California Environmental Protection Agency

Air Resources Board

SOP MLD 058

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF AROMATIC AND HALOGENATED COMPOUNDS 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 AROMATIC AND HALOGENATED 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 aromatic and halogenated 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 23, 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 passes through a Nafion™ dryer to remove moisture from the gas stream. It is trapped on a cryotrap at -130 degrees centigrade (ºC). At this temperature, the desired components are solidified, while fixed gases, such as nitro

gen (N_2), oxygen (O_2), carbon dioxide (CO_2), and methane (CH_4) pass through the cryotrap to the vent. The system is purged with ultrapure N_2 to flush sample remaining in the tubing or valving on to the cryotrap, and to remove any excess light impurities. After purging, the cryotrap is rapidly heated to 200ºC to transfer/desorb the contents and retrap them on the cryofocuser at -130°C. The cryofocuser is rapidly heated up to 200°C to inject the sample onto a DB-VRX 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 23, 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 as soon as possible. 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 23, lists the compounds addressed by this procedure.

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, cryotrap, 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 Cryogenic Concentrator system, containing:

4.1.2.1 A 700 µl, $^1/_8$-inch cryotrap, constructed of nickel tubing and packed with 60/80-mesh silanized glass beads.

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 A continuous, self-regenerating, in-line Nafion™ sample dryer, from Perma Pure Inc.

4.1.7 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-VRX 60 m by 0.25 mm i.d., with 1.40 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. 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. Table 2, page 24, lists

the NIST Standards associated with this SOP. Appendix V, page 89, lists the concentrations of the NIST 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. Table 2, page 24, lists the Control Standards associated with this SOP. Appendix V, page 89, 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 and in cryotrap purging.

5.5 One high pressure gas cylinder of Grade 5 or better Nitrogen (N_2) for use in sample line purging, sample loop purging, and leak testing. This N_2 can also be used as the dry, countercurrent gas for the in-line Nafion™ dryer.

5.6 One Liquid Nitrogen (LN_2) Dewar for cooling the cryotrap, the cryofocuser, and the GC column oven. This N_2 can also be used as the dry, countercurrent gas for the in-line Nafion™ dryer and/or the system blank.

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 Cryogenic 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 5).

6.2 Varian 3800 Concentrator

6.2.1 The Varian 3800 Concentrator's gas flow and automation configurations are shown in Figure 1, page 35, through Figure 6, page 40. The nomenclature and function of the Concentrator's thermal zones are shown in Table 3, page 25. A complete listing of the current Varian Star Workstation method, which includes all of the setpoints con

trolled by the Workstation, is given in Appendix III, page 59. 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 (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 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 4, page 27.

6.2.1.5 Front Injector Type 1079

This setting controls the programmed temperature of the Cryotrap/Front Cold 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 73. 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 4, page 27. The setpoint for the MFC is shown in Appendix I, page 55.

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 73.

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 6, page 32.

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 7, page 33.

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 59, 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 73, 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 cryotrap under control of the Star Chromatography Workstation method. The gas and sample flow and automation configurations for the cryotrap loading steps are shown in Figure 1, page 35, through Figure 4, page 38. The program times, relay # and status, and events are shown in Table 5, page 29.

7.3.2 After the Concentrator's cryotrap has finished loading, it is 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 35, and Figure 6, page 40.

7.3.3 A graphical representation of the concentration steps is shown in Figure 7, page 41.

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 7), 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 (mld058.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 8, page 42, through Figure 10, page 44.

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 five (5) times it's LOD, the analytical run associated with the system blank should be invalidated and the cause investigated.

9.1.4 If the individual concentrations of any target analytes detected in the system blank are greater than two (2) but less than five (5) times their LOD, each individual analyte result in the blank should be compared to each individual analyte result for each sample analyzed.

9.1.4.1 If the analyte result in the blank is less than five percent (5%) of the analyte result in the sample, no action should be taken.

9.1.4.2 If the analyte result in the blank is greater than five percent (5%) of the analyte result in the sample, the sample result should be invalidated.

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

9.1.6 The actions taken in response to system blank results are 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, on page 76.

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 several target analytes are shown in Figure 17, page 51, through Figure 22, page 53.

9.3.2.3 A typical dataset used for calculating control limits is given in Table 8, page 23.

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 system blank 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.

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 several target analytes are presented in Figure 11, page 45, through Figure 16, page 50. Correlation coefficient and highest calibrated concentration values for each target analyte are shown Appendix II, page 57.

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 - α) 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 57.

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.

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

Compound Name [2]	Abbr. [1]	Chemical Formula	CAS No.	Primary Ion	Secondary Ion(s)
1,3-Butadiene	Buta	C4H6	106-99-0	39	54
1,2-Dibromoethane	EDB	C2H4Br2	106-93-4	107	109
1,2-Dichloroethane	EDC	C2H4Cl2	107-06-2	62	64, 27
1,2-Dichloropropane	DCP	C3H6Cl2	78-87-5	63	62, 64, 65
1,1,1-Trichloroethane	TCEA	C2H3Cl3	71-55-6	97	99, 61
cis-1,3-Dichloropropene	c-DClprpene	C3H4Cl2	10061-01-5	75	77, 110
trans-1,3-Dichloropropene	t-DClprpene	C3H4Cl2	10061-02-6	75	77, 110
Benzene	Benz	C6H6	71-43-2	78	77, 50
Bromomethane	CH3Br	CH3Br	74-83-9	94	96, 93
Carbon tetrachloride	CCl4	CCl4	56-23-5	117	119
Chlorobenzene	ClBenz	C6H5Cl	108-90-7	112	77, 114
Chloroform	CHCl3	CHCl3	67-66-3	83	85, 47
Dichloromethane	DCM	CH2Cl2	75-09-2	49	84, 86
Ethylbenzene	EtBenz	C8H10	100-41-4	91	106
Trichlorofluoromethane	Freon 11	CCl3F	75-64-4	101	103,66,105
Dichlorodifluoromethane	Freon 12	C2H2Cl2F2	75-71-8	85	101, 103, 87
1,1,2-Trichloro-1,2,2-Trifluoroethane	Freon 113	C2Cl3F3	000076-13-1	101	103, 85, 151
m/*p*-Xylene [3]	m/p-Xyl	C8H10	108-38-3, 106-42-3	91	106
m-Dichlorobenzene	m-DCB	C6H4Cl2	541-73-1	146	148, 111
o-Dichlorobenzene	o-DCB	C6H4Cl2	95-50-1	146	148, 111
p-Dichlorobenzene	p-DCB	C6H4Cl2	106-46-7	146	148, 111
o-Xylene [3]	o-Xyl	C8H10	95-47-6	91	106
Perchloroethylene [4]	PERC	C2Cl4	127-18-4	166	164, 131
Styrene [5]	Sty	C8H8	100-42-5	104	78, 103
Toluene	Tol	C7H8	108-88-3	91	92
1,1,2-Trichloroethylene [6]	TCE	C2HCl3	79-01-6	130	132, 95
Vinyl Chloride [7]	VinCl	C2H3Cl	7S-01-4	62	64

(1) Abbr. = Abbreviation – sometimes used in lieu of the full name in the analytical software.
(2) Bromomethane (CH_3Br) and 1,2-Dichloropropane (DCP) can also be determined by this method.
(3) m-Xylene = 1,3-Dimethylbenzene; p-Xylene = 1,4-Dimethylbenzene; o-Xylene = 1,2-Dimethylbenzene
(4) Perchloroethylene = 1,1,2,2-Tetrachloroethylene = 1,1,2,2-Tetrachloroethene
(5) Styrene = Ethenylbenzene = Vinylbenzene
(6) 1,1,2-Trichloroethylene = 1,1,2-Trichloroethene
(7) Vinyl Choride = Chloroethene

Table 2: MLD058 Standards and Controls

Date Range	Standard Cylinder	Control Cylinder
11/01/00 – present	ALM046027 ALM029258	CC386

Table 3: Thermal Zones for the Varian 3800 Concentrator

Thermal Zone #	Status Label	GC Control Label	Function
1	Front: 1079	Front 1079	Cryotrap 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
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

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Table 4: Function of Valves for the Varian 3800 Concentrator

Valve/ Relay #	Name	Relay of 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 Line s or Transfer Internal Standard from Loop to Valve 2
1	Sample Valve	+ 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 Cryotrap to Valve 3
2	Sample Preconcentration Trap Valve	+ SPT Trap	Flow from Valve 1 through Cryotrap 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
3	Sample Preconcentration Trap Valve	+ 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
4	Series Bypass Valve	+ Bypass	Cryofocuser Isolated
5	Event A Valve	- Off	No Action
5	Event A Valve	+ On	Start Hewlett-Packard GC and MS Data Acquisition
6	Event B Valve	- Off	Sample Line to Vent
6	Event B Valve	+ On	Enable Leak test
7	Event C Valve	- Off	N2 Pressurization Gas Off
7	Event C Valve	+ On	N2 Pressurization Gas On

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Table 5: Program Times, Relay #'s, and Status for the Con-centrator

Time (minutes)	Relay # & Status	Events
0.00	-1-2-3-4-5-6-7-8	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 cryotrap (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**-2-3-4-5-6-7-8	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 cryotrap, through Valve 3, through the cryofocuser, back through Valve 3 to vent. He carrier gas flows through Valve 3 to the column.
4.00	**+1+2**-3-4-5-6-7-8	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 cryotrap and then through the MFC to vacuum. The N_2 purge gas flow remains blocked. ***This starts sample loading of the cryotrap.*** 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 5: Program Times, Relay #'s, and Status for the Concentrator

Time (minutes)	Relay # & Status	Events
7.00	-1**+2**-3-4-5-6-7-8	Valve 1 is turned off (-1) and Valve 2 remains on (**+2**): The sample flow is blocked and N_2 purge gas flows through the loop to Valve 2, through the cryotrap and then through the MFC to vacuum. This flushes the loop and any sample remaining in the lines to the cryotrap. ***This terminates sample loading of the cryotrap.*** 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.***
8.00	-1-2-3-4-5-6-7-8	Valve 2 is turned off (-2): 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 cryotrap, through Valve 3, through the cryofocuser, back through Valve 3 to vent. ***This starts the transfer of the cryotrap contents to the cryofocuser.*** He carrier gas flows through Valve 3 to the column.
11.00	-1-2**+3**-4**+5**-6-7-8	Valves 3 is turned on (**+3**) and Valve 5 is turned on (**+5**): 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 cryotrap, through Valve 3 to the vent. He carrier gas flows through Valve 3, through the cryofocuser, back through Valve 3 to the column. ***This stops transfer of the cryotrap contents to***

Table 5: Program Times, Relay #'s, and Status for the Concentrator

Time (minutes)	Relay # & Status	Events
		the cryofocuser and starts backflushing the cryofocuser contents to GC column. Valve 5 starts the Hewlett-Packard GC and MS Data Acquisition.
11.01	-1-2**+3**-4-5-6-7-8	Valve 5 is turned off (-5) and Valve 3 remains on (**+3**): This step is identical to the previous step at 11.00 minutes. It simply recycles the GC/MS start event to off.
16.00	-1-2-3-4-5-6-7-8	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 cryotrap (Front Cold Trap), through Valve 3, through the cryofocuser (Middle Cold Trap), back through Valve 3 to vent. This forward flushes the cryotrap and cryofocuser to vent. He carrier gas flows through Valve 3 to the column.

