-	-	-	+	-	-	-
14.90	-	-	+	+	-	-	-
15.00	-	-	+	-	-	-	-
20.00	-	-	-	-	-	-	-

V1 Sample Valve
V2 Sample Preconcentration Trap Valve
V3 Sample Preconcentration Trap Valve
V4 Series Bypass Valve
V5 Event A Valve
V6 Event B Valve
V7 Event C Valve

Figure 3: Starts Loading Multisorbent Trap
Time: 2.00

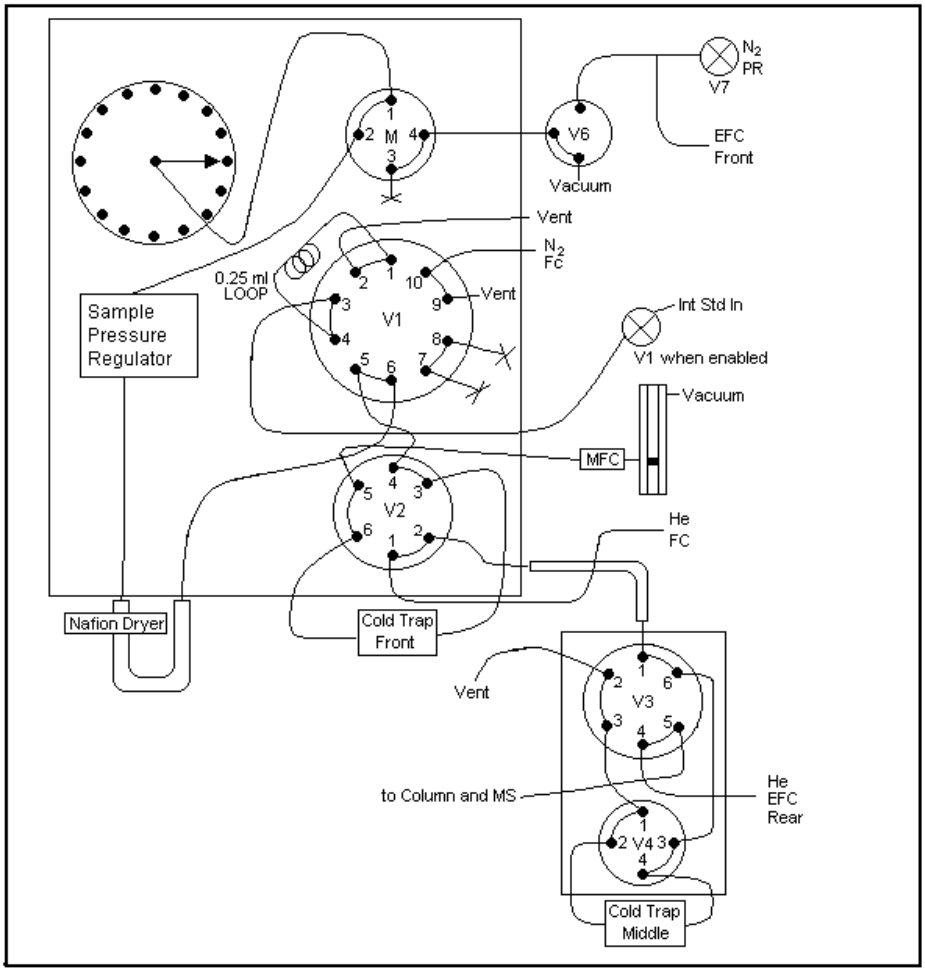


Sample Delivery Program

	Time	V1	V2	V3	V4	V5	V6	V7
	0.00	-	-	-	-	-	-	-
	0.01	+	-	-	-	-	-	-
*	2.00	+	+	-	-	-	-	-
	3.00	+	+	-	-	+	-	-
*	4.00	+	+	-	-	-	-	-
	5.00	-	+	-	-	-	-	-
	11.00	-	-	-	-	-	-	-
	14.00	-	-	-	+	-	-	-
	14.90	-	-	+	+	-	-	-
	15.00	-	-	+	-	-	-	-
	20.00	-	-	-	-	-	-	-

V1 Sample Valve
V2 Sample Preconcentration Trap Valve
V3 Sample Preconcentration Trap Valve
V4 Series Bypass Valve
V5 Event A Valve
V6 Event B Valve
V7 Event C Valve

Figure 4: Loading Multisorbent Trap and starts GC/MS Data Acquisition Time: 3.00 min

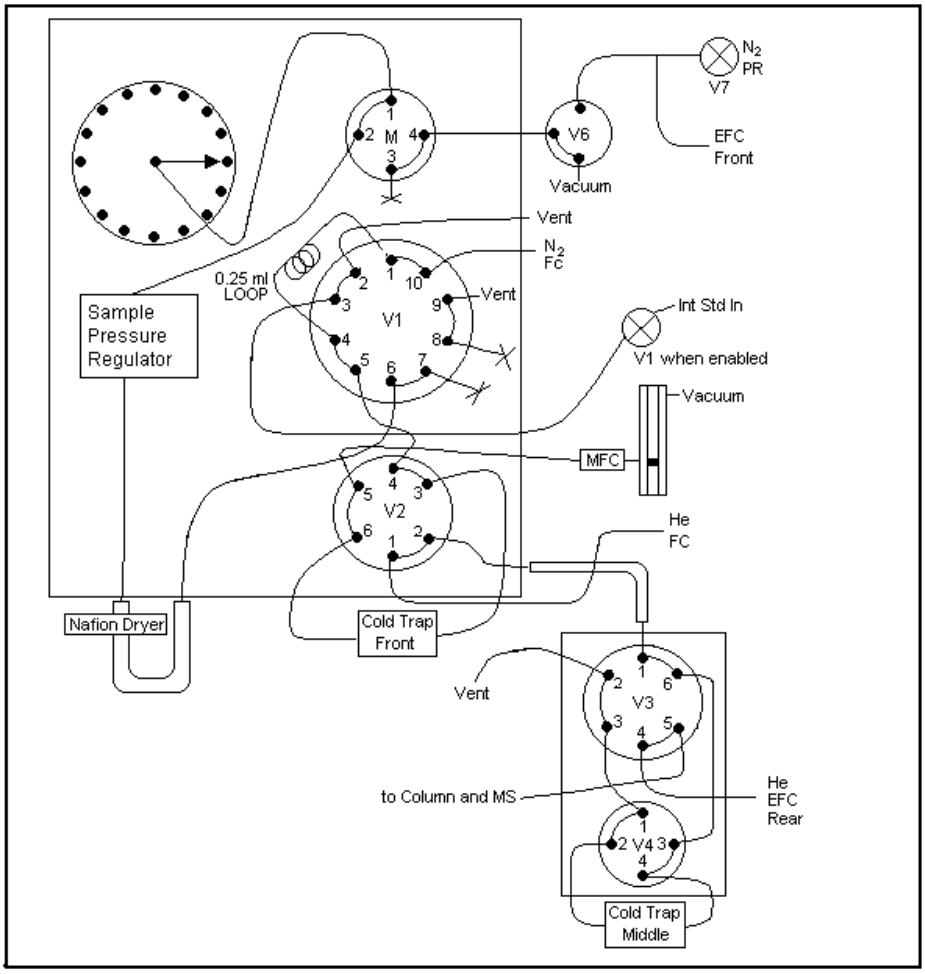


Sample Delivery Program

Time	V1	V2	V3	V4	V5	V6	V7
0.00	-	-	-	-	-	-	-
0.01	+	-	-	-	-	-	-
2.00	+	+	-	-	-	-	-
* 3.00	+	+	-	-	+	-	-
4.00	+	+	-	-	-	-	-
5.00	-	+	-	-	-	-	-
11.00	-	-	-	-	-	-	-
14.00	-	-	-	+	-	-	-
14.90	-	-	+	+	-	-	-
15.00	-	-	+	-	-	-	-
20.00	-	-	-	-	-	-	-

V1 Sample Valve
V2 Sample Preconcentration Trap Valve
V3 Sample Preconcentration Trap Valve
V4 Series Bypass Valve
V5 Event A Valve
V6 Event B Valve
V7 Event C Valve

Figure 5: Stops loading and starts N2 Purge of Sorbent Trap
Time: 5.00 min

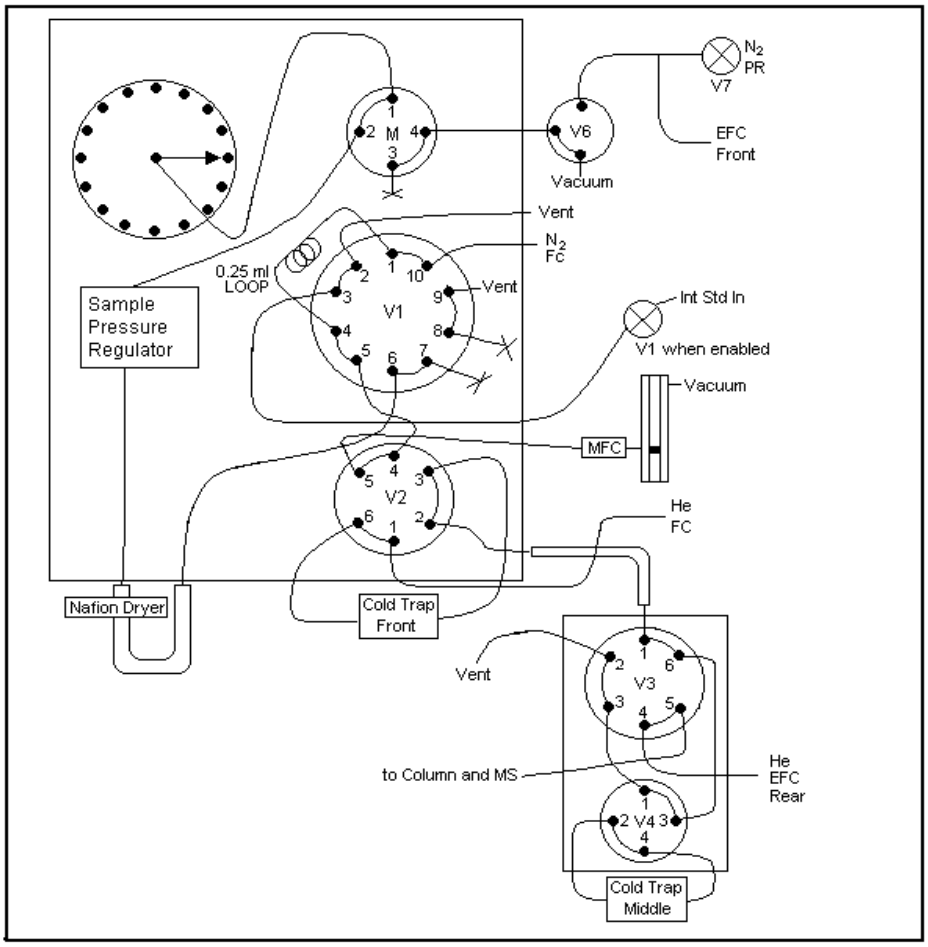


Sample Delivery Program

Time	V1	V2	V3	V4	V5	V6	V7
0.00	-	-	-	-	-	-	-
0.01	+	-	-	-	-	-	-
2.00	+	+	-	-	-	-	-
3.00	+	+	-	-	+	-	-
4.00	+	+	-	-	-	-	-
* 5.00	-	+	-	-	-	-	-
11.00	-	-	-	-	-	-	-
14.00	-	-	-	+	-	-	-
14.90	-	-	+	+	-	-	-
15.00	-	-	+	-	-	-	-
20.00	-	-	-	-	-	-	-

V1 Sample Valve
V2 Sample Preconcentration Trap Valve
V3 Sample Preconcentration Trap Valve
V4 Series Bypass Valve
V5 Event A Valve
V6 Event B Valve
V7 Event C Valve

Figure 6: Stops Transfer of Trap contents to Cryofocuser
Time: 14.00 min

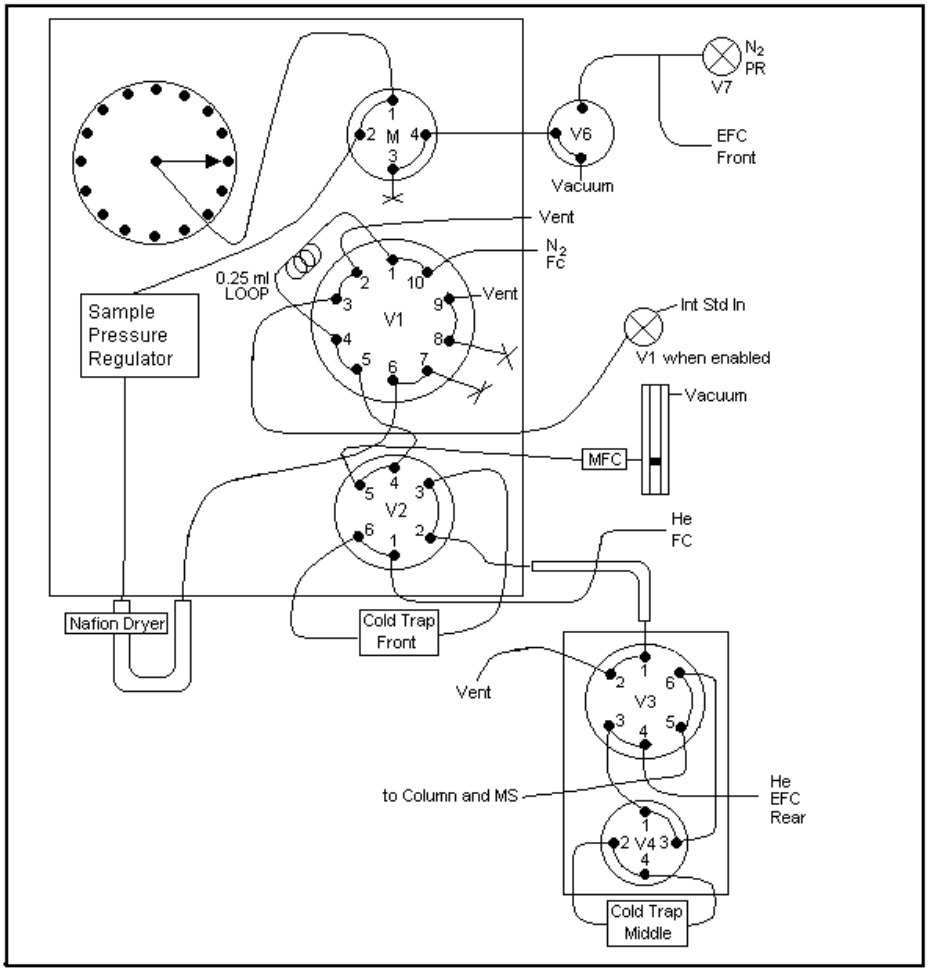


Sample Delivery Program

Time	V1	V2	V3	V4	V5	V6	V7
0.00	-	-	-	-	-	-	-
0.01	+	-	-	-	-	-	-
2.00	+	+	-	-	-	-	-
3.00	+	+	-	-	+	-	-
4.00	+	+	-	-	-	-	-
5.00	-	+	-	-	-	-	-
11.00	-	-	-	-	-	-	-
14.00	-	-	-	+	-	-	-
14.90	-	-	+	+	-	-	-
15.00	-	-	+	-	-	-	-
20.00	-	-	-	-	-	-	-

V1 Sample Valve
V2 Sample Preconcentration Trap Valve
V3 Sample Preconcentration Trap Valve
V4 Series Bypass Valve
V5 Event A Valve
V6 Event B Valve
V7 Event C Valve

Figure 7: Isolates Cryofocuser
Time: 14.90 min

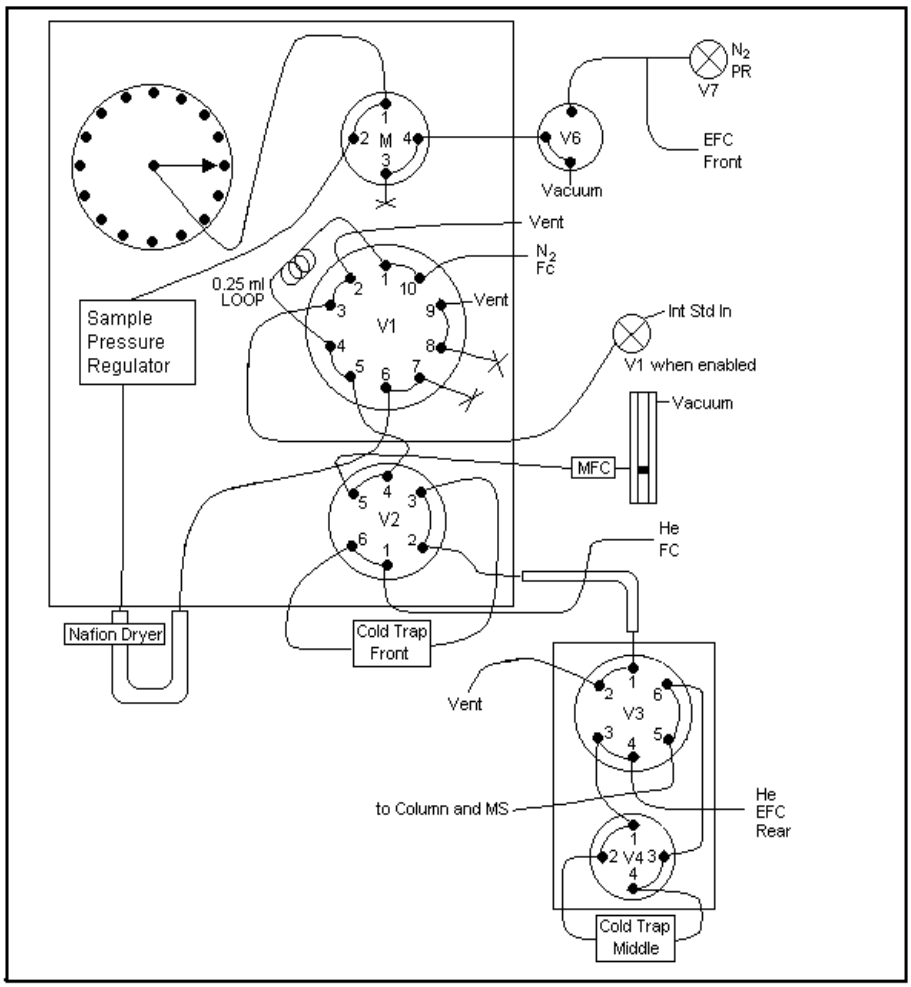


Sample Delivery Program

Time	V1	V2	V3	V4	V5	V6	V7
0.00	-	-	-	-	-	-	-
0.01	+	-	-	-	-	-	-
2.00	+	+	-	-	-	-	-
3.00	+	+	-	-	+	-	-
4.00	+	+	-	-	-	-	-
5.00	-	+	-	-	-	-	-
11.00	-	-	-	-	-	-	-
14.00	-	-	-	+	-	-	-
14.90	-	-	+	+	-	-	-
15.00	-	-	+	-	-	-	-
20.00	-	-	-	-	-	-	-

V1 Sample Valve
V2 Sample Preconcentration Trap Valve
V3 Sample Preconcentration Trap Valve
V4 Series Bypass Valve
V5 Event A Valve
V6 Event B Valve
V7 Event C Valve

Figure 8: Desorbs Cryofocuser Contents to GC Column and MS
Time: 15.0 mins



Sample Delivery Program

Time	V1	V2	V3	V4	V5	V6	V7
0.00	-	-	-	-	-	-	-
0.01	+	-	-	-	-	-	-
2.00	+	+	-	-	-	-	-
3.00	+	+	-	-	+	-	-
4.00	+	+	-	-	-	-	-
5.00	-	+	-	-	-	-	-
11.00	-	-	-	-	-	-	-
14.00	-	-	-	+	-	-	-
14.90	-	-	+	+	-	-	-
15.00	-	-	+	-	-	-	-
20.00	-	-	-	-	-	-	-

V1 Sample Valve
V2 Sample Preconcentration Trap Valve
V3 Sample Preconcentration Trap Valve
V4 Series Bypass Valve
V5 Event A Valve
V6 Event B Valve
V7 Event C Valve

Figure 9. Concentrator Programming Sequence

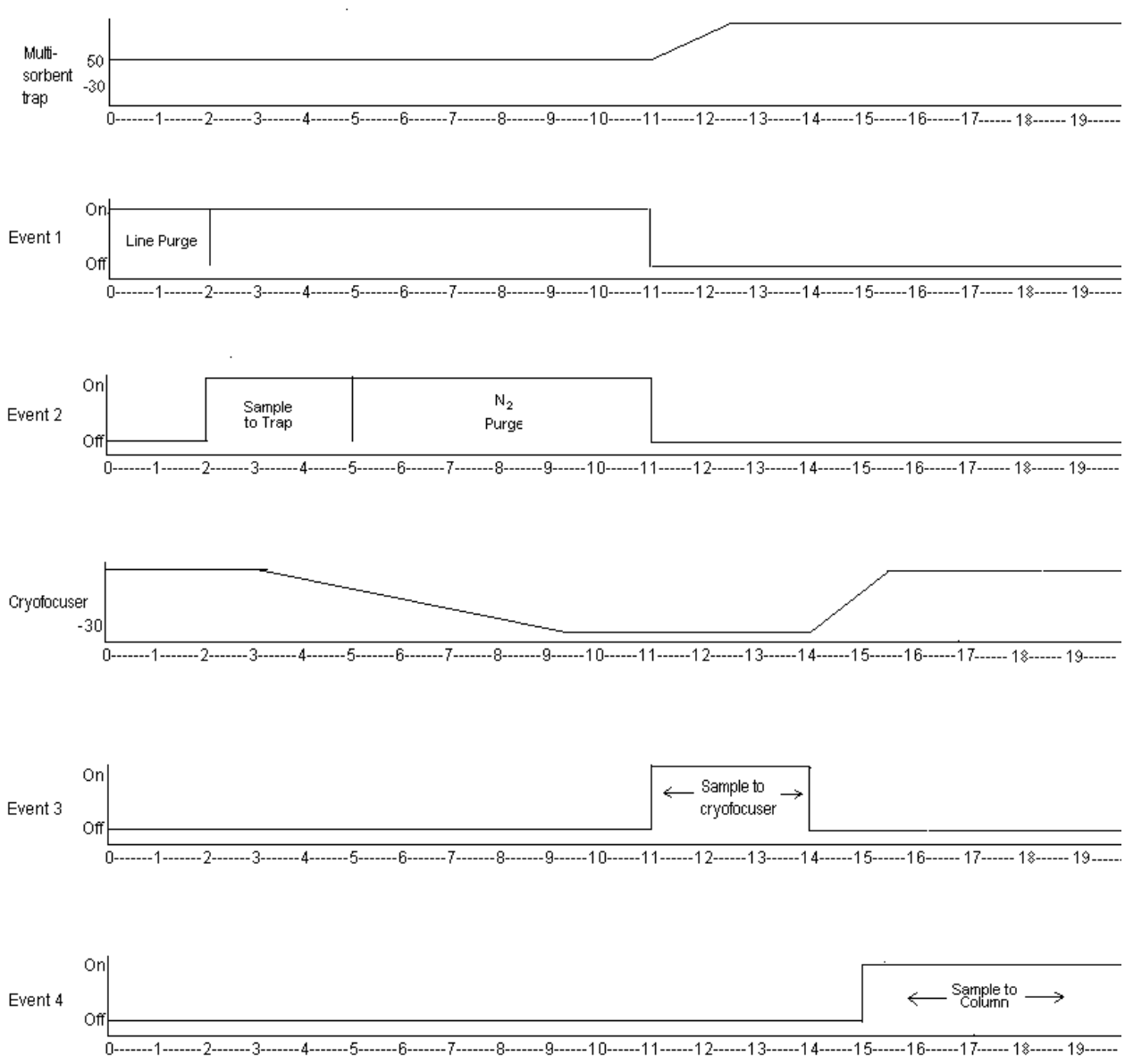


Figure 10. Typical Calibration Standard TIC, CC50604 Gas Mixture

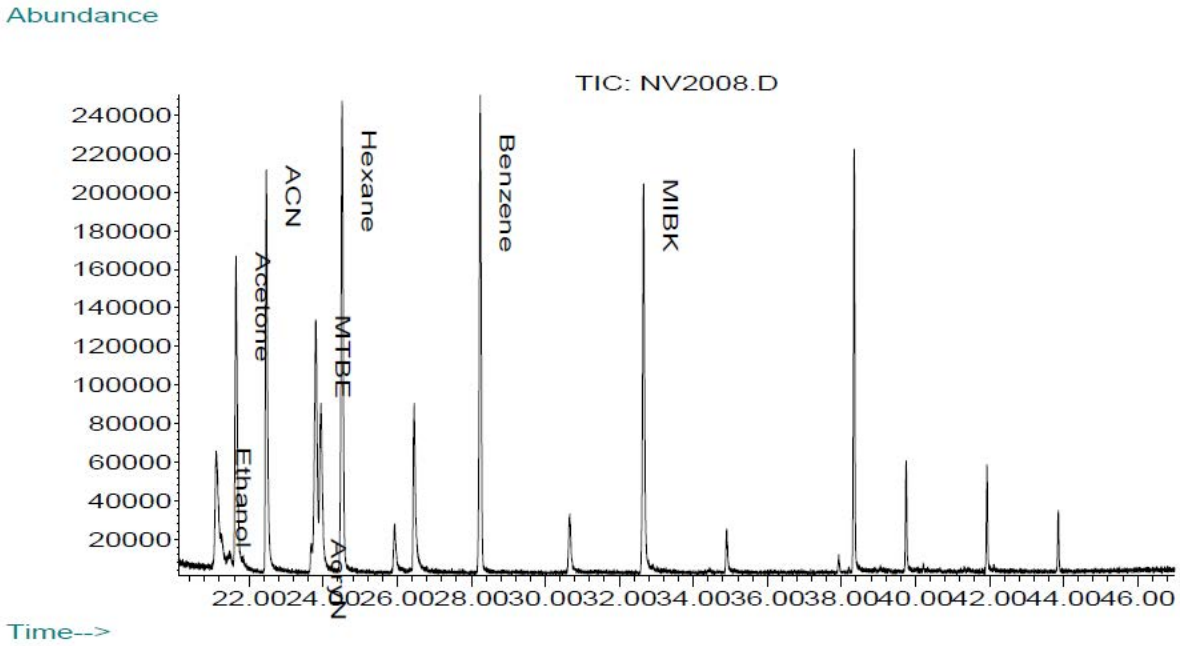


Figure 11: Typical Ambient Air TIC, Long Beach Sample.