Table 6: 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 7: BFB Ion Abundance Criteria

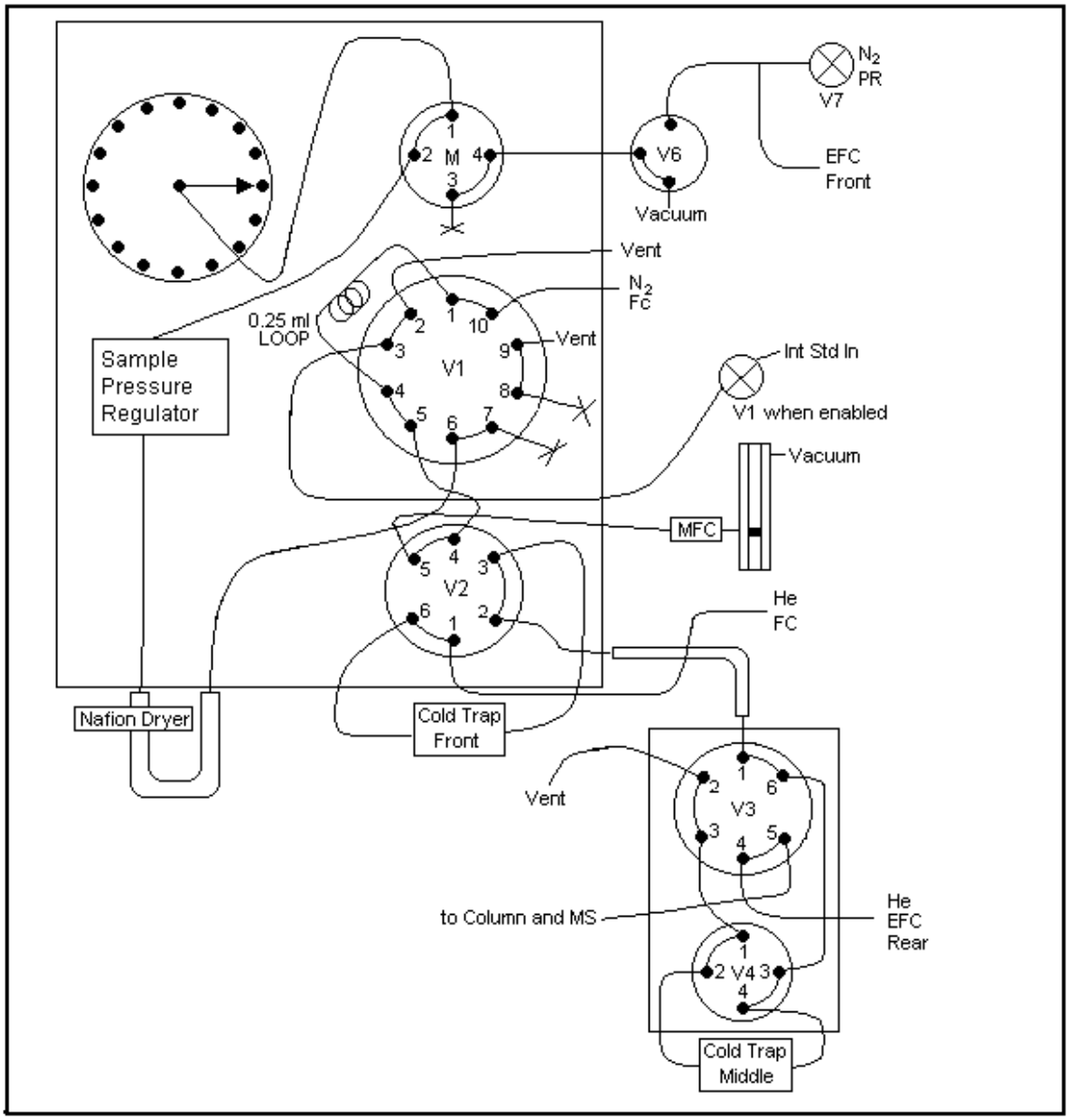
m/z	Ion Abundance Criteria
50	8.0 to 4.0 Per cent of m/z 95
75	30.0 to 66.0 Percent of m/z 95
95	Base peak, 100 Percent Relative Abundance
96	5.0 to 9.0 Percent of m/z 95 (see note)
173	Less than 2.0 Percent of m/z 174
174	50.0 to 120 Percent of m/z 95
175	4.0 to 9.0 Percent of m/z 174
176	93.0 to 101.0 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 8: Precision Measurements for MLD058

	Compound					
File Name	**Buta**	**CCl4**	**Benz**	**TCE**	**Styrene**	**p-DCB**
tct1017.d	1.23	0.13	3.41	0.34	5.11	3.35
tct1018.d	1.11	0.13	3.40	0.34	5.08	2.85
oc1903.d	1.11	0.14	3.36	0.33	5.15	3.76
oc2304.d	1.19	0.13	3.41	0.34	5.16	3.11
oc3004.d	1.18	0.13	3.45	0.33	5.61	3.17
oc3004b.d	1.18	0.13	3.46	0.33	5.59	3.39
nv0103.d	1.19	0.14	3.50	0.32	5.66	2.97
nv0103b.d	1.29	0.14	3.51	0.33	5.69	3.12
nv0103c.d	1.30	0.14	3.51	0.33	5.64	3.01
nv0105b.d	1.31	0.15	3.49	0.33	5.70	3.12
nv0103d.d	1.32	0.14	3.54	0.32	5.62	2.85
nv0203.d	1.25	0.13	3.43	0.33	5.74	3.30
nv0203b.d	1.24	0.13	3.43	0.33	5.61	3.01
nv0203c.d	1.19	0.13	3.45	0.32	5.62	2.99
nv0203d.d	1.17	0.13	3.43	0.33	5.55	3.19
nv0203e.d	1.21	0.13	3.44	0.34	5.59	3.04
nv0203f.d	1.18	0.13	3.42	0.32	5.54	2.96
nv0603.d	1.15	0.14	3.45	0.35	5.56	2.81
nv0603b.d	1.19	0.14	3.46	0.36	5.71	2.62
nv0603c.d	1.16	0.14	3.47	0.34	5.48	2.59
nv0603d.d	1.13	0.14	3.49	0.36	5.44	2.53
nv0603e.d	1.15	0.14	3.49	0.35	5.43	2.33
Average:	1.20	0.14	3.45	0.34	5.51	3.00
Std. Dev.:	0.062	0.006	0.043	0.012	0.204	0.317
%RSD:	5.13	4.40	1.24	3.54	3.70	10.57
Std. Dev. at 5%RSD		0.01	0.17	0.02	0.28	
UCL:	1.39	0.16	3.97	0.39	6.34	3.96
UWL:	1.32	0.15	3.80	0.37	6.06	3.64
LWL:	1.08	0.12	3.11	0.30	4.96	2.37
LCL:	1.02	0.12	2.94	0.28	4.69	2.05

Figure 1: Idle State (All Valves OFF)
Time: 0.00 min and 16.00 min

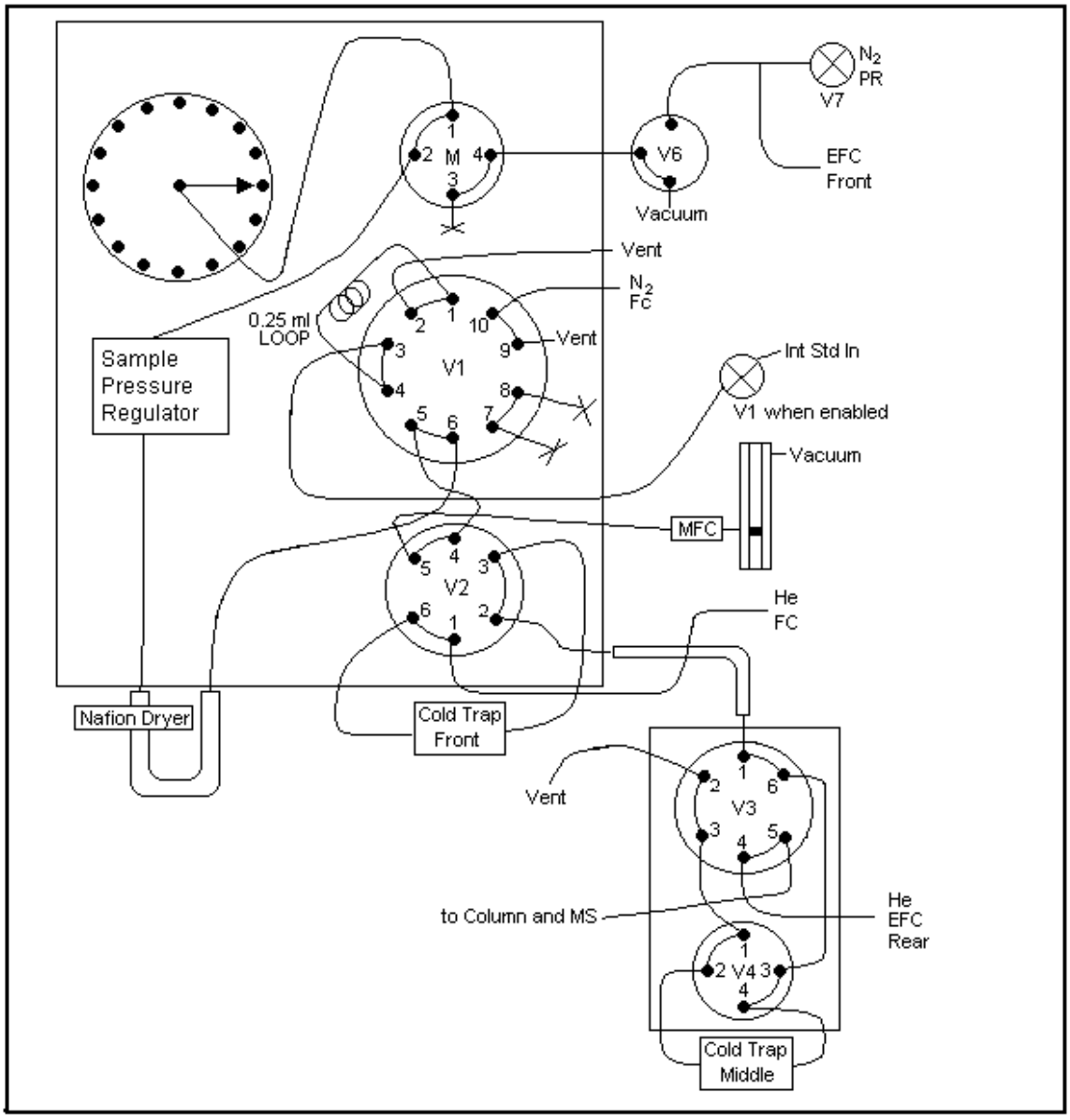


Sample Delivery Program

Time	V1	V2	V3	V4	V5	V6	V7
0.00	-	-	-	-	-	-	-
0.01	+	-	-	-	-	-	-
4.00	+	+	-	-	-	-	-
7.00	-	+	-	-	-	-	-
8.00	-	-	-	-	-	-	-
11.00	-	-	+	-	+	-	-
11.01	-	-	+	-	-	-	-
16.00	-	-	-	-	-	-	-