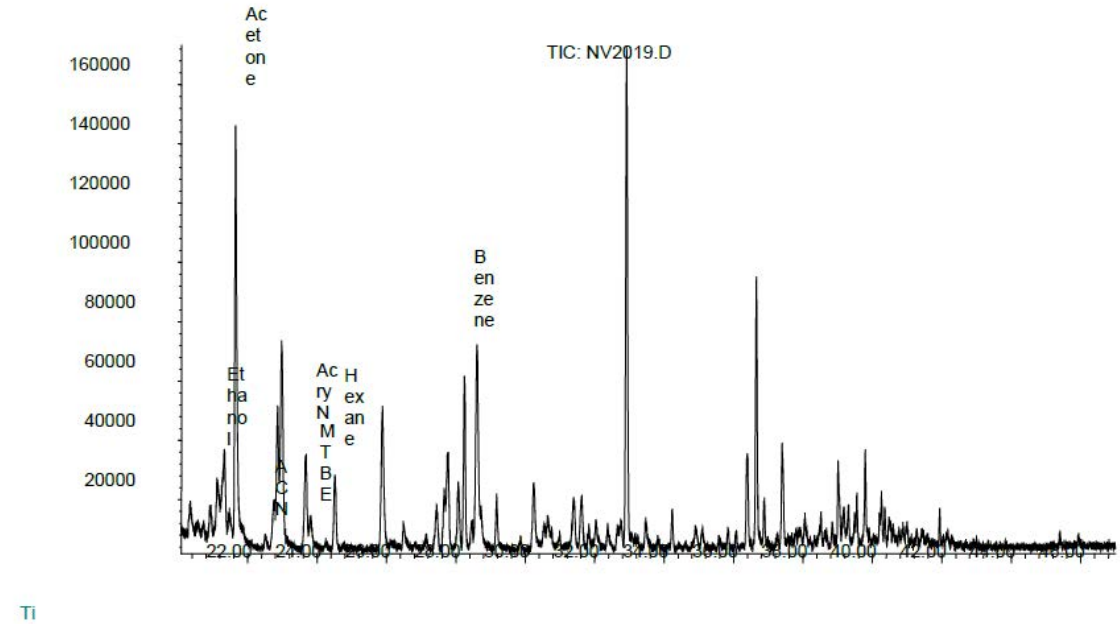


Figure 12: Typical Mass Spectrum, Acetone

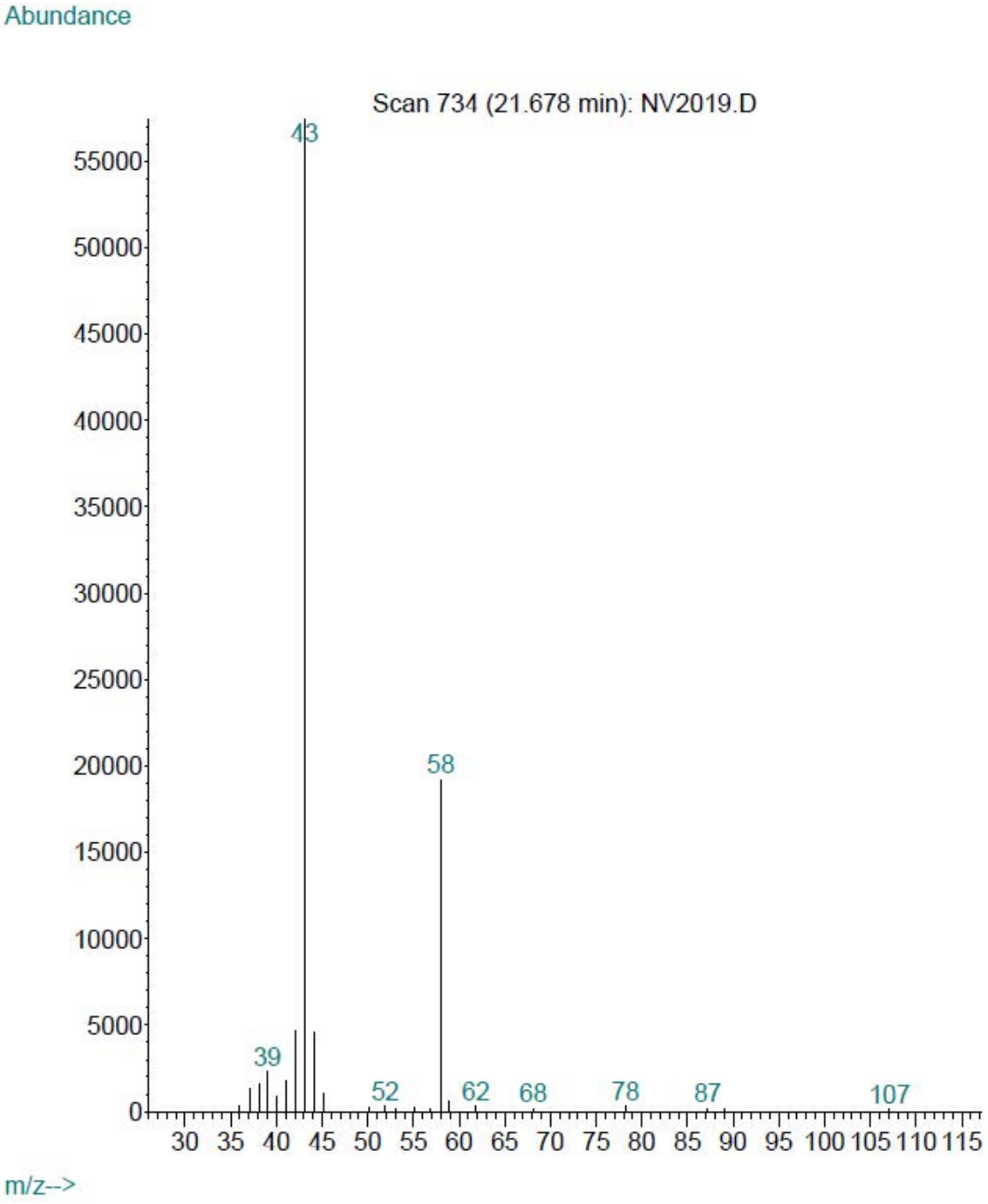


Figure 13: Acrolein Multipoint Analysis (10/22/03 – ALM069798
3.01 ppb

LEVELS OF CONCENTRATION (PPB)					
cc	**25**	**50**	**100**	**150**	**300**
ppb	**0.502**	**1.003**	**2.007**	**3.010**	**6.020**
1st Run	2725	5297	10963	16647	34836
2nd	2956	5660	10621	16159	34068
3rd	2574	5570	10353	15872	34279
Mean=	2752	5509	10646	16226	34394
Std.Dev.=	192	189	306	392	397
%RSD=	7.0	3.4	2.9	2.4	1.2
# Obs. =	3	3	3	3	3

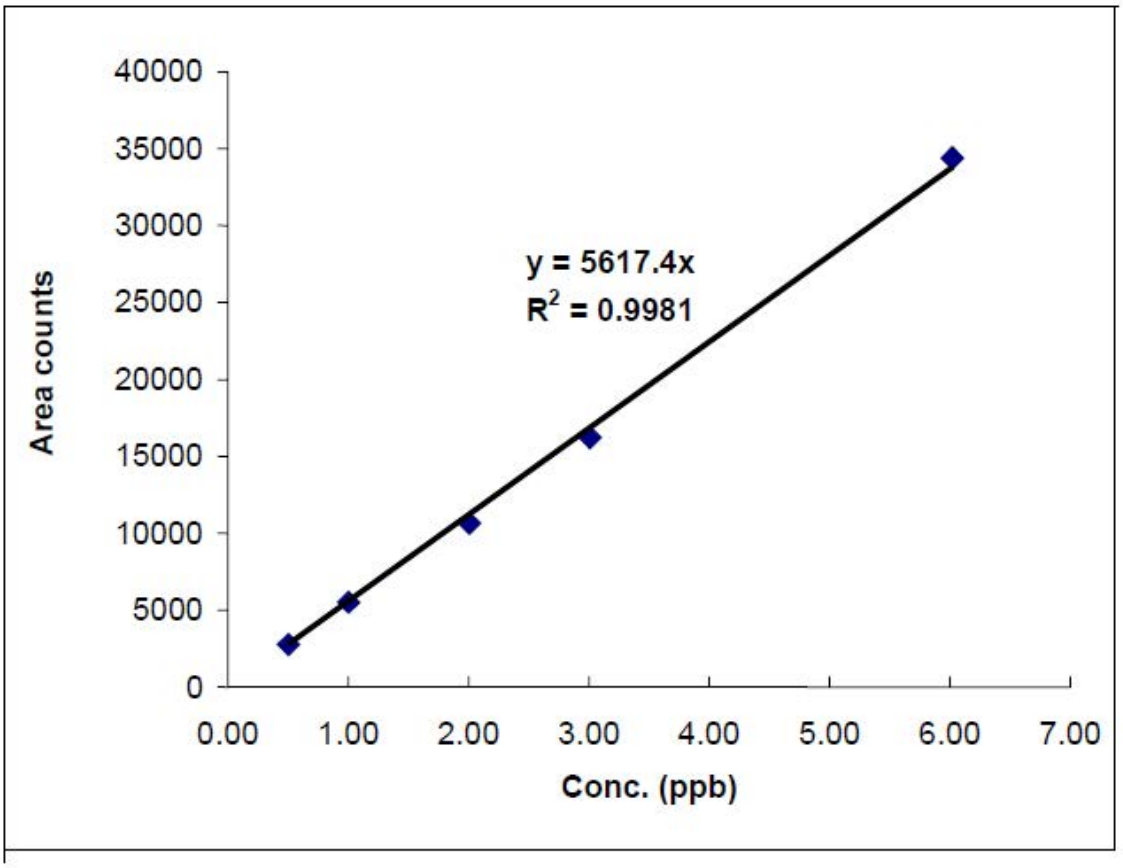


Figure 14: Ethanol Multipoint Analysis (03/11/03) – CC50604
30 ppb

LEVELS OF CONCENTRATION (PPB)					
cc	**25**	**50**	**150**	**200**	**300**
ppb	**5.000**	**10.000**	**30.000**	**40.000**	**60.000**
1st Run	29009	53893	153431	201777	308912
2nd	28321	50630	156982	189902	317477
3rd	28304	48100	160072	198264	328727
Mean=	28545	50874	156828	196648	318372
Std.Dev.=	402	2904	3323	6100	9938
%RSD=	1.4	5.7	2.1	3.1	3.1
# Obs. =	3	3	3	3	3

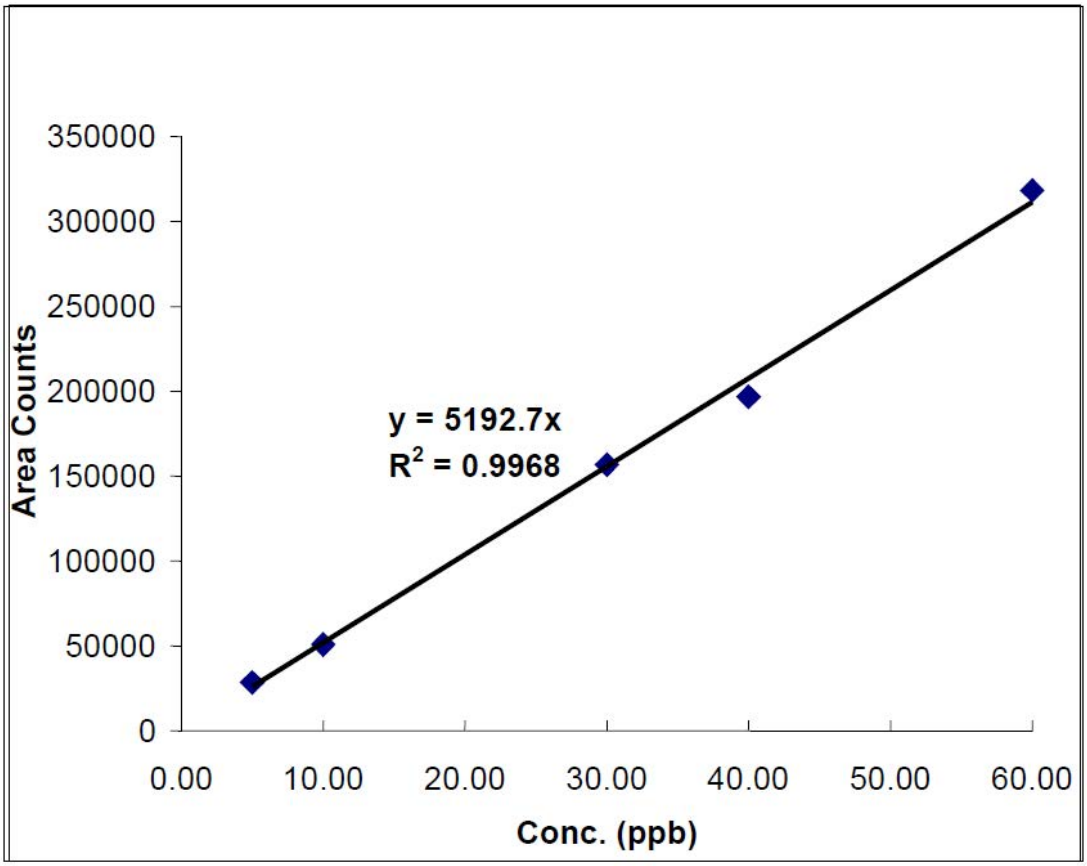


Figure 15: Acetone Multipoint Analysis (3/11/03) – CC50604
10.0 ppb

LEVELS OF CONCENTRATION (PPB)					
cc	**25**	**50**	**150**	**200**	**300**
ppb	**1.667**	**3.333**	**10.000**	**13.333**	**20.000**
1st Run	75092	135818	415917	592473	906216
2nd	71419	135000	418240	599978	910896
3rd	68762	133866	414744	590280	919560
Mean=	71758	134895	416300	594244	912224
Std.Dev.=	3179	980	1779	5086	6770
%RSD=	4.4	0.7	0.4	0.9	0.7
# Obs. =	3	3	3	3	3

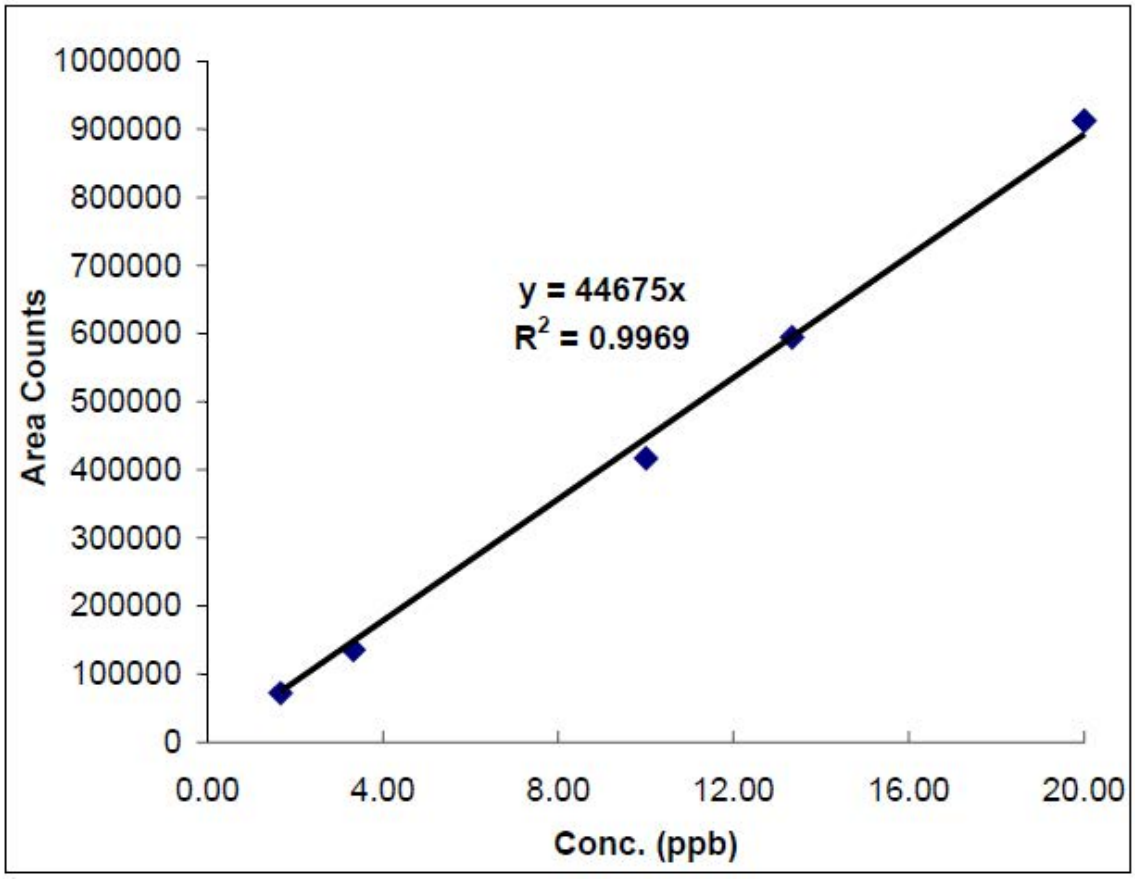


Figure 16: Acetonitrile Multipoint Analysis (3/11/03) – CC50604
15.0 ppb

LEVELS OF CONCENTRATION (PPB)					
cc	**25**	**50**	**150**	**200**	**300**
ppb	**2.500**	**5.000**	**15.000**	**20.000**	**30.000**
1st Run	65828	119753	358820	482681	739275
2nd	61177	120424	353132	490058	743130
3rd	58558	114277	364630	489153	752261
Mean=	61854	118151	358861	487297	744889
Std.Dev.=	3682	3372	5749	4023	6669
%RSD=	6.0	2.9	1.6	0.8	0.9
# Obs. =	3	3	3	3	3

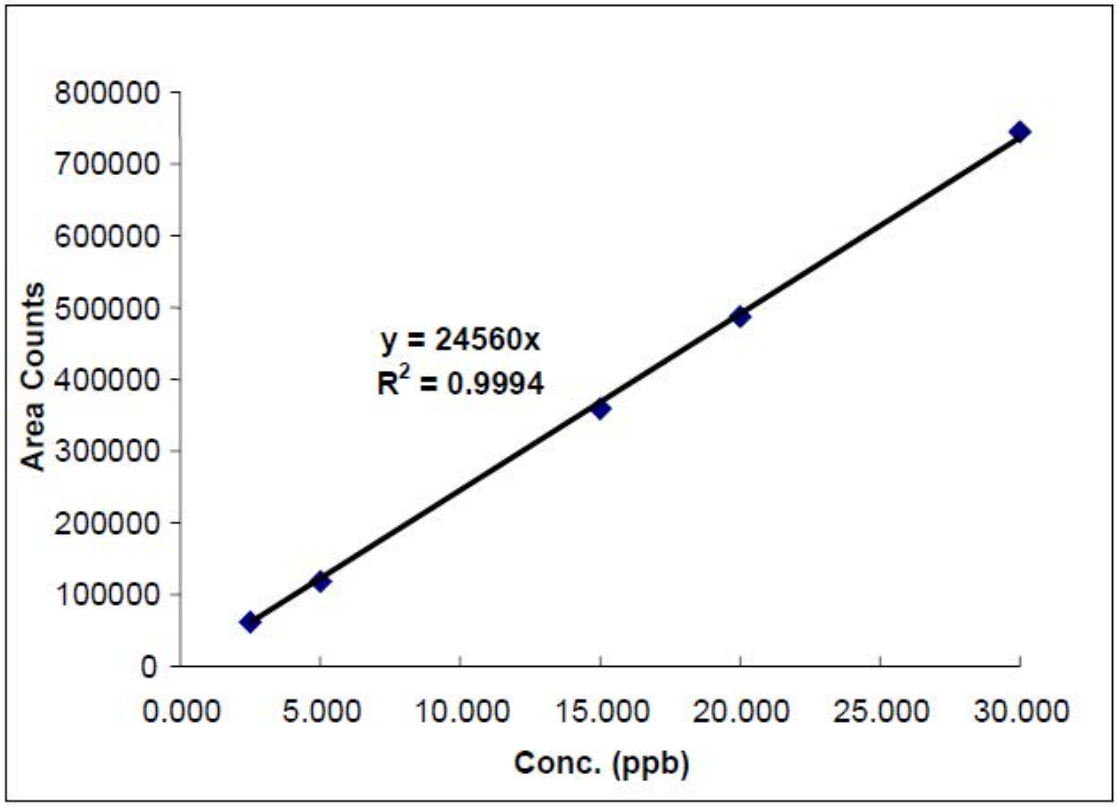


Figure 17: Acrylonitrile Multipoint Analysis (3/11/03) – CC50604
2.00 ppb

LEVELS OF CONCENTRATION (PPB)					
cc	**25**	**50**	**150**	**200**	**300**
ppb	**0.333**	**0.667**	**2.000**	**2.667**	**4.000**
1st Run	6721	8068	23069	29957	48953
2nd	5129	8131	22359	31677	49398
3rd	4565	7303	21673	31164	50342
Mean=	5472	7834	22367	30933	49564
Std.Dev.=	1118	461	698	883	709
%RSD=	20.4	5.9	3.1	2.9	1.4
# Obs. =	3	3	3	3	3