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: Purge Sample Line
Time: 0.01 min

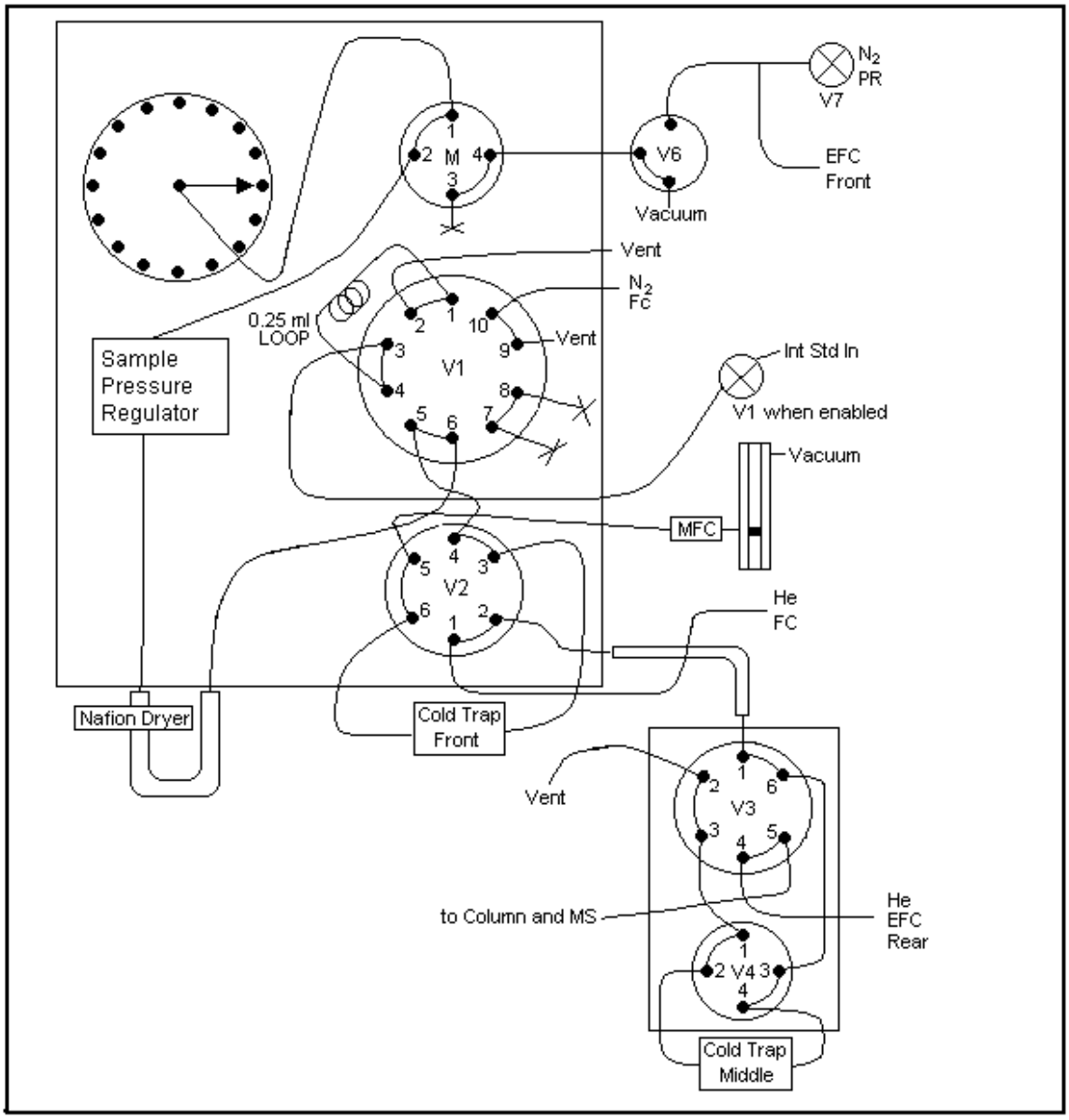


Sample Delivery Program

Time	V1	V2	V3	V4	V5	V6	V7
0.00	-	-	-	-	-	-	-
0.01	+	-	-	-	-	-	-
4.00	+	+	-	-	-	-	-
7.00	-	+	-	-	-	-	-
8.00	-	-	-	-	-	-	-
11.00	-	-	+	-	+	-	-
11.01	-	-	+	-	-	-	-
16.00	-	-	-	-	-	-	-

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: Start Loading Cryotrap
Time: 4.00 min

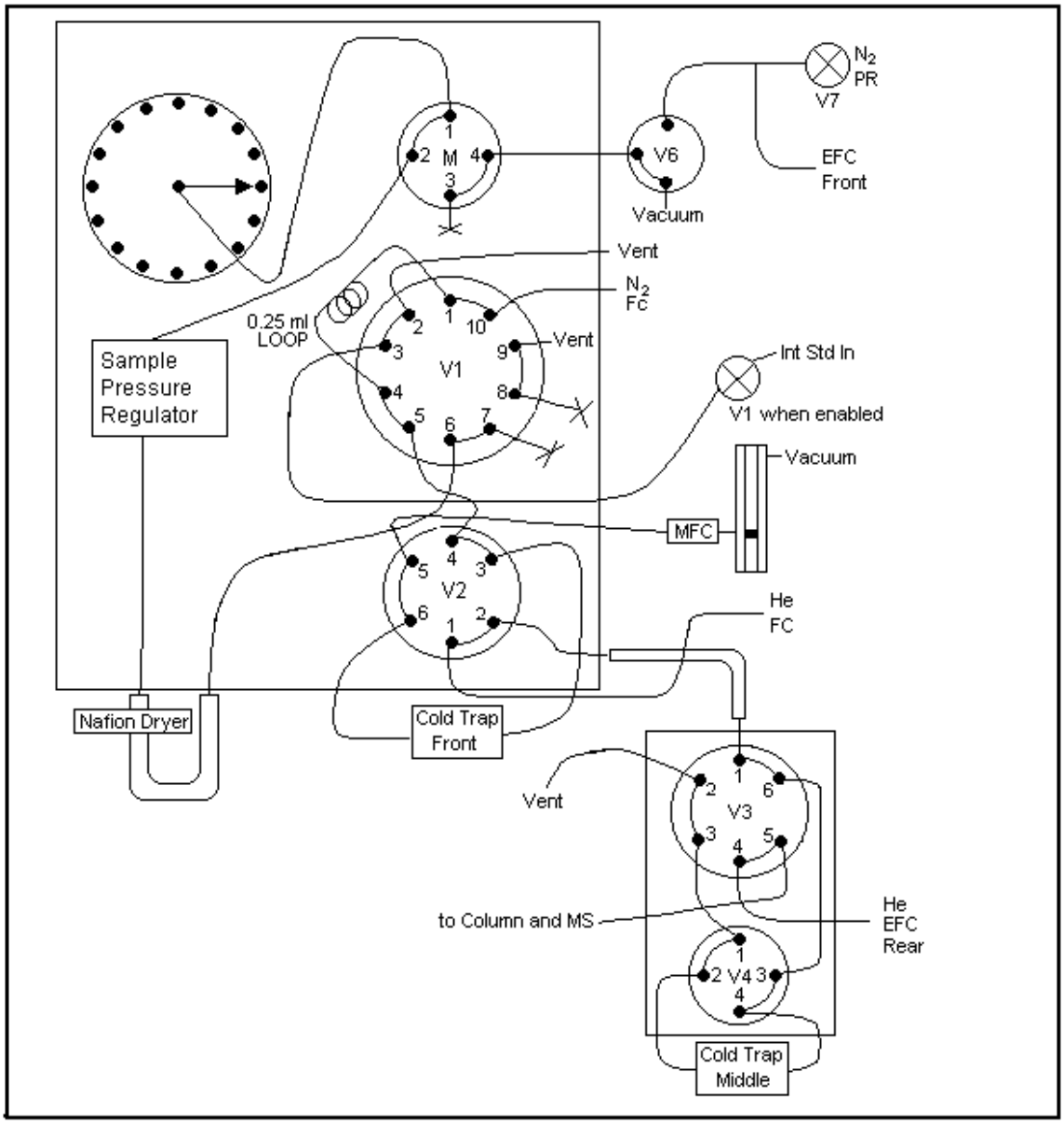


Sample Delivery Program

Time	V1	V2	V3	V4	V5	V6	V7
0.00	-	-	-	-	-	-	-
0.01	+	-	-	-	-	-	-
4.00	+	+	-	-	-	-	-
7.00	-	+	-	-	-	-	-
8.00	-	-	-	-	-	-	-
11.00	-	-	+	-	+	-	-
11.01	-	-	+	-	-	-	-
16.00	-	-	-	-	-	-	-

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: Cryotrap Purge
Time: 7.00 min