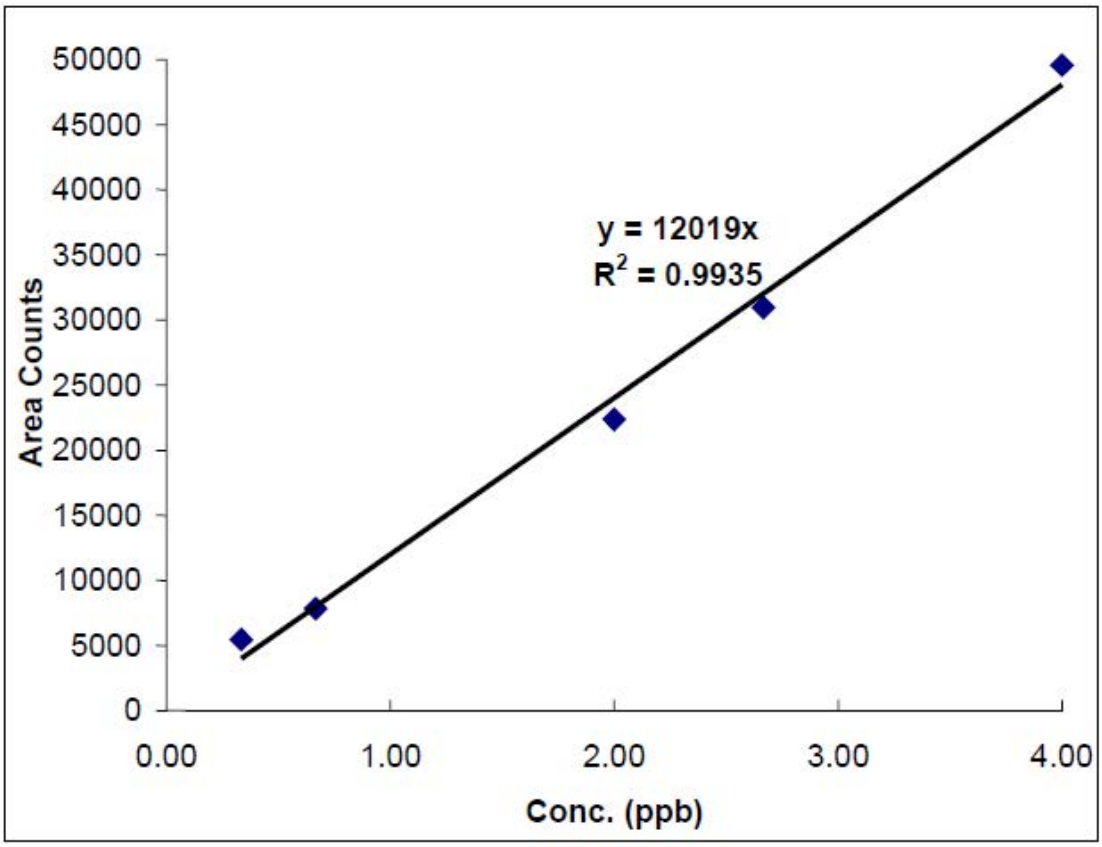


Figure 18: Acrolein Control Chart

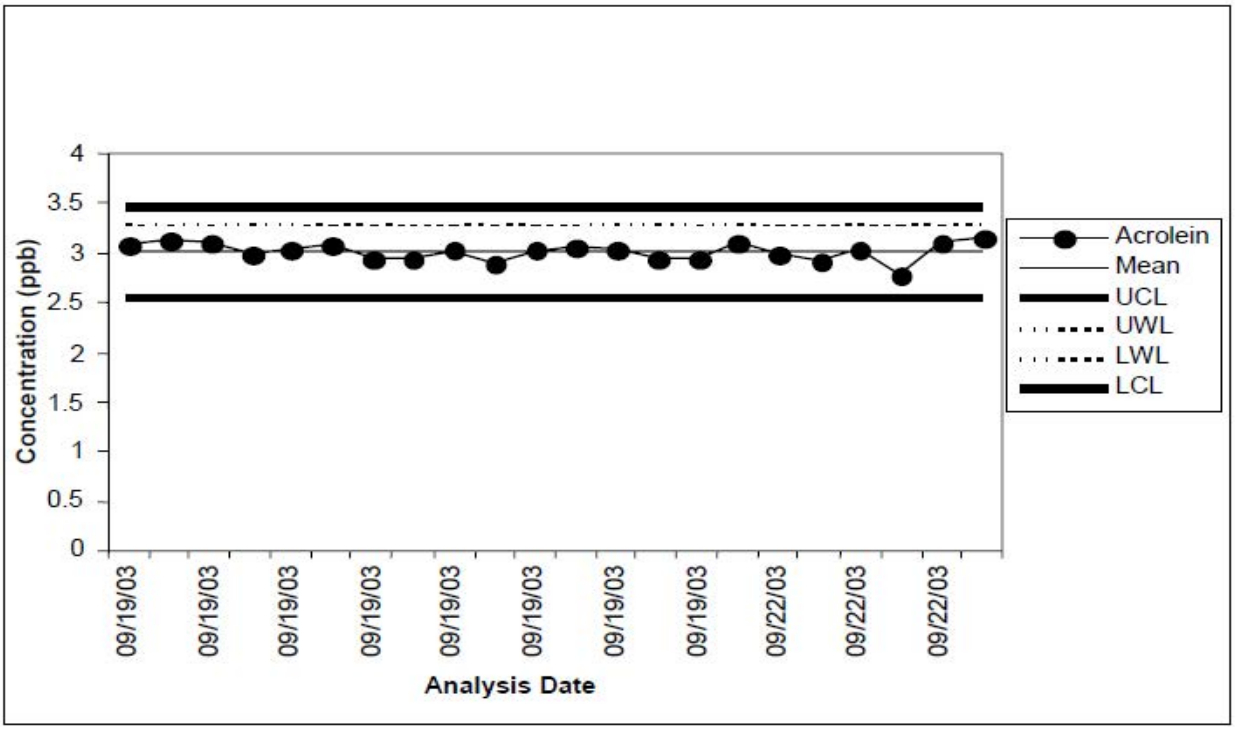


Figure 19: Ethanol Control Chart

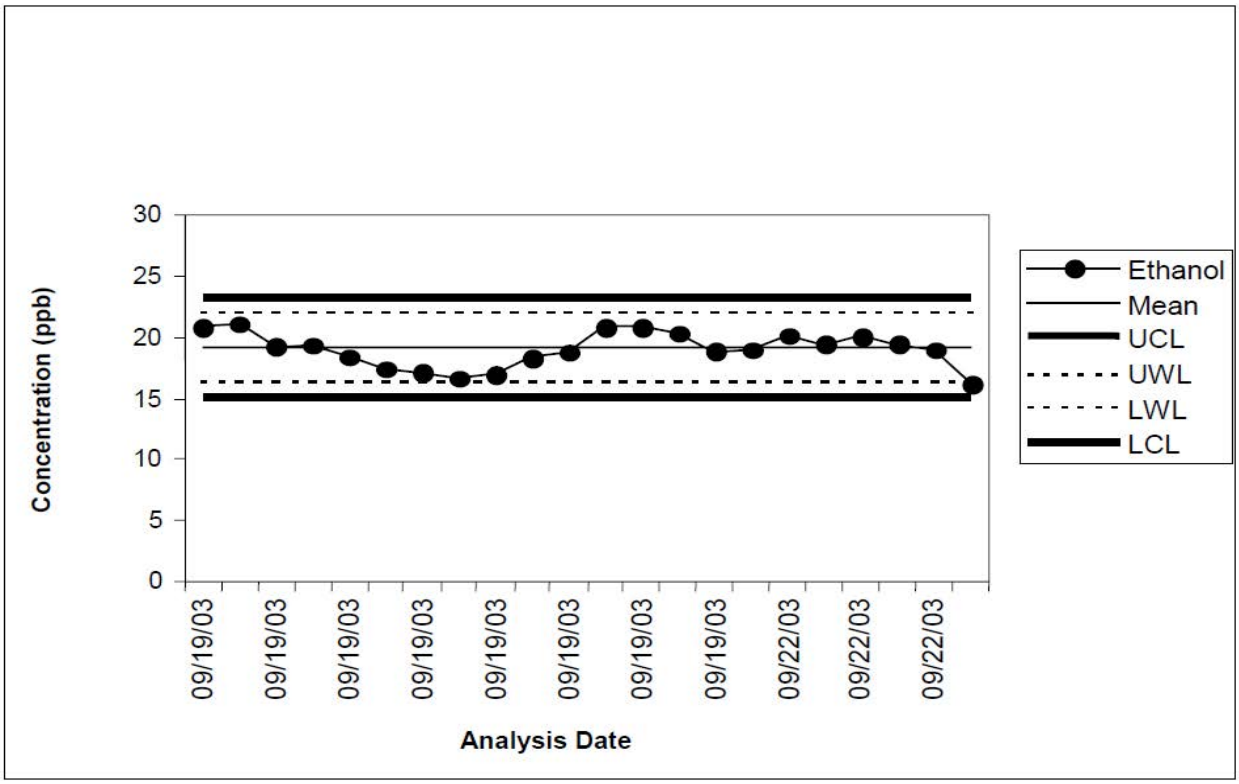


Figure 20: Acetone Control Chart

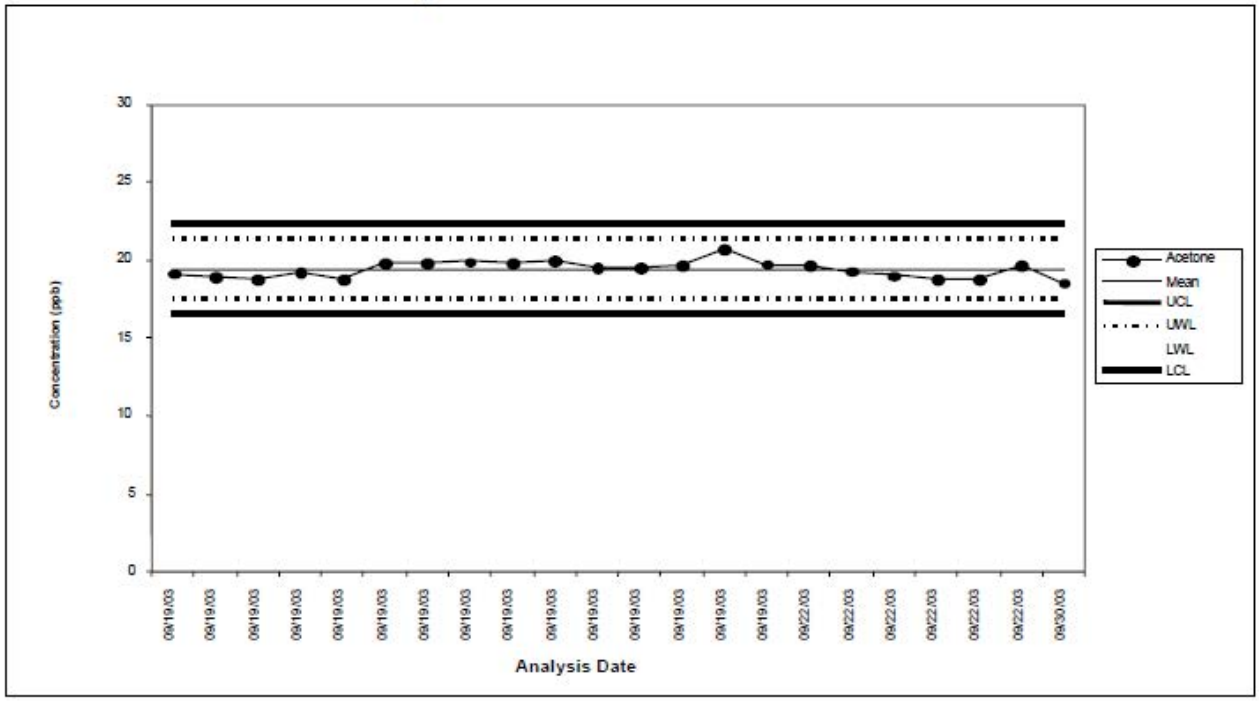


Figure 21: Acetonitrile Control Chart

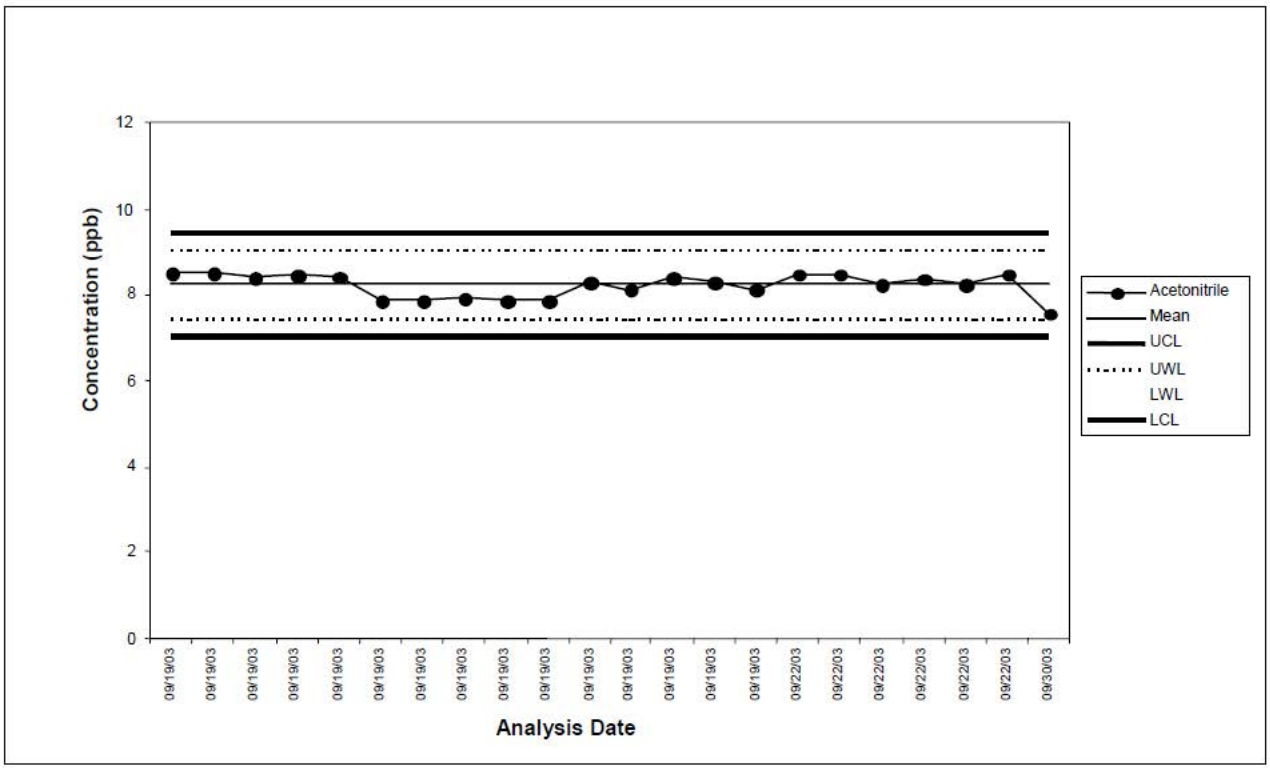
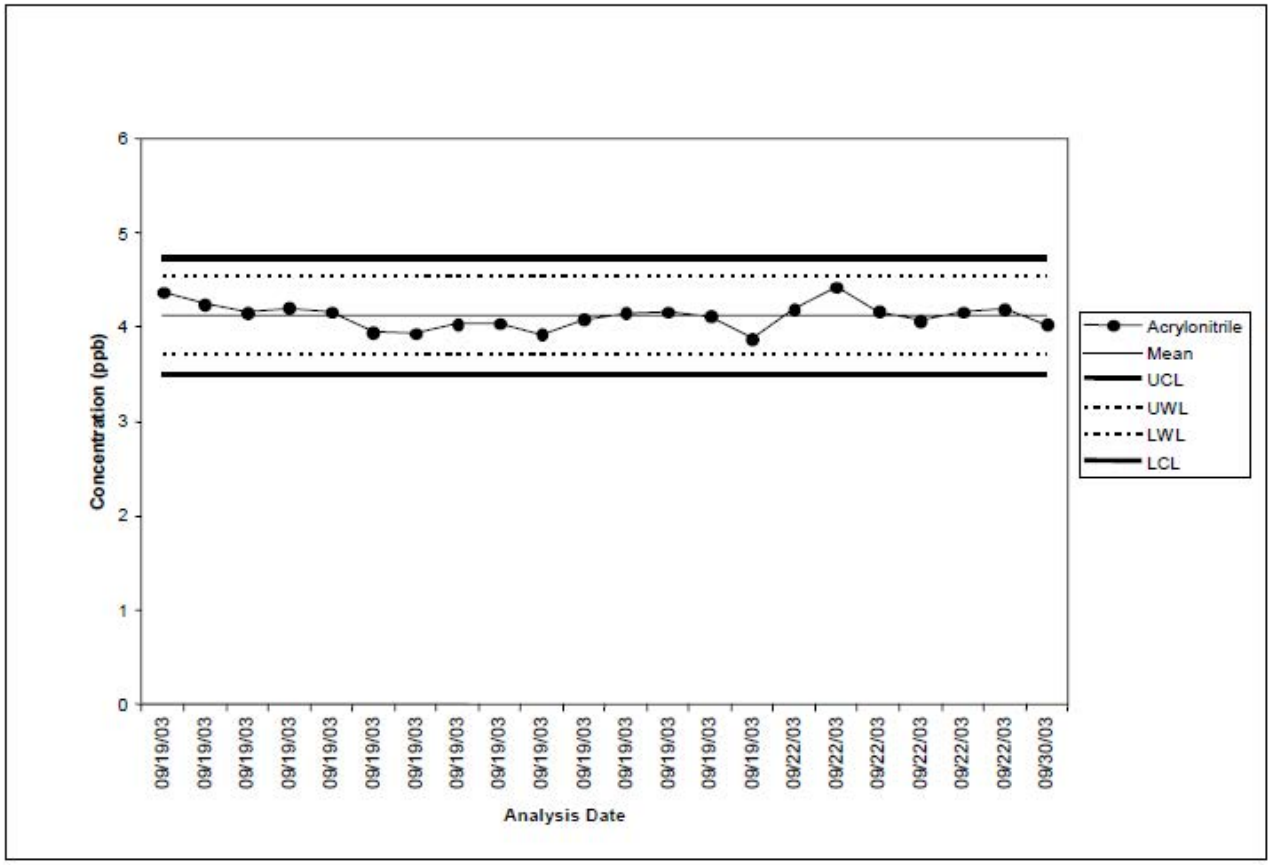


Figure 22: Acrylonitrile Control Chart



Appendix I: Additional Setpoints

He Carrier Gas:

Set Rear Type 3 Electronic Flow Controller to 1.2 cm^3/minute

N_2 Purge Gas:

Set digital gauge on Flow Controller to 16.0 (~ cm^3/minute)

He Purge Gas:

Set digital gauge on Flow Controller to 7.05 (~ cm^3/minute)

Nafion Dryer Purge:

Set digital gauge on Flow Controller to 7.05 (~ cm^3/minute)

Mass Flow Controller (MFC):

Set sampling flow rate to 50 cm^3/minute

Set .....50.1% of full scale
Read .....50.6% of full scale

Note: 100 cm^3/minute equals 100% full scale

Required Regulator Pressures:

He - Carrier Gas and Purge Gas .....60 psi

N_2 - Purge Gas and Nafion™ Dryer Gas.....60 psi

Appendix II: Target Analyte LODs and Highest Calibration Concentration

Target compound	Recommended Published LOD	Replicate LOD	Multipoint Analysis Data	
			Correlation coefficient,R	Linear range
Acrolein	0.30	0.14	0.999	6.
Ethanol	0.50	0.28	0.9984	60
Acetone	0.30	0.12	0.9984	20
Acetonitrile	0.30	0.12	0.9997	30
Acrylonitrile	0.30	0.05	0.9967	4

Appendix III: Varian Star Chromatography Workstation

A Varian GC Star Workstation includes an Intel compatible PC, an Ethernet network adapter, Microsoft 9.X or NT 4.0 operating system, and Varian Star Chromatography software, Version 5.51. The chromatography software operates under Microsoft Windows 9.X or Microsoft Windows NT 4.0. The Star Workstation automates control of the Varian/Lotus Sorbent Concentration and Cryofocuser System, including concentration of the sample, introduction of the concentrated sample onto the gas chromatographic column, and setting the column carrier gas flow. For a more detailed discussion of the Star Workstation software, including setting up methods, sequences, and sample lists, refer to the manuals on the “Varian Star Chromatography Workstation”, Version 5.51 CD-ROM and the “Varian Saturn GC/MS Workstation – System Software”, Version 5.51 CD-ROM. Additional resources are the “Ultra Trace Hydrocarbon System Operator’s Manual”, the “Stream Selector Valve Control Software for Varian Workstation Operator’s Manual”, and the "Varian GC Star Workstation Manual", all by Randall Bramston-Cook of Lotus Consulting.

A Hewlett-Packard ChemStation, running Hewlett-Packard Analytical MSD Productivity ChemStation Software, is used to automate the control of the Hewlett-Packard Model 6890 Gas Chromatograph with a Model 5973 Mass Selective Detector (MSD).

Each Gas Chromatograph (GC) serviced by the Star Chromatography Workstation is assigned a separate address. Each Workstation can be linked to a maximum of four (4) GCs. In a single GC environment, the Varian/Lotus 3800 Cryogenic Concentrator would normally have an address of 44. The instrument setpoints are stored on the Workstation as methods. Method MLD066S.MTH is used for normal operation. Other methods include IDLE66.MTH for system standby, SBAKEOUT.MTH for conditioning/bakeout of the system. They are used in automated sequences along with method MLD066S.

Copies of the current Star GC Chromatography Workstation analytical, idle and bakeout methods are listed. Although there are sections for data handling and reporting, they are not used in this analysis, and are shown in lighter type. Examples of a sample list and a sequence list are also shown.

Varian Star Workstation

```
Star Chromatography Workstation - Method Listing   Mon Dec 15
09:41:10 2003

Method: MLD066S.mth
********************************************************************************
3800 GC
**********************
Module Address: 44

Middle Valve Oven
-----------------
      Oven Power: On
     Temperature: 120 C

Rear Valve Oven
-----------------
      Oven Power: On
     Temperature: 50 C

Valve Table
-----------
     Valve 1: Sample Valve
             Initial: Off
            0.01 min: On
            2.00 min: On
            3.00 min: On
            4.00 min: On
            5.00 min: Off
           11.00 min: Off
           14.00 min: Off
           14.90 min: Off
           15.00 min: Off
           20.00 min: Off

     Valve 2: Sample Preconcentration Trap Valve
             Initial: SPT Desorb
            0.01 min: SPT Desorb
            2.00 min: SPT Trap
            3.00 min: SPT Trap
            4.00 min: SPT Trap
            5.00 min: SPT Trap
           11.00 min: SPT Desorb
           14.00 min: SPT Desorb
           14.90 min: SPT Desorb
           15.00 min: SPT Desorb
           20.00 min: SPT Desorb
```

```
Valve 3: Sample Preconcentration Trap Valve
        Initial: SPT Desorb
       0.01 min: SPT Desorb
       2.00 min: SPT Desorb
       3.00 min: SPT Desorb
       4.00 min: SPT Desorb
       5.00 min: SPT Desorb
      11.00 min: SPT Desorb
      14.00 min: SPT Desorb
      14.90 min: SPT Trap
      15.00 min: SPT Trap
      20.00 min: SPT Desorb

Valve 4: Series Bypass Valve
        Initial: Series
       0.01 min: Series
       2.00 min: Series
       3.00 min: Series
       4.00 min: Series
       5.00 min: Series
      11.00 min: Series
      14.00 min: Bypass
      14.90 min: Bypass
      15.00 min: Series
      20.00 min: Series

Valve 5: Event A Valve
        Initial: Off
       0.01 min: Off
       2.00 min: Off
       3.00 min: On
       4.00 min: Off
       5.00 min: Off
      11.00 min: Off
      14.00 min: Off
      14.90 min: Off
      15.00 min: Off
      20.00 min: Off

Valve 6: Event B Valve
        Initial: Off
       0.01 min: Off
       2.00 min: Off
       3.00 min: Off
       4.00 min: Off
```

```
             5.00 min: Off
            11.00 min: Off
            14.00 min: Off
            14.90 min: Off
            15.00 min: Off
            20.00 min: Off

     Valve 7: Event C Valve
             Initial: Off
            0.01 min: Off
            2.00 min: Off
            3.00 min: Off
            4.00 min: Off
            5.00 min: Off
           11.00 min: Off
           14.00 min: Off
           14.90 min: Off
           15.00 min: Off
           20.00 min: Off

 Front Injector Type 1079
------------------------
            Oven Power: On
               Coolant: On
     Enable Coolant at: 300 C
       Coolant Timeout: 20.00 min

     Temp     Rate       Hold      Total
      (C)    (C/min)    (min)      (min)
     --------------------------------
      125        0      11.00      11.00
      325      200      28.00      40.00

Middle Injector Type 1079
------------------------
            Oven Power: On
               Coolant: On
     Enable Coolant at: 300 C
       Coolant Timeout: 20.00 min

     Temp     Rate       Hold      Total
      (C)    (C/min)    (min)      (min)
     --------------------------------
      200        0       3.00       3.00
      -30      200       9.85      14.00
```

```
     325      200      24.23      40.00

  Rear Injector Type 1041
-------------------------
      Oven Power: On
     Temperature: 150 C

  Rear Injector EFC Type 3
--------------------------
     Flow     Rate       Hold      Total
 (ml/min) (ml/min/min) (min)      (min)
 ------------------------------------
      2.0      0.0      45.00      45.00

Column Oven

               Coolant: Off
     Enable Coolant at: 50 C
       Coolant Timeout: 20.00 min
    Stabilization Time: 0.50 min

     Temp     Rate       Hold      Total
      (C)    (C/min)    (min)      (min)
     --------------------------------
       50      0.0      48.00      48.00

 Front FID Detector
-------------------
      Oven Power: Off
     Temperature: 50 C
     Electronics: On
   Time Constant: Fast

      Time     Range  Autozero
      (min)
      ----------------------
    Initial    12       no

Output Port A
--------------
      Time     Signal    Attenuation
      (min)    Source
      ---------------------------
    Initial    Front           1
```

Varian Star Workstation

```
Output Port B
-------------
      Time    Signal   Attenuation
      (min)   Source
      ---------------------------
    Initial    Front          1

Output Port C
-------------
      Time    Signal   Attenuation
      (min)   Source
      ---------------------------
    Initial    Front          1

Data Acquisition
----------------
      Detector Bunch Rate : 128 points (0.3 Hz)
           Monitor Length : 16 bunched points (51.2 sec)
       Front FID/TSD Scale: 1 Volts
      Middle FID/TSD Scale: 1 Volts
        Rear FID/TSD Scale: 1 Volts
```