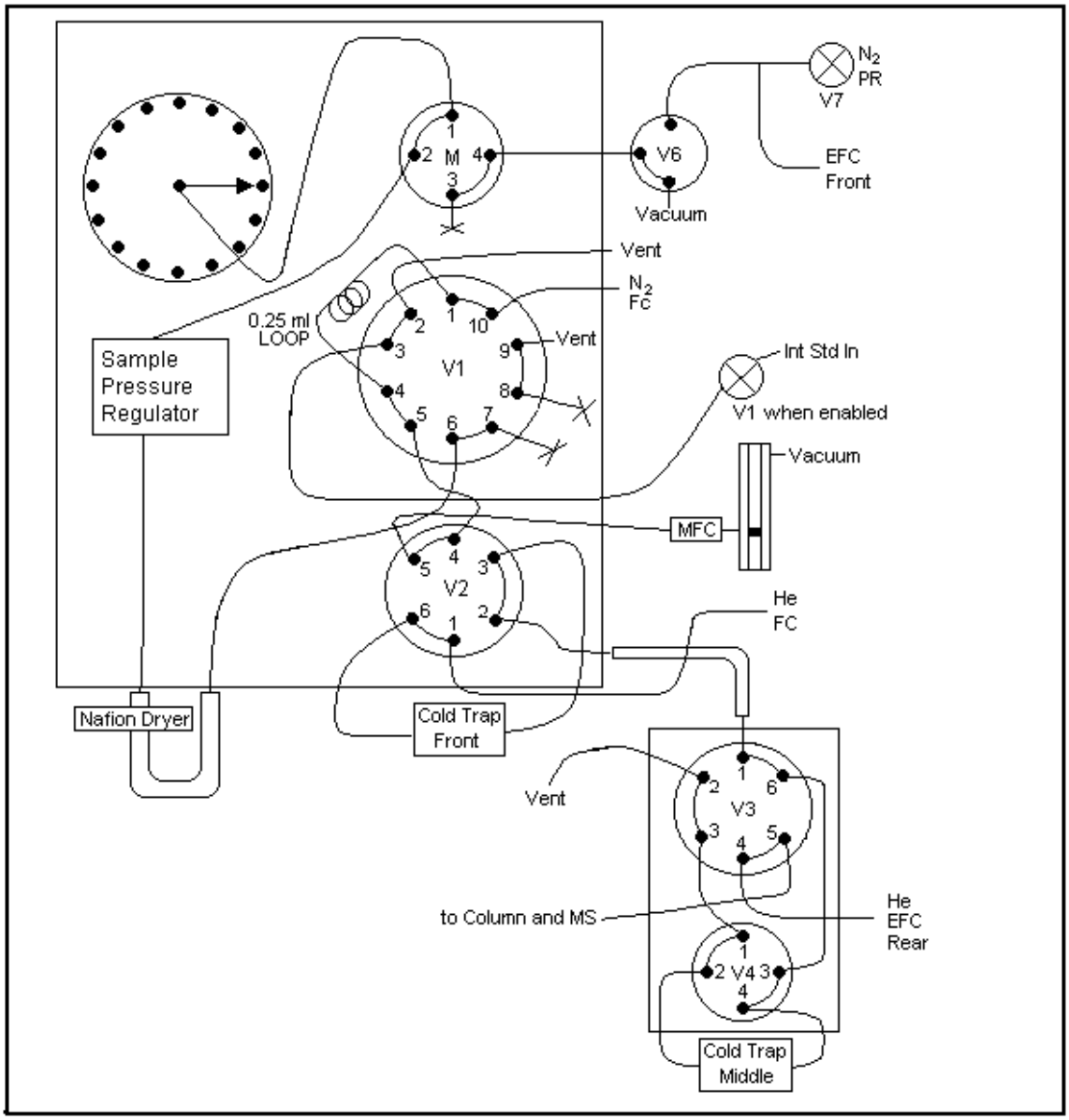


Sample Delivery Program

Time	V1	V2	V3	V4	V5	V6	V7
0.00	-	-	-	-	-	-	-
0.01	+	-	-	-	-	-	-
4.00	+	+	-	-	-	-	-
7.00	-	+	-	-	-	-	-
8.00	-	-	-	-	-	-	-
11.00	-	-	+	-	+	-	-
11.01	-	-	+	-	-	-	-
16.00	-	-	-	-	-	-	-

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: Transfer from Cryotrap to Cryofocuser
Time: 8.00 min

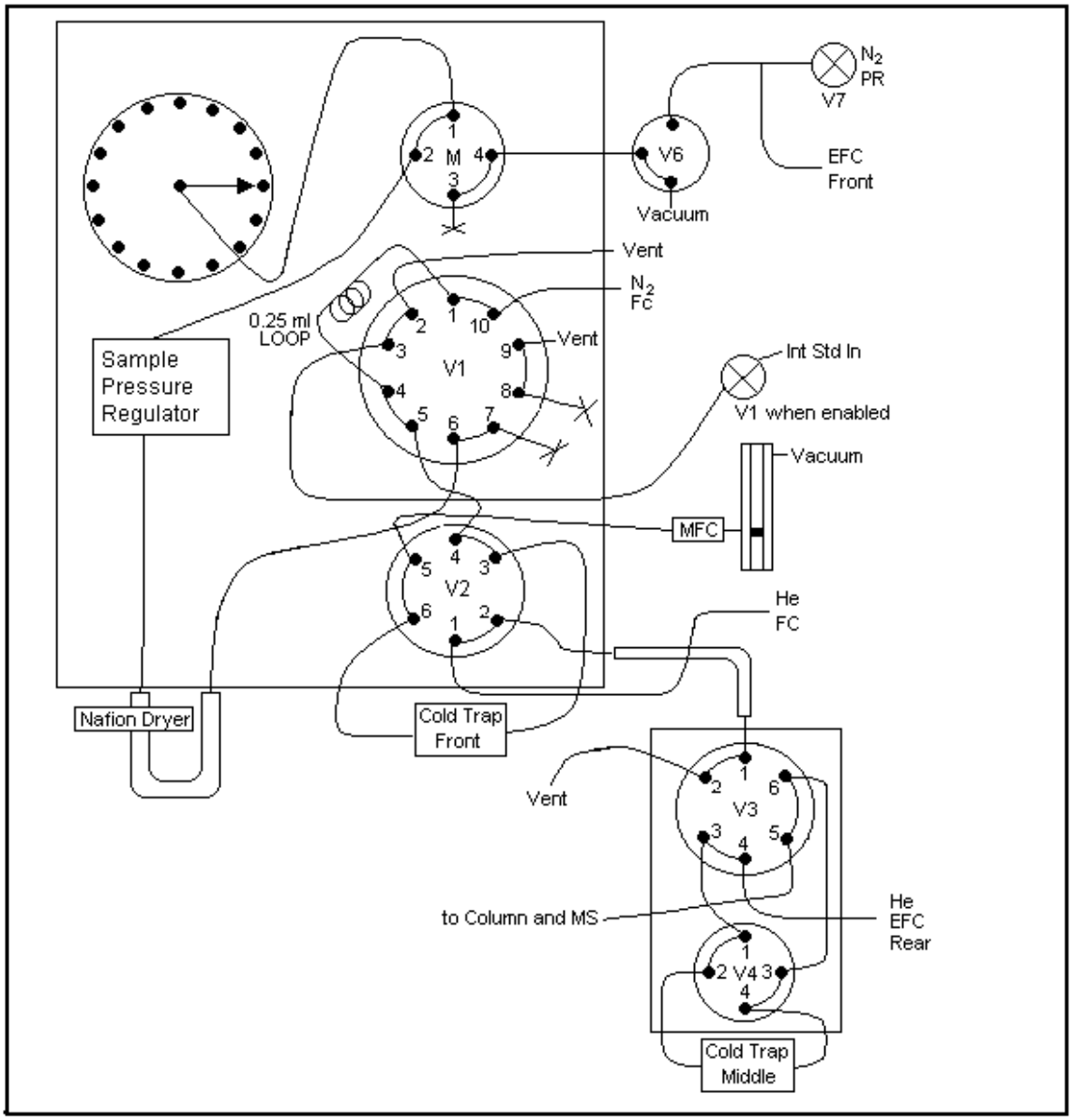


Sample Delivery Program

Time	V1	V2	V3	V4	V5	V6	V7
0.00	-	-	-	-	-	-	-
0.01	+	-	-	-	-	-	-
4.00	+	+	-	-	-	-	-
7.00	-	+	-	-	-	-	-
8.00	-	-	-	-	-	-	-
11.00	-	-	+	-	+	-	-
11.01	-	-	+	-	-	-	-
16.00	-	-	-	-	-	-	-

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: Desorb Cryofocuser to Column / Start GC Time: 11.00 and 11.01 min



Sample Delivery Program

Time	V1	V2	V3	V4	V5	V6	V7
0.00	-	-	-	-	-	-	-
0.01	+	-	-	-	-	-	-
4.00	+	+	-	-	-	-	-
7.00	-	+	-	-	-	-	-
8.00	-	-	-	-	-	-	-
11.00	-	-	+	-	+	-	-
11.01	-	-	+	-	-	-	-
16.00	-	-	-	-	-	-	-

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: Concentrator Programming Sequence

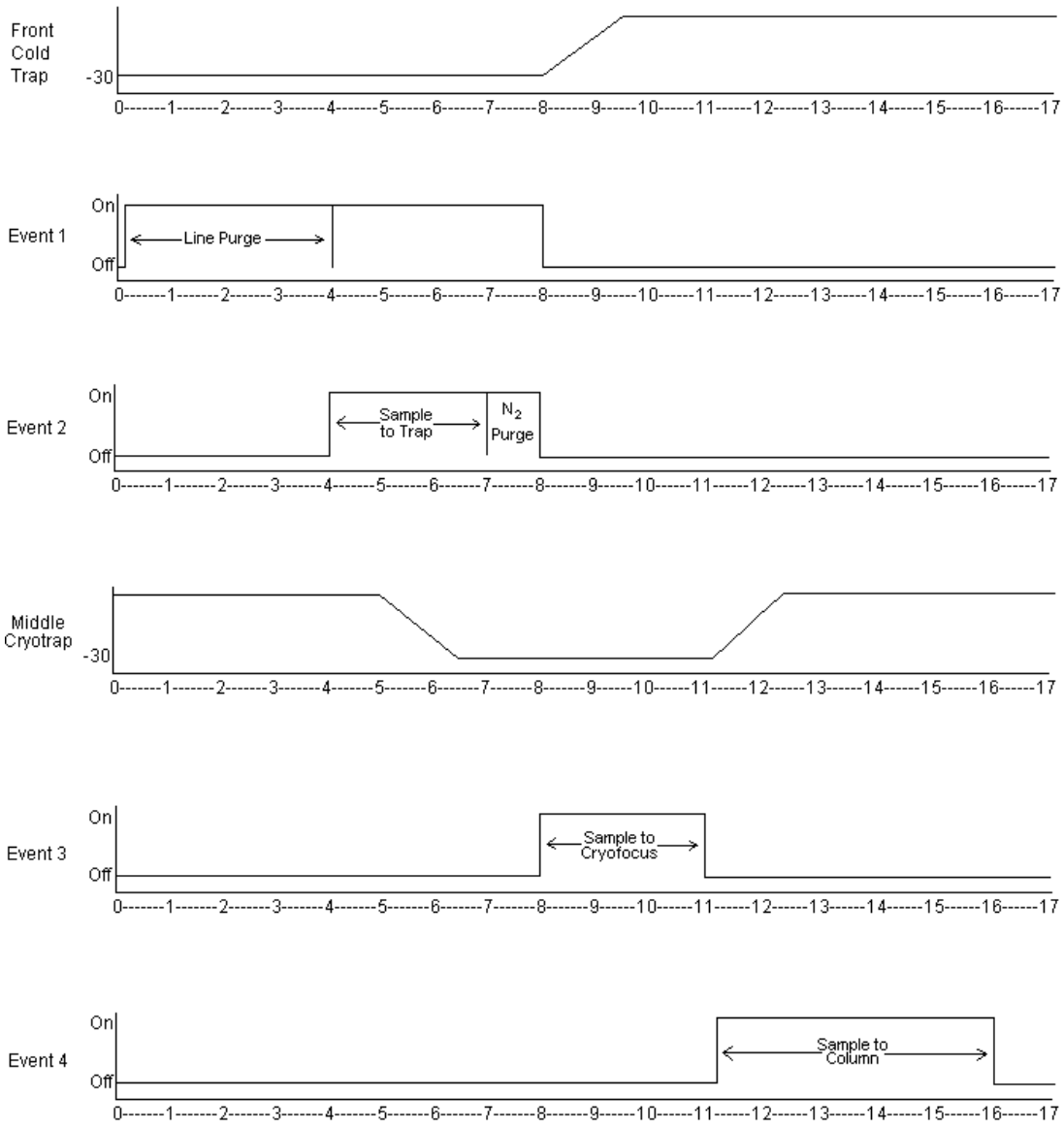


Figure 8: Typical Calibration Standard TIC

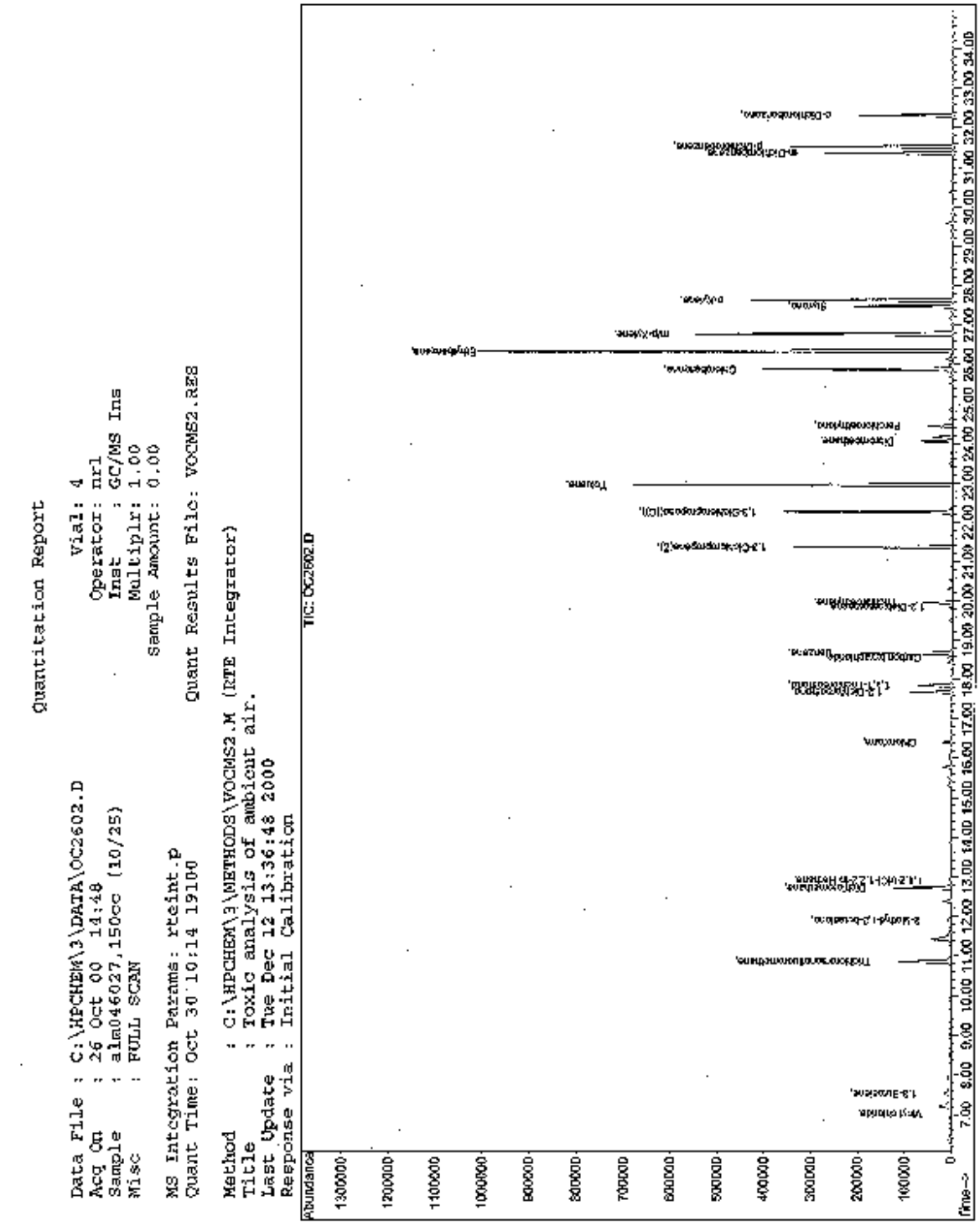


Figure 9: Typical Ambient Air TIC

Figure 10: Typical Mass Spectrum

```
File       : C:\HPCHEM\3\DATA\OC2602.D
Operator   : nrl
Acquired   : 26 Oct 00  14:48      using AcqMethod VOCMS2
Instrument :   GC/MS Ins
Sample Name: alm046027,150cc (10/25)
Misc Info  : FULL SCAN
Vial Number: 4
```

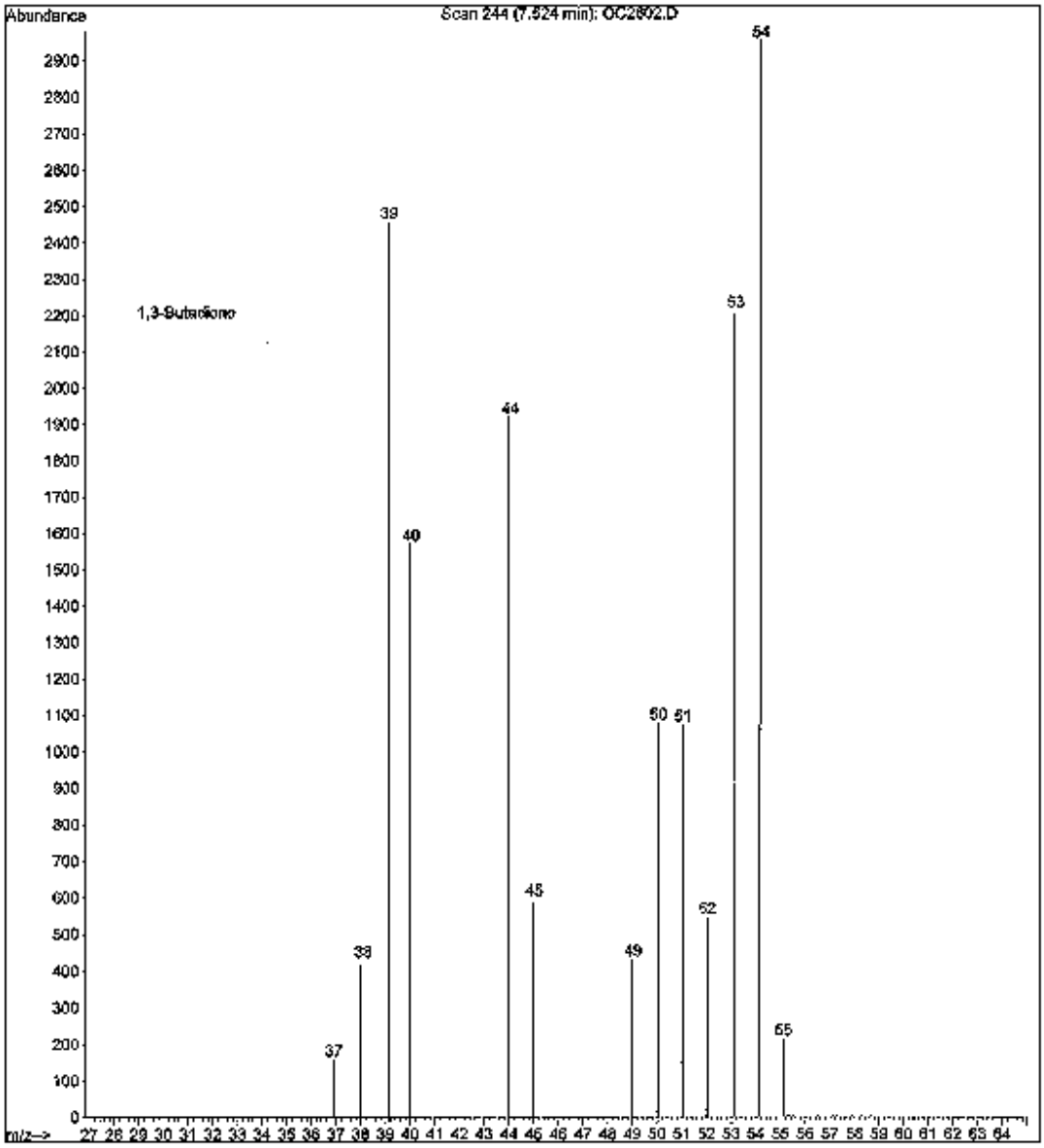


Figure 11: 1,3 Butadiene Multipoint Analysis (10/26/00) - ALM046027

Buta 0.84 ppb

LEVELS OF CONCENTRATION (PPB)						
cc	**25**	**50**	**100**	**150**	**300**	**600**
ppb	**0.14**	**0.28**	**0.56**	**0.84**	**1.68**	**3.36**
1st Run	1074	2691	7203	10182	22169	46409
2nd	741	3040	5964	10167	20609	41716
3rd	782	4128	6265	10220	21161	39365
Mean=	866	3286	6477	10190	21313	42497
Std.Dev.=	182	750	646	27	791	3586
%RSD=	21.0	22.8	10.0	0.3	3.7	8.4
# Obs. =	3	3	3	3	3	3

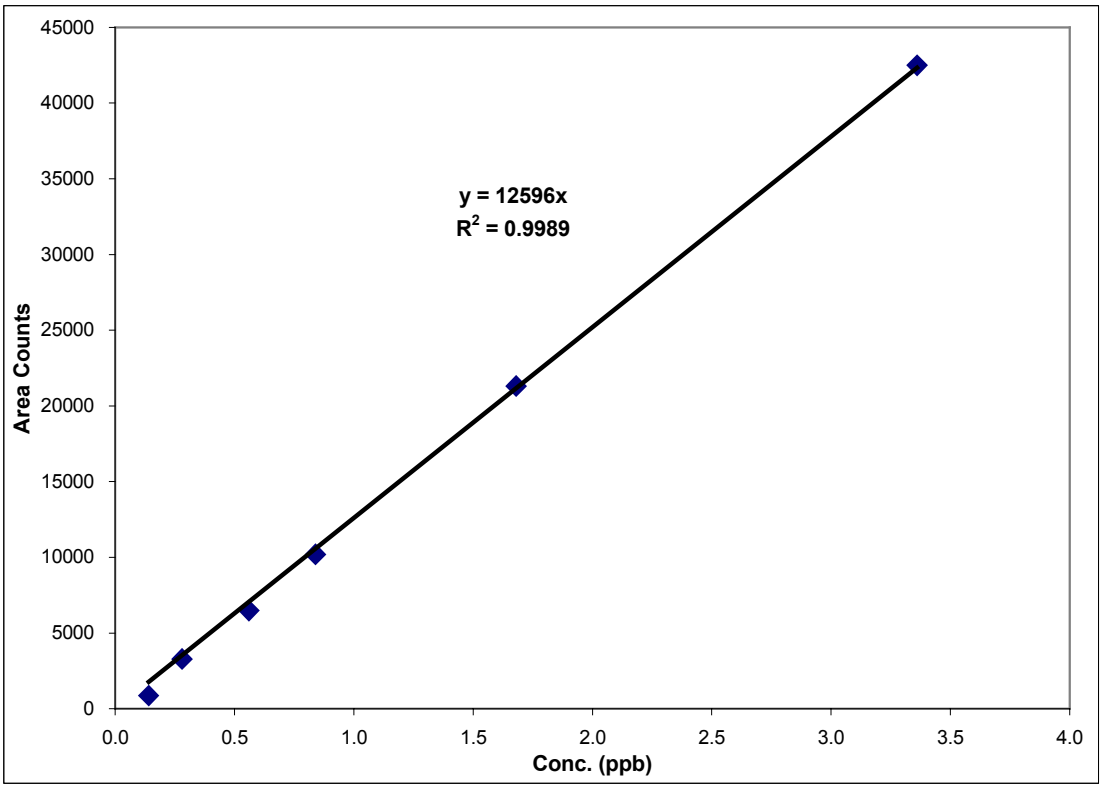


Figure 12: Carbon Tetrachloride Multipoint Analysis (10/26/00)