Varian Star Workstation

```
 Star Chromatography Workstation - Method Listing   Mon Dec 15
09:43:53 2003

Method: idle66.mth
**********************
    3800 GC
**********************
Module Address: 44

Middle Valve Oven
-----------------
      Oven Power: On
     Temperature: 120 C

  Rear Valve Oven
-----------------
      Oven Power: On
     Temperature: 50 C

Valve Table
-----------
     Valve 1: Sample Valve
             Initial: Off
            0.20 min: Off
           15.00 min: Off
           15.10 min: Off

     Valve 2: Sample Preconcentration Trap Valve
             Initial: SPT Desorb
            0.20 min: SPT Desorb
           15.00 min: SPT Desorb
           15.10 min: SPT Desorb

     Valve 3: Sample Preconcentration Trap Valve
             Initial: SPT Desorb
            0.20 min: SPT Desorb
           15.00 min: SPT Desorb
           15.10 min: SPT Desorb

     Valve 4: Series Bypass Valve
             Initial: Series
            0.20 min: Series
           15.00 min: Series
           15.10 min: Series
```

Varian Star Workstation

```
     Valve 5: Event A Valve
              Initial: Off
             0.20 min: On
            15.00 min: Off
            15.10 min: Off

     Valve 6: Event B Valve
              Initial: Off
             0.20 min: Off
            15.00 min: Off
            15.10 min: Off

     Valve 7: Event C Valve
              Initial: Off
             0.20 min: Off
            15.00 min: Off
            15.10 min: Off

 Front Injector Type 1079
-------------------------
              Oven Power: On
                 Coolant: On
     Enable Coolant at: 250 C
       Coolant Timeout: 20.00 min

     Temp     Rate       Hold      Total
      (C)    (C/min)    (min)      (min)
     --------------------------------
      180        0       0.20       0.20

Middle Injector Type 1079
-------------------------
              Oven Power: On
                 Coolant: On
     Enable Coolant at: 250 C
       Coolant Timeout: 20.00 min

     Temp     Rate       Hold      Total
      (C)    (C/min)    (min)      (min)
     --------------------------------
      200        0       0.10       0.10


Rear Injector Type 1041
-----------------------
```

Varian Star Workstation

```
      Oven Power: On
     Temperature: 150 C

Rear Injector EFC Type 3
-------------------------
     Flow    Rate       Hold      Total
 (ml/min) (ml/min/min) (min)      (min)
 ----------------------------------------
      2.0      0.0       1.00       1.00

Column Oven
-----------
               Coolant: Off
     Enable Coolant at: 50 C
       Coolant Timeout: 20.00 min
    Stabilization Time: 0.10 min

     Temp     Rate       Hold      Total
      (C)   (C/min)    (min)      (min)
     --------------------------------
       50      0.0      45.00      45.00

 Front FID Detector
-------------------
      Oven Power: Off
     Temperature: 50 C
     Electronics: Off
   Time Constant: Fast

      Time     Range  Autozero
      (min)
      ----------------------
    Initial     12      yes

Output Port A
--------------
      (min)   Source
      ---------------------------
    Initial    Front          1



Output Port B
--------------
      Time    Signal   Attenuation
```

Varian Star Workstation

```
      (min)    Source
      ----------------------------
    Initial    Front          1

Output Port C
-------------
      Time     Signal   Attenuation
      (min)    Source
      ----------------------------
    Initial    Front          1

Data Acquisition
----------------
      Detector Bunch Rate : 4 points (10.0 Hz)
           Monitor Length : 64 bunched points (6.4 sec)
       Front FID/TSD Scale: 1 Volts
      Middle FID/TSD Scale: 1 Volts
        Rear FID/TSD Scale: 1 Volts
```

Varian Star Workstation

```
Star Chromatography Workstation - Method Listing   Mon Dec 15
09:42:41 2003

Method: SBAKEOUT.mth
*************
    Notes
*************
THIS IS A 20 MIN RUN TO CONDITION THE VARIAN3800 STAR ATD SYATEM
BEFORE AN ANALYTICAL METHOD IS ACTIVATED TO RUN A SAMPLE LIST.
**********************
    3800 GC
**********************
Module Address: 44

Middle Valve Oven
-----------------
      Oven Power: On
     Temperature: 120 C

  Rear Valve Oven
-----------------
      Oven Power: On
     Temperature: 50 C

Valve Table
-----------
     Valve 1: Sample Valve
              Initial: Off
             1.00 min: Off
            20.00 min: Off

     Valve 2: Sample Preconcentration Trap Valve
              Initial: SPT Desorb
             1.00 min: SPT Desorb
            20.00 min: SPT Desorb

     Valve 3: Sample Preconcentration Trap Valve
              Initial: SPT Desorb
             1.00 min: SPT Desorb
            20.00 min: SPT Desorb

     Valve 4: Series Bypass Valve
              Initial: Series
             1.00 min: Series
            20.00 min: Series
```

```
     Valve 5: Event A Valve
             Initial: Off
            1.00 min: On
           20.00 min: Off

     Valve 6: Event B Valve
             Initial: Off
            1.00 min: Off
           20.00 min: Off

     Valve 7: Event C Valve
             Initial: Off
            1.00 min: Off

 Front Injector Type 1079
-------------------------
              Oven Power: On
                 Coolant: On
     Enable Coolant at: 250 C
       Coolant Timeout: 20.00 min

     Temp     Rate       Hold      Total
      (C)    (C/min)    (min)      (min)
     --------------------------------
      325        0      20.00      20.00

Middle Injector Type 1079
-------------------------
              Oven Power: On
                 Coolant: On
     Enable Coolant at: 250 C
       Coolant Timeout: 20.00 min

     Temp     Rate       Hold      Total
      (C)    (C/min)    (min)      (min)
     --------------------------------
      325        0      20.00      20.00

Rear Injector Type 1041
-----------------------
      Oven Power: On
     Temperature: 150 C

Rear Injector EFC Type 3
------------------------
```

Flow (ml/min)	Rate (ml/min/min)	Hold (min)	Total (min)
2.0	0.0	20.00	20.00

Column Oven

Coolant: Off
Enable Coolant at: 50 C
Coolant Timeout: 20.00 min
Stabilization Time: 0.10 min

Temp (C)	Rate (C/min)	Hold (min)	Total (min)
50	0.0	20.00	20.00

Front FID Detector

Oven Power: Off
Temperature: 50 C
Electronics: Off
Time Constant: Fast

Time (min)	Range	Autozero
Initial	12	no

Output Port A

Time (min)	Signal Source	Attenuation
Initial	Front	1

Output Port B

Time (min)	Signal Source	Attenuation
Initial	Front	1

Varian Star Workstation

```
Output Port C
-------------
      Time     Signal    Attenuation
      (min)    Source
      ----------------------------
    Initial     Front           1

Data Acquisition
----------------
      Detector Bunch Rate : 4 points (10.0 Hz)
           Monitor Length : 64 bunched points (6.4 sec)
       Front FID/TSD Scale: 1 Volts
      Middle FID/TSD Scale: 1 Volts
        Rear FID/TSD Scale: 1 Volts
```

Varian Star Workstation

```
Varian Star Workstation - Generic SampleList  Mon Dec 15
09:46:23 2003

SampleList:   C:\Star\data\DEC0403.smp

Created:      Thu Dec 04 13:52:08 2003
Modified:     Fri Dec 05 09:47:56 2003
```

Amount Line	Sample Type	Sample Name	Inj.	AutoLink	Standard
1	AutoLink	c:\star\ssvauto.exe Other parameters: -i			
2	Analysis	BLANK	1	below	1
	AutoLink	Command c:\star\ssvauto.exe			
3	Activate Method	C:\Star\METHODS\MLD066S25cc.mth			
4	Analysis	AAL069919#1054	1	below	2
	AutoLink	Command c:\star\ssvauto.exe			
5	Analysis	CC50604 25CC #1061	1	below	3
	AutoLink	Command c:\star\ssvauto.exe			
6	Activate Method	C:\Star\METHODS\MLD066S50cc.mth			
7	Analysis	CC50604 50CC	1	below	3
	AutoLink	Command c:\star\ssvauto.exe			
8	Activate Method	C:\Star\METHODS\MLD066S75cc.mth			
9	Analysis	CC50604 75CC	1	below	3
	AutoLink	Command c:\star\ssvauto.exe			
10	Activate Method	C:\Star\METHODS\MLD066S100.mth			
11	Analysis	CC50604 100CC	1	below	3
	AutoLink	Command c:\star\ssvauto.exe			
12	Activate Method	C:\Star\METHODS\MLD066S.mth			
13	Analysis	CC50604 150CC	1	below	3
	AutoLink	Command c:\star\ssvauto.exe			

```
14          Analysis     ALM069798 #1072     1     below              4
            AutoLink  Command c:\star\ssvauto.exe
15          Analysis           5669BFREG     1     below              5
            AutoLink  Command c:\star\ssvauto.exe
16          Analysis           5670BFCOL     1     below              6
17          Analysis           5671RUREG     1     below              7
            AutoLink  Command c:\star\ssvauto.exe
18          Analysis           5672RUCOL     1     below              8
            AutoLink  Command c:\star\ssvauto.exe
19          Analysis              5673RS     1     below              9
            AutoLink  Command c:\star\ssvauto.exe
20          Analysis              5674CX     1     below             11
            AutoLink  Command c:\star\ssvauto.exe
21          Analysis              5675CV     1     below             12
            AutoLink  Command c:\star\ssvauto.exe
22          Analysis           5654BFREG     1     below             13
            AutoLink  Command c:\star\ssvauto.exe
23          Analysis           5655BFCOL     1     below             14
            AutoLink  Command c:\star\ssvauto.exe
24   Activate Method  C:\Star\METHODS\MLD066S25cc.mth
25          Analysis      5642SV RR 25CC     1     below             10
            AutoLink  Command c:\star\ssvauto.exe
26   Activate Method  C:\Star\METHODS\MLD066S.mth
27          Analysis            5669DUP     1     below              5
            AutoLink  Command c:\star\ssvauto.exe
                      AutoLink  Command c:\star\ssvauto.exe
```

Varian Star Workstation

```
Varian Star Workstation - Sequence Listing  Mon Dec 15 09:47:38
2003

Sequence:     C:\Star\voc.seq

Created:      Wed Aug 13 12:32:26 2003
Modified:     Fri Dec 05 10:41:12 2003

********************************************************************************
   Line            Action            Method

   ====            ======            ======

     1             Inject            c:\star\methods\sbakeout.mth
     2             Inject            c:\star\methods\mld066s.mth
     3  Print Message Log
     4             Inject            c:\star\methods\idle66.mth
```

Appendix IV: Hewlett-Packard GC/MS ChemStation

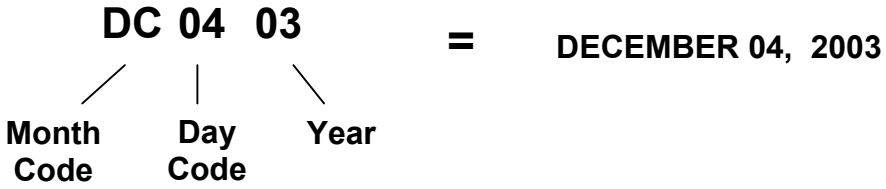
A Hewlett-Packard GC/MS ChemStation includes an Intel compatible PC, an Ethernet network adapter, a GPIB interface card, Microsoft 9.X or NT 4.0 operating system, and Hewlett-Packard Analytical MSD Productivity ChemStation Software, Version A.03.00 or B.03.00. The A software operates under Microsoft Windows 9.X, and the B operates under Microsoft Windows NT 4.0. They are functionally equivalent.

The Hewlett-Packard ChemStation automates control of the Hewlett-Packard Model 6890 Gas Chromatograph and it's associated Model 5973 Mass Selective Detector (MSD). This includes controlling the temperature of the GC column oven, the GC to MSD transfer line, and all operating and data acquisition parameters of the MSD. This software is also used for the analysis and reporting of the acquired MS data. For a more detailed discussion of the ChemStation software, including setting up methods, sequences, and sample lists, and data analysis, refer to the manuals, on the CD-ROM, “HP 5973 MSD Reference Collection”, Revision C.00.00, by Hewlett-Packard. A Varian Star GC Chromatography Workstation, running Varian Star Chromatography software, is used to automate the control of the Lotus/Varian 3800 Concentrator.

The instrument setpoints are stored on the ChemStation as methods. Method MLD066.M is used for normal operation. Method IDLE.M and IDLE1 are used for system standby and bakeout steps. Both methods are used in automated sequences. Method MLD066.M also includes data handling and reporting sections.

A copy of the current Hewlett-Packard ChemStation analytical and idle methods, including sections for data handling and reporting, are listed. An example SAMPLE.S sequence list screen is also shown.

The analytical data files collected by the Hewlett-Packard ChemStation are named in the following manner:



The applicable month codes are:

January	=	JA	May	=	MY	September	=	SE
February	=	FB	June	=	JN	October	=	OC
March	=	MR	July	=	JL	November	=	NV
April	=	AP	August	=	AG	December	=	DC

HP GC/MS Chemstation

```
Method Information For: C:\HPCHEM\1\METHODS\MLD066.M

Method Sections To Run:

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

Method Comments:
  This is a method for the analysis of ambient air for
OXYGENATES, ACETONITRILE AND ACRYLONITRILE.


                        END OF TOPLEVEL PARAMETERS
                        --------------------------
                        INSTRUMENT CONTROL PARAMETERS
                        -----------------------------
Sample Inlet:       GC
Injection Source:   External Device
Injection Location: Front
Mass Spectrometer:  Enabled

================================================================
                              HP6890 GC METHOD
================================================================

OVEN
   Initial temp:  60 'C (On)        Maximum temp:  260 'C
   Initial time:  8.00 min          Equilibration time:  0.50 min
   Ramps:
      #  Rate  Final temp Final time  CRYO (N2)
      1 40.00       -20       4.00     Cryo:  On
      2  5.00        80       0.00     Cryo fault: On
      3 10.00       200       2.00    Cryo timeout: 60.00 min (On)
      4  0.0(Off)                     Quick cryo cool:  On

   Post temp:  0 'C                   Ambient temp:  55 'C
   Post time:  0.00 min
   Run time:  48.00 min

FRONT INLET (HP PTV)              BACK INLET (SPLIT/SPLITLESS)
   Mode:  Split                    Mode:  Split
   Initial temp:  50 'C (Off)      Initial temp:  50 'C (Off)
```

```
   Cryo:  On                          Pressure:  0.00 psi (Off)
   Cryo use temp:  25 'C              Total flow:  45.0 mL/min
   Cryo Timeout:  30.00 min (On)      Gas saver:  Off
   Cryo Fault:  On                    Gas type:  Helium
   Pressure:  1.10 psi (Off)
   Split ratio:  50:1
   Split flow:  61.3 mL/min
   Total flow:  65.7 mL/min
   Gas saver:  Off
   Gas type:  Helium

COLUMN 1                              COLUMN 2
   Capillary Column                   (not installed)
   Model Number:  J & W DB-624
   30m x 0.32 mm i.d. and 1.8 um thick
   Max temperature:  260 'C
   Nominal length:  30.0 m
   Nominal diameter:  320.00 um

Method: MLD066.M              Mon Dec 15 09:52:18 2003
Page: 1
   Mode:  constant pressure
   Pressure:  1.10 psi
   Nominal initial flow:  1.2 mL/min
   Average velocity:  41 cm/sec
   Inlet:  Front Inlet
   Outlet:  MSD
   Outlet pressure:  vacuum

FRONT DETECTOR (NO DET)                BACK DETECTOR (NO DET)

SIGNAL 1                               SIGNAL 2
   Data rate:  20 Hz                      Data rate:  20 Hz
   Type:  test plot                       Type:  test plot
   Save Data:  Off                        Save Data:  Off
   Zero:  0.0 (Off)                       Zero:  0.0 (Off)
   Range:  0                              Range:  0
   Fast Peaks:  Off                       Fast Peaks:  Off
   Attenuation:  0                     Attenuation:  0

COLUMN COMP 1                          COLUMN COMP 2
   (No Detectors Installed)          (No Detectors Installed)

THERMAL AUX 2
   Use:  MSD Transfer Line Heater
```

```
    Description:  MSD
   Initial temp:  280 'C (On)
   Initial time:  0.00 min
      #  Rate  Final temp  Final time
      1   0.0(Off)
                                          POST RUN
                                            Post Time: 0.00 min
TIME TABLE
   Time       Specifier                   Parameter & Setpoint

                          7673 Injector

     Front Injector:
No parameters specified

     Back Injector:
        Sample Washes                 0
        Sample Pumps                  0
        Injection Volume            1.0 microliters
        Syringe Size               10.0 microliters
        PostInj Solvent A Washes      0
        PostInj Solvent B Washes      0
        Viscosity Delay               0 seconds
        Plunger Speed              Fast
        PreInjection Dwell         0.00 minutes
        PostInjection Dwell        0.00 minutes
```