CCl4 0.08 ppb

LEVELS OF CONCENTRATION (PPB)						
cc	**25**	**50**	**100**	**150**	**300**	**600**
ppb	**0.01**	**0.03**	**0.05**	**0.08**	**0.16**	**0.32**
1st Run	655	1634	3093	5103	10694	21070
2nd	677	1613	3409	5289	10205	20612
3rd	644	1669	3478	4988	10555	20512
Mean=	659	1639	3327	5127	10485	20731
Std.Dev.=	17	28	205	152	252	298
%RSD=	2.6	1.7	6.2	3.0	2.4	1.4
# Obs. =	3	3	3	3	3	3

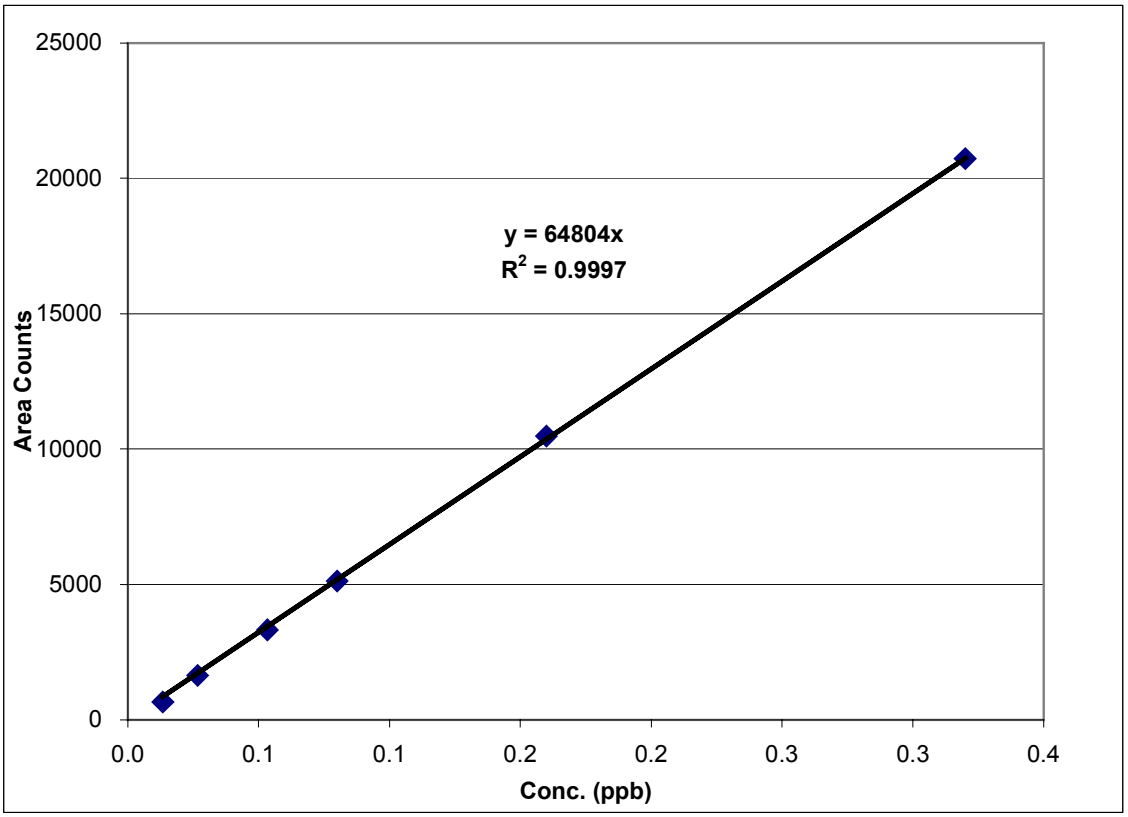


Figure 13: Benzene Multipoint Analysis (10/26/00)

Benzene 2.02 ppb

LEVELS OF CONCENTRATION (PPB)						
cc	**25**	**50**	**100**	**150**	**300**	**600**
ppb	**0.34**	**0.67**	**1.35**	**2.02**	**4.04**	**8.08**
1st Run	27288	56252	122003	177650	354181	720179
2nd	26908	58454	119299	175858	355111	719840
3rd	27096	59664	117910	176182	355156	718340
Mean=	27097	58123	119737	176563	354816	719453
Std.Dev.=	190	1730	2081	955	550	979
%RSD=	0.7	3.0	1.7	0.5	0.2	0.1
# Obs. =	3	3	3	3	3	3

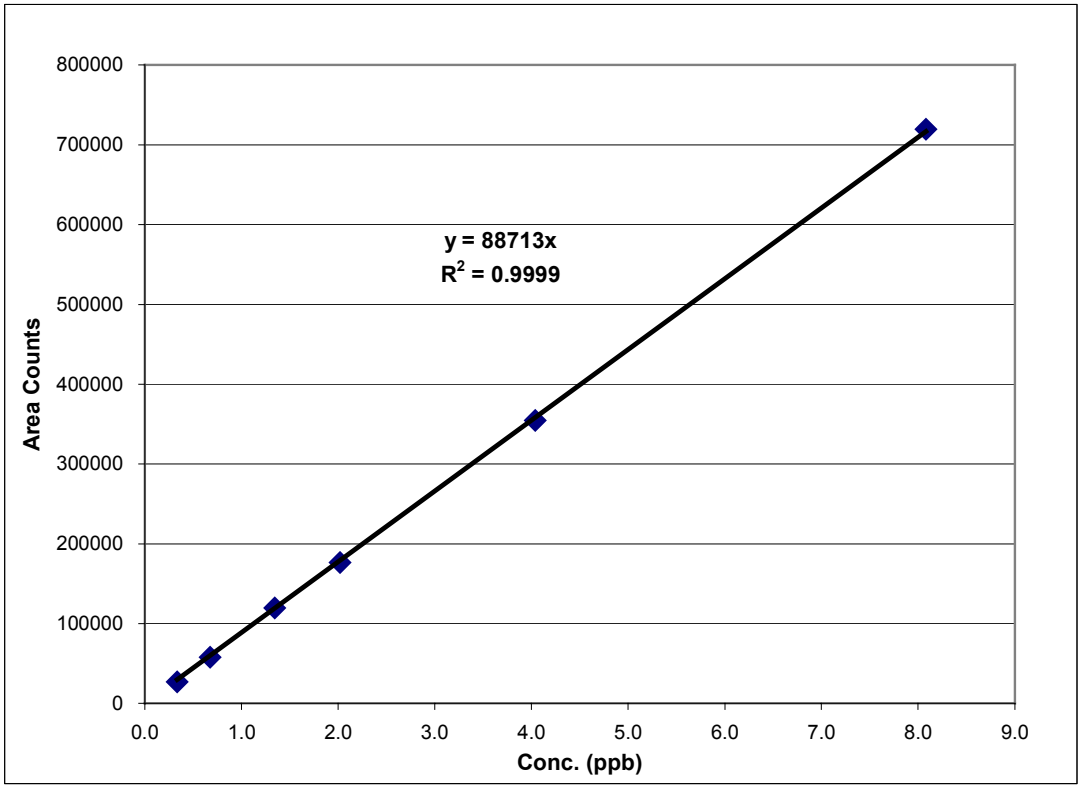


Figure 14: Trichloroethylene Multipoint Analysis (10/26/00)

TCE 0.56 ppb

LEVELS OF CONCENTRATION (PPB)						
cc	**25**	**50**	**100**	**150**	**300**	**600**
ppb	**0.09**	**0.19**	**0.37**	**0.56**	**1.12**	**2.24**
1st Run	3454	7451	15858	23595	46132	92914
2nd	3428	7434	15447	23302	46750	92833
3rd	3526	7837	15026	22993	46048	93355
Mean=	3469	7574	15444	23297	46310	93034
Std.Dev.=	51	228	416	301	383	281
%RSD=	1.5	3.0	2.7	1.3	0.8	0.3
# Obs. =	3	3	3	3	3	3

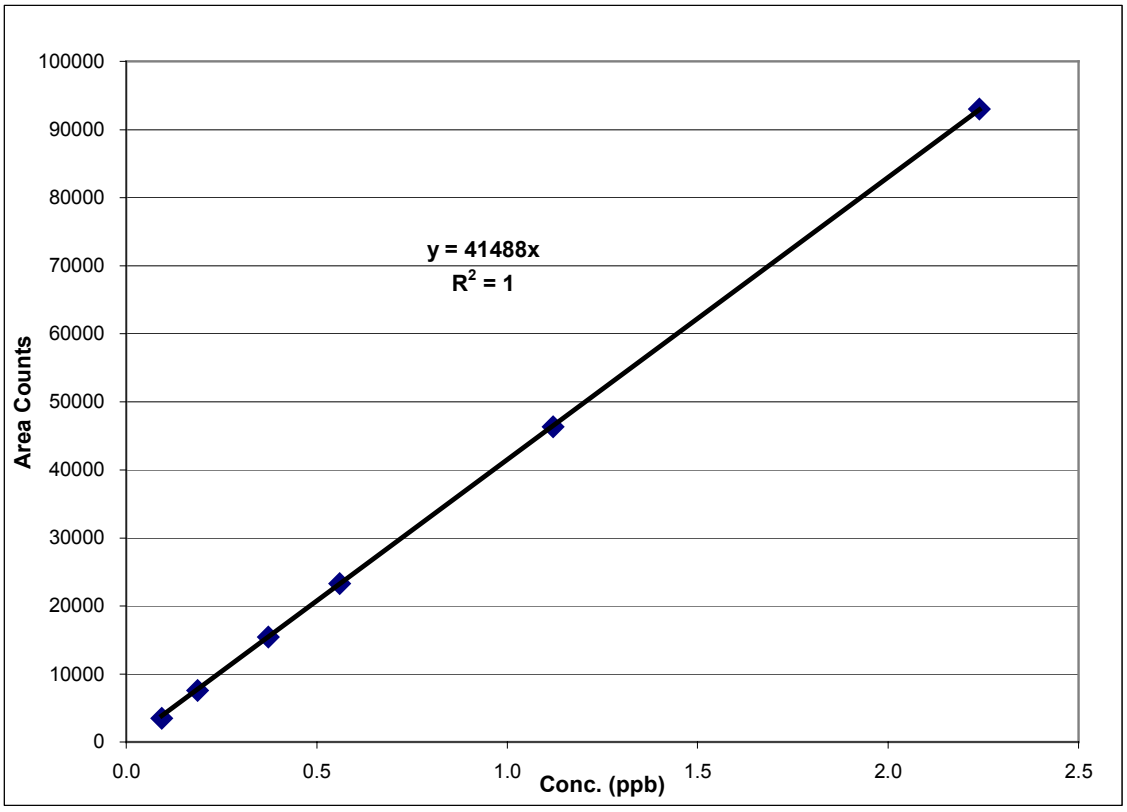


Figure 15: Styrene Multipoint Analysis (10/26/00)