MS ACQUISITION PARAMETERS

```
General Information
------- -----------
Tune File                : ATUNE.U
Acquistion Mode          : Scan

MS Information
-- -----------
Solvent Delay            : 20.00 min
EM Absolute              : False
EM Offset                : 106
Resulting EM Voltage     : 2435.3

Low Mass                 : 33
High Mass                : 200
Threshold                : 150
Sample #                 : 2       A/D Samples    4
```

HP GC/MS Chemstation

```
[MSZones]

MS Quad                    : 150 C   maximum 200 C
MS Source                  : 230 C   maximum 250 C
Timed Events
----- ------
[Timed MS Detector Entries]

Time (min)           State (MS on/off)
47.00                     Off


                        END OF MS ACQUISITION PARAMETERS
                      END OF INSTRUMENT CONTROL PARAMETERS
                        ---------------------------------


                        DATA ANALYSIS PARAMETERS
                        ------------------------

Method Name: C:\HPCHEM\3\METHODS\MLD066.M

Percent Report Settings
-----------------------
Sort By: Retention Time
Output Destination
    Screen:  No
    Printer: Yes
    File:    No

Integration Events: Meth Default
Generate Report During Run Method:  No

Signal Correlation Window: 0.020

Qualitative Report Settings
---------------------------
Peak Location of Unknown: Apex

Library to Search      Minimum Quality
C:\DATABASE\NIST98.L    0

Integration Events: RTEINT.p

Report Type: Summary
```

HP GC/MS Chemstation

```
Output Destination
    Screen:  No
    Printer: Yes
    File:    No

Generate Report During Run Method:  No

Quantitative Report Settings
----------------------------
Report Type: Summary

Output Destination
    Screen:  Yes
    Printer: No
    File:    No

Generate Report During Run Method:  Yes

Analysis Method for Oxygenates
Calibration Last Updated: Mon Dec 08 09:16:24 2003

Reference Window: 10.00 Percent
Non-Reference Window: 5.00 Percent
Correlation Window: 0.02 minutes
Default Multiplier: 1.00
Default Sample Concentration: 0.00

Compound Information
```

```
 1)  Acrolein                                        ( )
Ret. Time  21.04 min., Extract & Integrate from  20.84 to  21.24
min.
Signal       Rel Resp.   Pct. Unc.(abs)    Integration
Tgt   56.00                              *** METH DEFAULT ***
Q1    55.00     72.90       20.0         *** METH DEFAULT ***
Lvl ID   Conc (ppbv)  Response
1            9.120        72782
2        not used for this compound
3        not used for this compound
4        not used for this compound
5        not used for this compound
Qualifier Peak Analysis ON
Curve Fit: Linear, forced through origin
```

```
------------
```

```
 2)  Ethanol                                          ( )
Ret. Time  21.10 min., Extract & Integrate from  20.90 to  21.30
min.
Signal       Rel Resp.   Pct. Unc.(abs)    Integration
Tgt   45.00                                *** METH DEFAULT ***
Q1    46.00     10.00       20.0          *** METH DEFAULT ***
Q2    43.00      8.60       20.0          *** METH DEFAULT ***
Lvl ID   Conc (ppbv)  Response
1           30.000       189728
2        not used for this compound
3        not used for this compound
4        not used for this compound
5        not used for this compound
Qualifier Peak Analysis ON
Curve Fit: Linear, forced through origin
------------------------------------------------------------------
------------
 3)  Acetone                                          ( )
Ret. Time  21.63 min., Extract & Integrate from  21.43 to  21.83
min.
Signal       Rel Resp.   Pct. Unc.(abs)    Integration
Tgt   43.00                                *** METH DEFAULT ***
Q1    58.00     29.90       20.0          *** METH DEFAULT ***
Lvl ID   Conc (ppbv)  Response
1           10.000       454778
2        not used for this compound
3        not used for this compound
4        not used for this compound
5        not used for this compound
Qualifier Peak Analysis ON
Curve Fit: Linear, forced through origin
------------------------------------------------------------------
------------
 4)  ACN                                              ( )
Ret. Time  22.46 min., Extract & Integrate from  22.26 to  22.66
min.
Signal       Rel Resp.   Pct. Unc.(abs)    Integration
Tgt   41.00                               *** METH DEFAULT ***
Q1    39.00     10.60       20.0          *** METH DEFAULT ***
Lvl ID   Conc (ppbv)  Response
1           15.000       440488
2        not used for this compound
3        not used for this compound
4        not used for this compound
5        not used for this compound
```

```
Qualifier Peak Analysis ON
Curve Fit: Linear, forced through origin
------------------------------------------------------------------
------------
 5)  AcryN                                              ( )
Ret. Time  23.67 min., Extract & Integrate from  23.47 to  23.87
min.
Signal       Rel Resp.   Pct. Unc.(abs)    Integration
Tgt   53.00                               *** METH DEFAULT ***
Q1    52.00     43.20       20.0          *** METH DEFAULT ***
Q2    51.00     17.70       20.0          *** METH DEFAULT ***
Lvl ID   Conc (ppbv)  Response
1            2.000        19894
2        not used for this compound
3        not used for this compound
4        not used for this compound
5        not used for this compound
Qualifier Peak Analysis ON
Curve Fit: Linear, forced through origin
------------------------------------------------------------------
------------
6)  MTBE                                               ( )
Ret. Time  23.79 min., Extract & Integrate from  23.59 to  23.99
min.
Signal       Rel Resp.   Pct. Unc.(abs)    Integration
Tgt   73.00                               *** METH DEFAULT ***
Q1    57.00      7.30       10.0          *** METH DEFAULT ***
Q2    41.00     15.70       10.0          *** METH DEFAULT ***
Lvl ID   Conc (ppbv)  Response
1            0.830        19234
2            1.670        45037
3            2.500        78114
4            3.330       118736
5            5.000       213904
Qualifier Peak Analysis ON
Curve Fit: Quadratic, forced through origin
------------------------------------------------------------------
------------
 7)  Hexane                                            ( )
Ret. Time  24.51 min., Extract & Integrate from  24.31 to  24.71
min.
Signal       Rel Resp.   Pct. Unc.(abs)    Integration
Tgt   57.00                               *** METH DEFAULT ***
Q1    56.00     61.60       20.0          *** METH DEFAULT ***
Q2    86.00     18.50       20.0          *** METH DEFAULT ***
```

```
Lvl ID   Conc (ppbv)  Response
1            5.000       156081
2        not used for this compound
3        not used for this compound
4        not used for this compound
5        not used for this compound
Qualifier Peak Analysis ON
Curve Fit: Linear, forced through origin
-------------------------------------------------------------------
-----------
 8)  Benzene                                          ( )
Ret. Time  28.24 min., Extract & Integrate from  28.04 to  28.44
min.
Signal       Rel Resp.   Pct. Unc.(abs)    Integration

Tgt   78.00                                *** METH DEFAULT ***
Q1    77.00     10.50       10.0          *** METH DEFAULT ***
Lvl ID   Conc (ppbv)  Response
1            5.000       380868
2        not used for this compound
3        not used for this compound
4        not used for this compound
5        not used for this compound
Qualifier Peak Analysis ON
Curve Fit: Linear, forced through origin
-------------------------------------------------------------------
-----------
9)  MIBK                                             ( )
Ret. Time  32.65 min., Extract & Integrate from  32.45 to  32.85
min.
Signal       Rel Resp.   Pct. Unc.(abs)    Integration
Tgt   43.00                                *** METH DEFAULT ***
Q1    58.00     16.30       20.0          *** METH DEFAULT ***
Q2    85.00      7.00       20.0          *** METH DEFAULT ***
Q3   100.00      5.80       20.0          *** METH DEFAULT ***

Lvl ID   Conc (ppbv)  Response
1            5.000       241219
2        not used for this compound
3        not used for this compound
4        not used for this compound
5        not used for this compound
Qualifier Peak Analysis ON
Curve Fit: Linear, forced through origin
-------------------------------------------------------------------
```

HP GC/MS Chemstation

```
 Method Information For: C:\HPCHEM\1\METHODS\IDLE.M

Method Sections To Run:

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

Method Comments:
  This is a method for setting temperature zones to standby con-
ditions.

                     END OF TOPLEVEL PARAMETERS
                     --------------------------
                    INSTRUMENT CONTROL PARAMETERS
                    -----------------------------

Sample Inlet:       GC
Injection Source:   External Device
Injection Location: Front
Mass Spectrometer:  Enabled

================================================================
                          HP6890 GC METHOD
================================================================

OVEN
   Initial temp:  100 'C (On)   Maximum temp:  260 'C
   Initial time:  33.00 min     Equilibration time:  0.50 min
   Ramps:
      #  Rate  Final temp  Final time   CRYO (N2)
      1   0.0(Off)                     Cryo:  On
   Post temp:  0 'C                    Cryo fault:  On
   Post time:  0.00 min             Cryo timeout:  60.00 min (On)
   Run time:  33.00 min                Quick cryo cool:  On
                                       Ambient temp:  55 'C

FRONT INLET (HP PTV)                   BACK INLET (SPLIT/SPLITLESS)
   Mode:  Split                        Mode:  Split
   Initial temp:  87 'C (Off)          Initial temp:  50 'C (Off)
   Cryo:  Off                          Pressure:  0.00 psi (Off)
   Cryo use temp:  25 'C               Total flow:  45.0 mL/min
```

```
   Cryo Timeout:  30.00 min (On)    Gas saver:  Off

   Cryo Fault:  On                  Gas type:  Helium
   Pressure:  7.32 psi (Off)
   Split ratio:  50:1
   Split flow:  98.6 mL/min
   Total flow:  103.6 mL/min
   Gas saver:  Off
   Gas type:  Helium

COLUMN 1                                  COLUMN 2
   Capillary Column                      (not installed)
   Model Number:  J & W DB-624
   30m x 0.32 mm i.d. and 1.8 um thick
   Max temperature:  260 'C
   Nominal length:  30.0 m
   Nominal diameter:  320.00 um
   Nominal film thickness:  1.80 um
   Mode:  constant pressure
   Pressure:  7.32 psi
   Average velocity:  52 cm/sec
   Inlet:  Front Inlet
   Outlet:  MSD
   Outlet pressure:  vacuum

FRONT DETECTOR (NO DET)                   BACK DETECTOR (NO DET)

SIGNAL 1                                  SIGNAL 2
   Data rate:  20 Hz                         Data rate:  20 Hz
   Type:  test plot                          Type:  test plot
   Save Data:  Off                           Save Data:  Off
   Zero:  0.0 (Off)                          Zero:  0.0 (Off)
   Range:  0                                 Range:  0
   Fast Peaks:  Off                          Fast Peaks:  Off
   Attenuation:  0                           Attenuation:  0

COLUMN COMP 1                             COLUMN COMP 2
   (No Detectors Installed)              (No Detectors Installed)

THERMAL AUX 2
   Use:  MSD Transfer Line Heater
   Description:  MSD
   Initial temp:  280 'C (On)
   Initial time:  0.00 min
      #  Rate  Final temp  Final time
```

```
     1    0.0 (Off)

                                          POST RUN
                                        Post Time: 0.00 min
TIME TABLE
   Time        Specifier                 Parameter & Setpoint

                          7673 Injector

     Front Injector:
No parameters specified

     Back Injector:
        Sample Washes                 0
        Sample Pumps                  0
        Injection Volume            1.0 microliters
        Syringe Size               10.0 microliters
        PostInj Solvent A Washes      0
        PostInj Solvent B Washes      0
        Viscosity Delay               0 seconds
        Plunger Speed              Fast
        PreInjection Dwell         0.00 minutes
        PostInjection Dwell        0.00 minutes

MS ACQUISITION PARAMETERS

General Information
------- -----------
Tune File                : ATUNE.U
Acquistion Mode          : Scan

MS Information
-- -----------
Solvent Delay            : 3.00 min
EM Absolute              : False
EM Offset                : 106
Resulting EM Voltage     : 2435.3

[Scan Parameters]

Low Mass                 : 35
Threshold                : 150
Sample #                 : 2       A/D Samples    4

[MSZones]
```

```
MS Quad                    : 150 C   maximum 200 C
MS Source                  : 230 C   maximum 250 C

Timed Events
----- ------
[Timed MS Detector Entries]

Time (min)          State (MS on/off)
45.00                    Off


                   END OF MS ACQUISITION PARAMETERS

                   END OF INSTRUMENT CONTROL PARAMETERS
                   -----------------------------------

                          DATA ANALYSIS PARAMETERS
                          -----------------------

Method Name: C:\HPCHEM\1\METHODS\IDLE.M

Percent Report Settings
-----------------------
Sort By: Retention Time

Output Destination
    Screen:  No
    Printer: Yes
    File:    No

Integration Events: AutoIntegrate
Generate Report During Run Method:  No
Signal Correlation Window: 0.020

Qualitative Report Settings
---------------------------
Peak Location of Unknown: Apex
Library to Search      Minimum Quality
DEMO.L                  0

Integration Events: AutoIntegrate
Report Type: Summary
Output Destination
    Screen:  No
    Printer: Yes
```

HP GC/MS Chemstation

```
     File:    No

Generate Report During Run Method:  No

Quantitative Report Settings
----------------------------
Report Type: Summary
Output Destination
    Screen:  Yes
    Printer: No
    File:    No

Generate Report During Run Method:  No

Calibration Last Updated:

Reference Window: 10.00 Percent
Non-Reference Window: 5.00 Percent
Correlation Window: 0.02 minutes
Default Multiplier: 1.00
Default Sample Concentration: 0.00

Compound Information
--------------------
*** Empty Quantitation Database ***

                  END OF DATA ANALYSIS PARAMETERS
                  -------------------------------
```