Styrene 4.10 ppb

LEVELS OF CONCENTRATION (PPB)						
cc	**25**	**50**	**100**	**150**	**300**	**600**
ppb	**0.68**	**1.37**	**2.73**	**4.10**	**8.20**	**16.40**
1st Run	18082	43464	100902	152001	311683	645898
2nd	18768	45579	99443	150340	327374	665468
3rd	18518	48480	98896	150501	318771	668414
Mean=	18456	45841	99747	150947	319276	659927
Std.Dev.=	347	2518	1037	916	7858	12238
%RSD=	1.9	5.5	1.0	0.6	2.5	1.9
# Obs. =	3	3	3	3	3	3

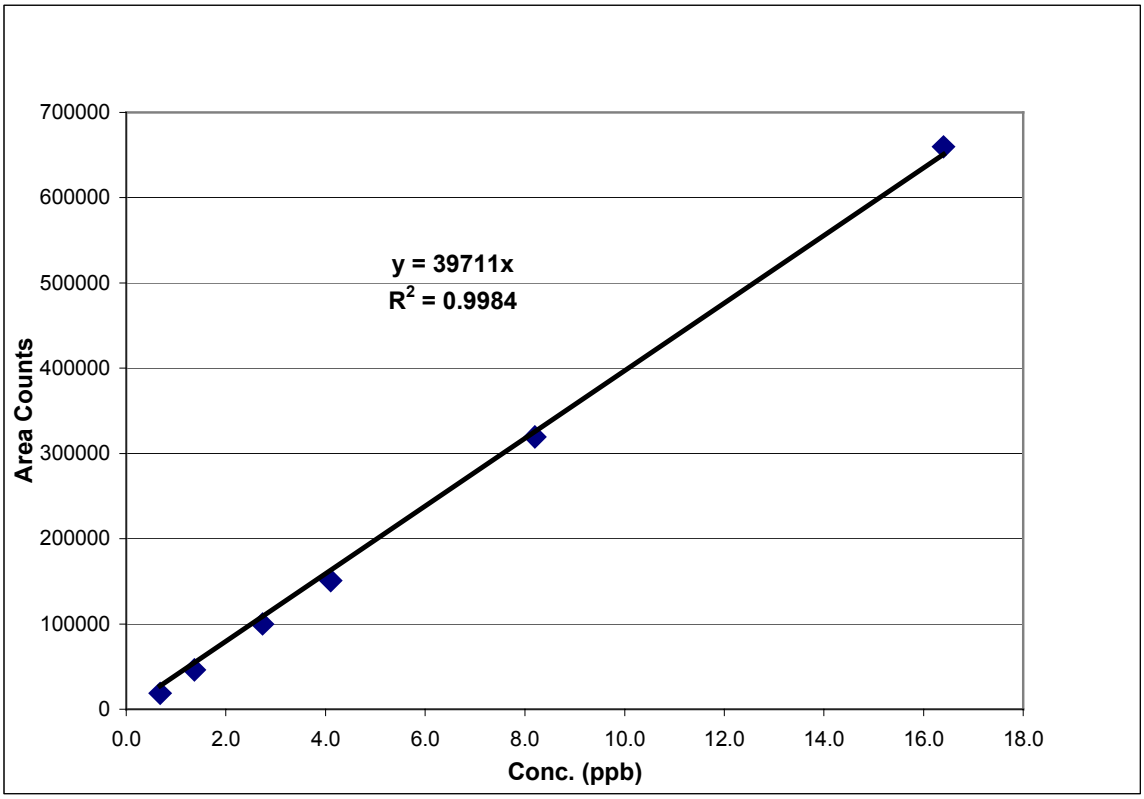


Figure 16: p-Dichlorobenzene Multipoint Analysis (10/26/00)

p-DCB 5.16 ppb

LEVELS OF CONCENTRATION (PPB)						
cc	**25**	**50**	**100**	**150**	**300**	**600**
ppb	**0.86**	**1.72**	**3.44**	**5.16**	**10.32**	**20.64**
1st Run	30523	74909	150768	213218	320746	625148
2nd	31553	74495	158275	211843	461606	801550
3rd	35477	76065	156581	200166	410096	911391
Mean=	32518	75156	155208	208409	397483	779363
Std.Dev.=	2614	814	3937	7172	71272	144406
%RSD=	8.0	1.1	2.5	3.4	17.9	18.5
# Obs. =	3	3	3	3	3	3