HP GC/MS Chemstation

```
Method Information For: C:\HPCHEM\1\METHODS\IDLE1.M

Method Sections To Run:

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

Method Comments:
  This is a method for setting temperature zones to standby con-
ditions.

                    END OF TOPLEVEL PARAMETERS
                    --------------------------
                   INSTRUMENT CONTROL PARAMETERS
                   -----------------------------

Sample Inlet:       GC
Injection Source:   External Device
Injection Location: Front
Mass Spectrometer:  Enabled

================================================================
                              HP6890 GC METHOD
================================================================
OVEN
   Initial temp:  200 'C (On)      Maximum temp:  260 'C
   Initial time:  20.00 min     Equilibration time:  0.50 min
   Ramps:

   #  Rate  Final temp  Final time   CRYO (N2)
   1   0.0(Off)                     Cryo:  On
   Post temp:  0 'C                 Cryo fault:  On
   Post time:  0.00 min          Cryo timeout:  60.00 min (On)
   Run time:  20.00 min             Quick cryo cool:  On
                                    Ambient temp:  55 'C

FRONT INLET (HP PTV)                BACK INLET (SPLIT/SPLITLESS)
   Mode:  Split                     Mode:  Split
   Initial temp:  87 'C (Off)       Initial temp:  50 'C (Off)
   Cryo:  Off                       Pressure:  0.00 psi (Off)
   Cryo use temp:  25 'C            Total flow:  45.0 mL/min
   Cryo Timeout:  30.00 min (On)        Gas saver:  Off
```

```
   Cryo Fault:  On                        Gas type:  Helium
   Pressure:  7.32 psi (Off)
   Split ratio:  50:1
   Split flow:  66.2 mL/min
   Total flow:  70.5 mL/min
   Gas saver:  Off
   Gas type:  Helium

COLUMN 1                                   COLUMN 2
   Capillary Column                       not installed)
   Model Number:  J & W DB-624
   30m x 0.32 mm i.d. and 1.8 um thick
   Max temperature:  260 'C
   Nominal length:  30.0 m
   Nominal diameter:  320.00 um
   Nominal film thickness:  1.80 um
   Mode:  constant pressure
   Pressure:  7.32 psi
   Average velocity:  45 cm/sec
   Inlet:  Front Inlet
   Outlet:  MSD
   Outlet pressure:  vacuum

FRONT DETECTOR (NO DET)            BACK DETECTOR (NO DET)

SIGNAL 1                           SIGNAL 2
   Data rate:  20 Hz                  Data rate:  20 Hz
   Type:  test plot                   Type:  test plot
   Save Data:  Off                    Save Data:  Off
   Zero:  0.0 (Off)                   Zero:  0.0 (Off)
   Range:  0                          Range:  0
   Fast Peaks:  Off                   Fast Peaks:  Off
   Attenuation:  0                    Attenuation:  0

COLUMN COMP 1                      COLUMN COMP 2
   (No Detectors Installed)       No Detectors Installed)

THERMAL AUX 2
   Use:  MSD Transfer Line Heater
   Description:  MSD
   Initial temp:  280 'C (On)
   Initial time:  0.00 min
      #  Rate  Final temp  Final time
      1   0.0(Off)
                                          POST RUN
```

```
                                        Post Time: 0.00 min
TIME TABLE
   Time       Specifier                 Parameter & Setpoint

                        7673 Injector
     Front Injector:
No parameters specified

     Back Injector:
        Sample Washes                     0
        Sample Pumps                      0
        Injection Volume                1.0 microliters
        Syringe Size                   10.0 microliters
        PostInj Solvent A Washes          0
        PostInj Solvent B Washes          0
        Viscosity Delay                   0 seconds
        Plunger Speed                  Fast
        PreInjection Dwell             0.00 minutes
        PostInjection Dwell            0.00 minutes
```

MS ACQUISITION PARAMETERS

```
General Information
------- -----------
Tune File                : ATUNE.U
Acquistion Mode          : Scan

MS Information
-- -----------
Solvent Delay            : 3.00 min
EM Absolute              : False
EM Offset                : 106
Resulting EM Voltage     : 2435.3

[Scan Parameters]

Low Mass                 : 35
Threshold                : 150
Sample #                 : 2       A/D Samples    4

[MSZones]

MS Quad                  : 150 C   maximum 200 C
MS Source                : 230 C   maximum 250 C

Timed Events
```

HP GC/MS Chemstation

```
----- ------
[Timed MS Detector Entries]

Time (min)          State (MS on/off)
15.00                    Off


                         END OF MS ACQUISITION PARAMETERS

                         END OF INSTRUMENT CONTROL PARAMETERS
                           ---------------------------------

                            DATA ANALYSIS PARAMETERS
                           ------------------------

Method Name: C:\HPCHEM\1\METHODS\IDLE1.M

Percent Report Settings
-----------------------
Sort By: Retention Time
Output Destination
    Screen:  No
    Printer: Yes
    File:    No

Integration Events: AutoIntegrate
Generate Report During Run Method:  No
Signal Correlation Window: 0.020
Qualitative Report Settings
---------------------------
Peak Location of Unknown: Apex
Library to Search      Minimum Quality
DEMO.L                  0

Integration Events: AutoIntegrate

Report Type: Summary
Output Destination
    Screen:  No
    Printer: Yes
    File:    No

Generate Report During Run Method:  No

Quantitative Report Settings
----------------------------
```

HP GC/MS Chemstation

```
Report Type: Summary
Output Destination
    Screen:  Yes
    Printer: No
    File:    No

Generate Report During Run Method:  Yes

Calibration Last Updated:

Reference Window: 10.00 Percent
Non-Reference Window: 5.00 Percent
Correlation Window: 0.02 minutes
Default Multiplier: 1.00
Default Sample Concentration: 0.00

Compound Information
--------------------

*** Empty Quantitation Database ***

                    END OF DATA ANALYSIS PARAMETERS
                    ------------------------------
```

HP GC/MS Chemstation

```
                Sequence list
              Comment: DEC0403.s
                   Operator: NRL
              Data Path: C:\HPCHEM\1\DATA\
              Pre-Seq Cmd:
              Post-Seq Cmd:

Method Sections To Run      On A Barcode Mismatch
 (X) Full Method              (X) Inject Anyway
 ( ) Reprocessing Only        ( ) Don't Inject
```

Line	Type	Vial	DataFile	Method	Sample Name
1	Sample	1	DE0401	IDLE1	bakeout
2	Sample	1	DE0402	MLD066	BLANK
3	Sample	2	DE0403	MLD066	AAL069919 #1054
4	Sample	3	DE0404	MLD066	CC50604A #1061 25CC
5	Sample	3	DE0405	MLD066	CC50604B #1061 50CC
6	Sample	3	DE0406	MLD066	CC50604C #1061 75CC
7	Sample	3	DE0407	MLD066	CC50604D #1061 100CC
8	Sample	3	DE0408	MLD066	CC50604E #1061 150CC
9	Sample	4	DE0409	MLD066	ALM069798 #1072
10	Sample	5	DE0410	MLD066	TX005669 BFREG
11	Sample	6	DE0411	MLD066	TX005670 BFCOL
12	Sample	7	DE0412	MLD066	TX005671 RUREG
13	Sample	8	DE0413	MLD066	TX005672 RUCOL
14	Sample	9	DE0414	MLD066	TX005673 RS
15	Sample	11	DE0415	MLD066	TX005674 CX
16	Sample	12	DE0416	MLD066	TX005675 CV
17	Sample	13	DE0417	MLD066	TX005654 BFREG
18	Sample	14	DE0418	MLD066	TX005655 BFCOL
19	Sample	10	DE0419	MLD066	XX5642 SV 25CC
20	Sample	5	DE0420	MLD066	TX005669 DUP
23	Sample	1	DE0423	IDLE	BLANK

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Appendix V: Calibration and Control Standards

Compounds	Calibration Standard			Control Standards	
	AAL070488 ppbv	ALM069798 ppbv	CA06063 ppbv	CC50604 ppbv	AAL069919 ppbv
Acrolein	2.18	5.6	11.2		54.7
Ethanol	40.5	22.9	41.3	30.0	
Acetone	27.2	20.5	30.0	10.0	
Acetonitrile	9.3	10.0	11.0	15.0	
Acrylonitrile	6.78	5.0	3.37	2.0	
t-butylmethyl ether (MTBE)	4.69	4.6	5.25	5.0	
Benzene	6.25	5.5	6.16	5.0	

ALM069798 - Calibration standard used from 7/01/2003 through 9/18/2003 and has been used as control standard from 9/19/2003 to the present

CC50604 and AAL069919 - Control standards used from 7/01/2003 through 9/18/2003 and used as calibration standards from 9/19/2003 through 11/14/2004.

AAL070488 - Calibration standard from 9/15/2004 to the present.

Appendix VI: Revision History

Revision Number	Approval Date	Comments
1.00	July 1, 2003	Initial SOP

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#A06

State of California
California Environmental Protection Agency
Air Resources Board
MLD/QMS-066 (NEW 4/14)

QUALITY MANAGEMENT DOCUMENT ADDENDUM

Section 1. ARB Document
☐ Quality Management Plan (QMP)
☐ Quality Assurance Project Plan (QAPP)
☒ Standard Operating Procedure (SOP)

Section 2. Information		
Submitter Name:	Steve Madden	
Submitter Signature/Date:		7/7/15

Section 3. Document Title *(specify exact title, revision #, and date of ARB Document(s) that your District proposes to modify)*	**Date**
SOP MLD066 Revision Number 1.0	July 1, 2003

Section 4. Revision(s)
(specify exact section(s), page number(s) and language in existing ARB document that will be modified and then specify modification (including any spreadsheets or forms).

Section 5.2, page 6, states

5.2 A certified National Institute of Standards (NIST) standard calibration mixture, or mixtures, containing all analytes of interest is being ordered. This standard, or standards, should be slightly higher in concentration than the typical sample and must be within the dynamic range of the GC/MS system. Appendix V, page 91, lists the concentrations of the current calibration standards associated with this SOP.

ARB modification to section 5.2, page 6, states -

5.2 A certified National Institute of Standards (NIST) standard calibration mixture, or mixtures, containing all analytes of interest. This standard, or standards, should be slightly higher in concentration than the typical sample and must be within the dynamic range of the GC/MS system. *An alternative standard, or standards, should be at concentrations higher than the typical sample and suitable for dilution to working calibration standard concentrations within the dynamic range of the GC/MS system using a gas mixing and dilution system (mixer/diluter). A second alternative standard, or*

standards, should be neat, undiluted analytes for preparation, with appropriate solvents, into liquid solutions suitable for dilution to working calibration standard concentrations within the dynamic range of the GC/MS system using a gas mixing and dilution system (mixer/diluter). This system is described in SOP MLD074, "Standard Operating Procedure for Preparation of Calibration and Control Standards Using a Gas Mixer/Dilution Apparatus."

The statement "~~is being ordered~~" is deleted. The sentence "~~Appendix V, page 91, lists the concentrations of the current calibration standards associated with this SOP.~~" Is deleted.

Section 5.3, page 6, states

5.3 A control standard mixture, or mixtures, containing all analytes of interest at concentrations within the calibration range of the GC System. Appendix V, page 91, lists the concentrations of the Control Standards associated with this SOP.

ARB modification to Section 5.3, page 6, states

5.3 A control standard mixture, or mixtures, containing all analytes of interest at concentrations within the calibration range of the *GC/MS* System. *An alternative standard, or standards, should be at concentrations higher than the typical sample and suitable for dilution to working control standard concentrations within the dynamic range of the GC/MS system using a gas mixing and dilution system (mixer/diluter). A second alternative standard, or standards, should be neat, undiluted analytes for preparation, with appropriate solvents, into liquid solutions suitable for dilution to working calibration standard concentrations within the dynamic range of the GC/MS system using a gas mixing and dilution system (mixer/diluter). This system is described in SOP MLD074, "Standard Operating Procedure for Preparation of Calibration and Control Standards Using a Gas Mixer/Dilution Apparatus."*

The statement "~~GC System~~" is replaced by "GC/MS System." The sentence "~~Appendix V, page 91, lists the concentrations of the Control Standards associated with this SOP~~" Is deleted.

Table "Appendix V: Calibration and Control Standards", page 91

This table is deleted.

Section 9.7.2, page 20, states

9.7.2 Providing blind Through the Probe audit samples to the NLB, in order to assess the accuracy of the entire sampling and analysis system, is the responsibility of the Quality Assurance Section (QAS) of the Quality Management Branch (QMB).

9.7.2.1 Through the Probe audit samples shall be treated as regular ambient air samples.

9.7.2.2 Replicate analyses of Through the Probe audit samples, unless the sample is picked as the analytical duplicate, should not be performed.

9.7.2.3 The concentration results of Through the Probe audit sample analysis shall be provided as quickly as possible to the QAS staff, and shall be included in the quarterly QC reports.

9.7.2.4 If after receiving the QAS Through the Probe Audit Report any results are considered substantially different from the preceding audit results, the OLS Supervisor in conjunction with the QAS Supervisor shall formulate an appropriate course of action.

9.7.2.5 All actions taken in response to Through the Probe audit should be approved by the OLS Supervisor.

9.7.2.6 The actions taken in response to the Through the Probe may be modified by the most current version of the Laboratory Quality Control Manual in effect.

ARB modification to section 9.7.2, page 20, states

Section 9.7.2 and all subsections are deleted

Table "**Table 7: Precision Measurements and Control Limits for MLD066 ALM069798", page 31**

The statement "ALM069798" is deleted.

Figures 13 through 17, pages 43 – 47, states

The statements "– ALM069798" and "– CC50604" are deleted.

Section 5. Justification for Deviation(s)
(provide explanation of why modification(s) to existing ARB document is necessary)

The modifications to Section 5.2, page 6, and Section 5.3, page 7, describing higher concentration calibration and control cylinders are necessary since the higher concentration standards have proved more stable than those of lower concentrations. Similarly, the use of neat, undiluted analytes for the preparation of liquid solutions is necessary for certain compounds. The mixer/diluter system make the use of these higher concentrations and liquid solutions feasible.

The deletions of Table Appendix V, and statements in Table 7, page 31, and Figures 13 – 17, pages 43 - 47 are in response to TSA comments concerning references to specific standard cylinders or lot numbers. Standards expire or are used up and are replaced with standards having different lot numbers.

The deletion of Section 9.7.2 and all subsections is necessary since "Through the Probe audit samples" are no longer provided by the Quality Assurance Section (QAS) of the Quality Management Branch (QMB).

Section 6. Attachment(s) ☐ *(specify attachment titles and number of pages, include modified spreadsheets or forms)*	**# of Pages**
None	

Section 7. ARB Approval		
Name/Phone Number:	Patrick Rainey	916 327-4756
Title:	Manager, Quality Management Section	
Signature/Date:		8/24/15
Addendum Number	A06 MLD066.1	

Completed form must be scanned/emailed or mailed to:

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prainey@arb.ca.gov