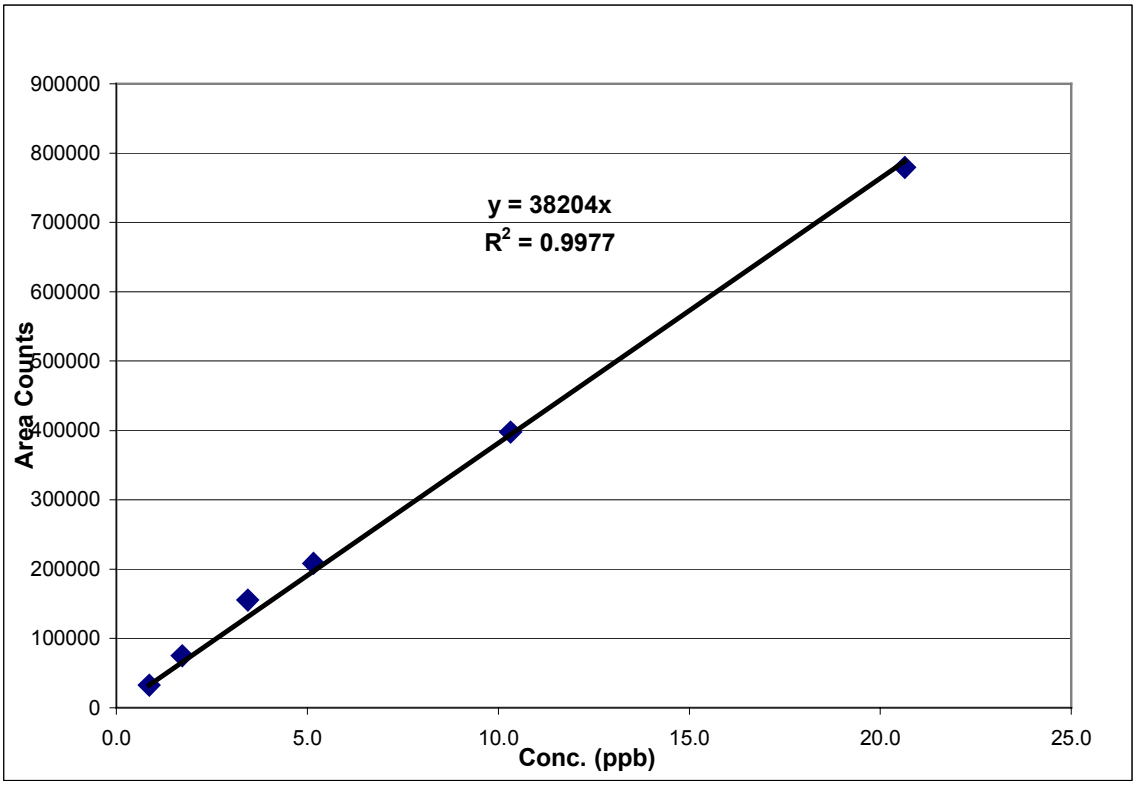


Figure 17: 1,3 Butadiene Control Chart

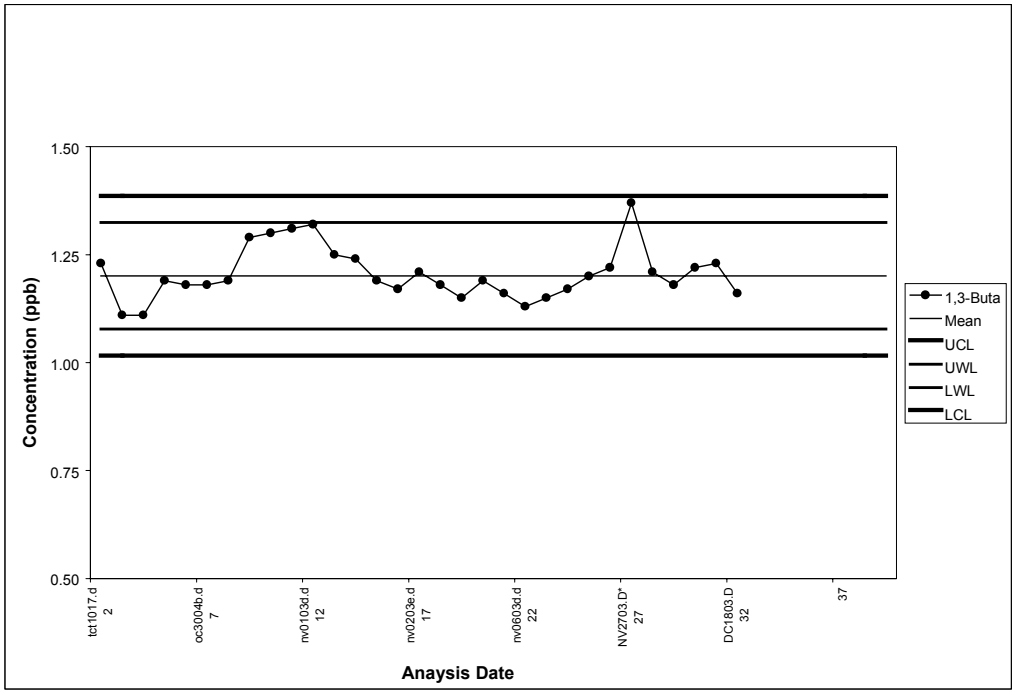


Figure 18: Carbon Tetrachloride Control Chart

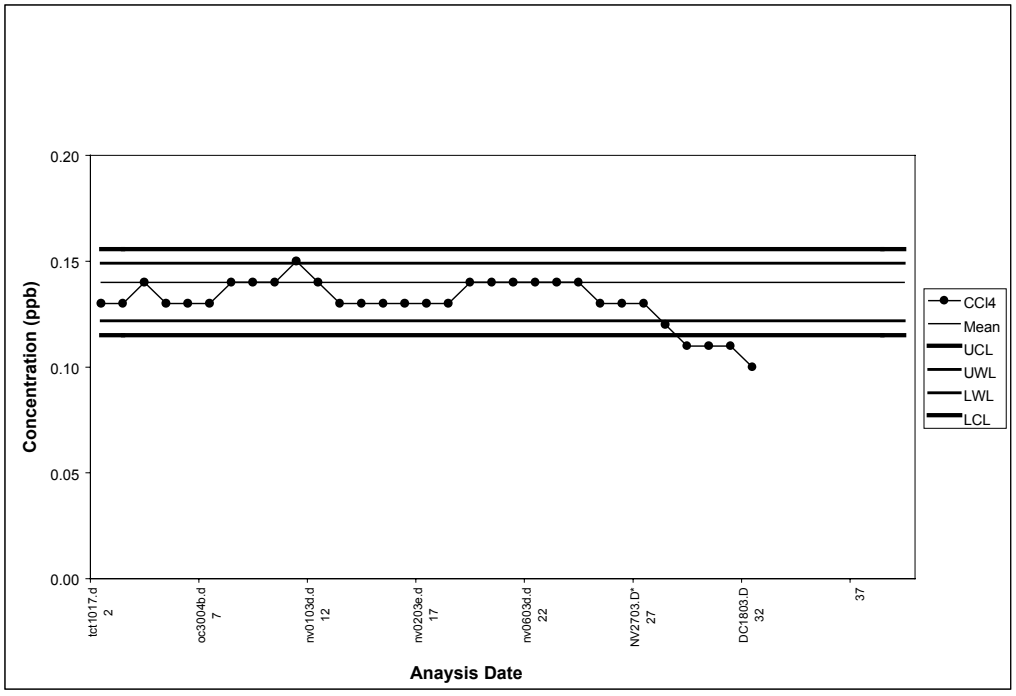


Figure 19: Benzene Control Chart

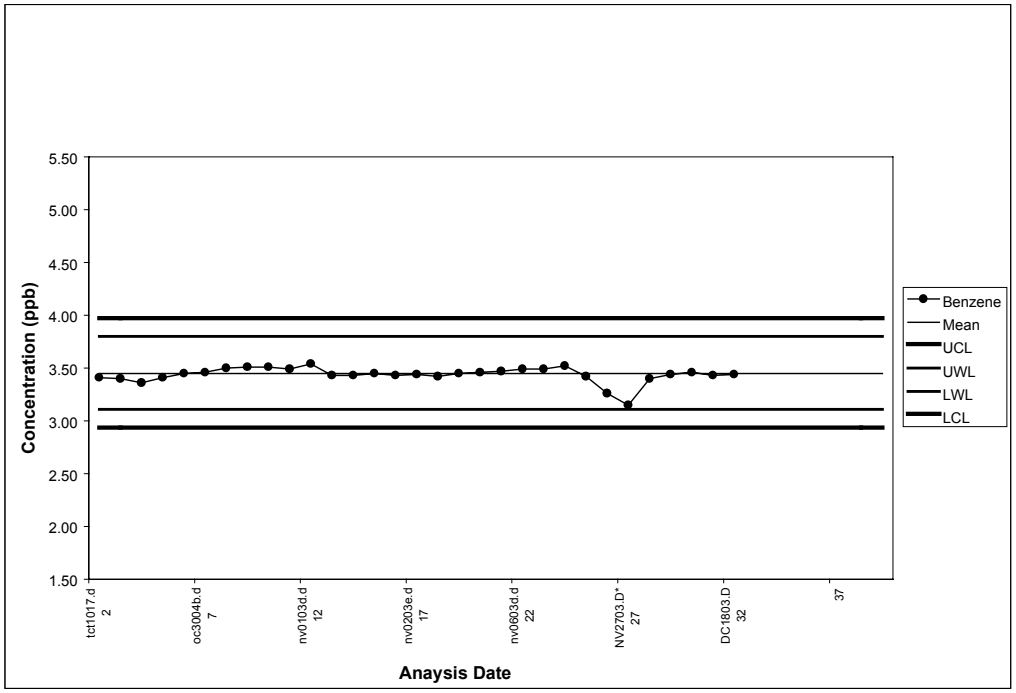


Figure 20: TCE Control Chart

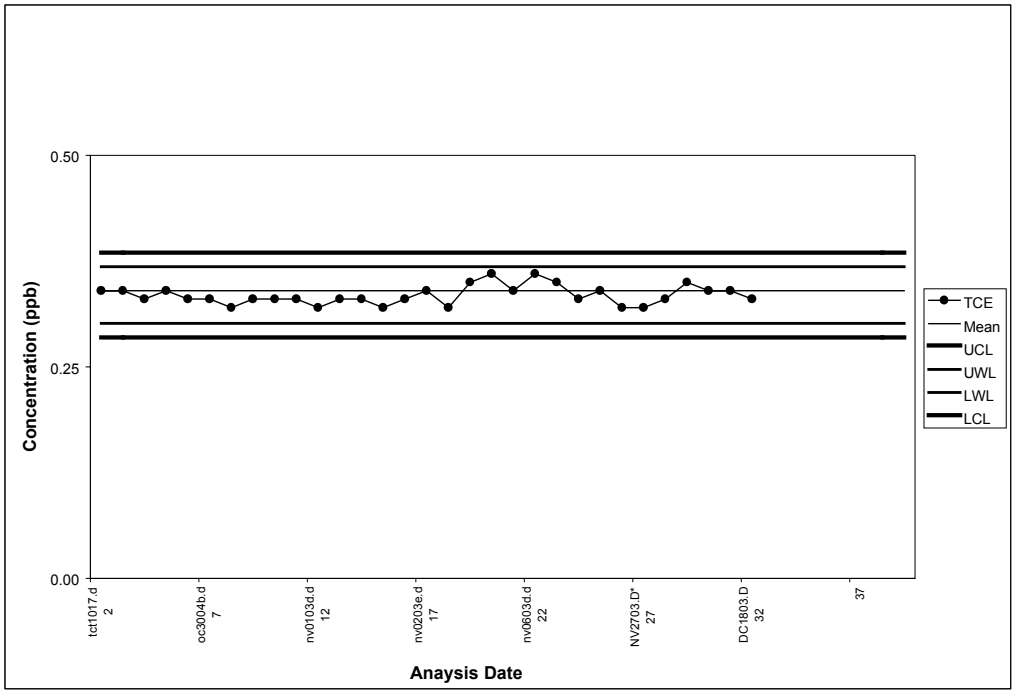


Figure 21: Styrene Control Chart

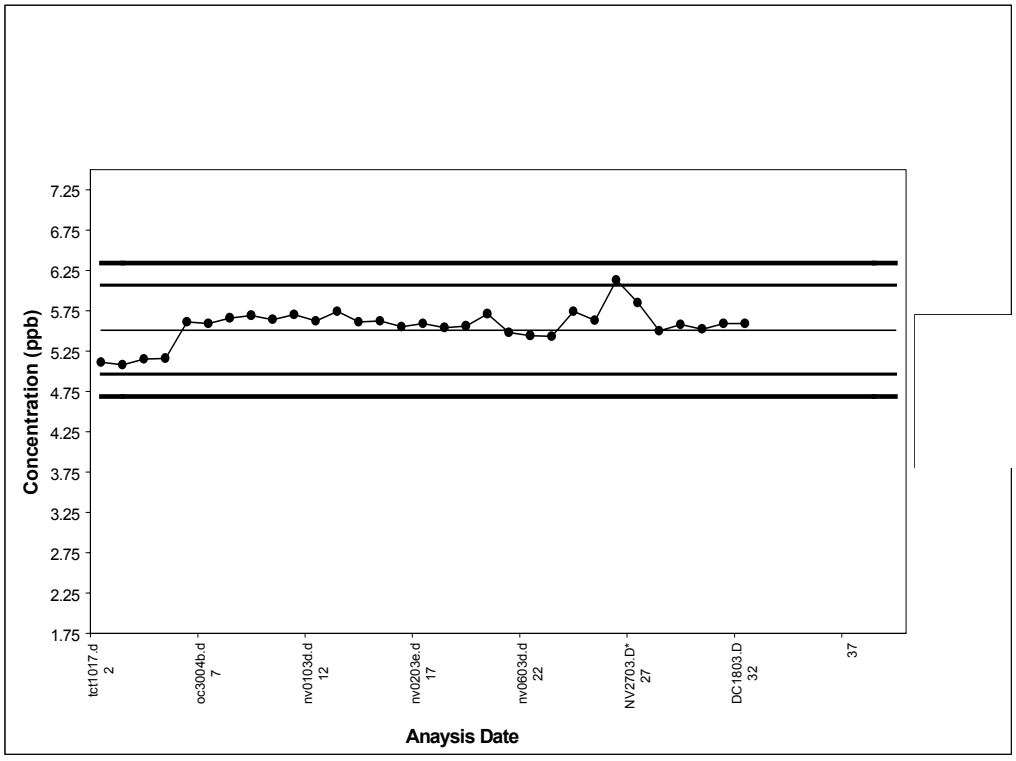
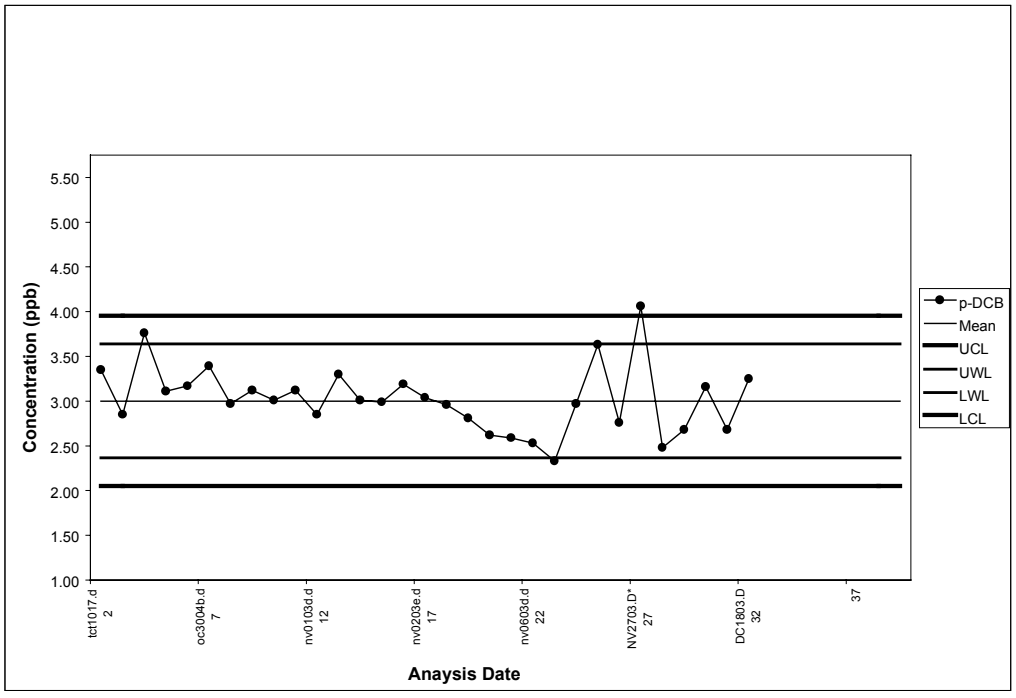


Figure 22: p-Dichlorobenzene Control Chart



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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

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Appendix II: Target Analyte LODs and Highest Calibration Concentration

ALM046027, 10/26/2000 - Varian 3800/HP6890/HP5973

			Multipoint Analysis	
Target Compound	**Published LOD (ppb)**	**Calculated LOD (ppb)**	**Correlation Coefficient R**	**Highest Calibrated Conc. (ppb)**
1,3-Butadiene	0.04	0.02	0.99945	3.36
Vinyl Chloride	NA	0.04	0.99800	1.08
Freon 11	NA	0.01	1.00000	8.00
Isoprene	NA	0.05	0.99925	2.92
Dichloromethane	1.0	0.03	0.99995	11.20
Chloroform	0.02	0.01	0.99995	0.96
1,2-Dichloroethane	NA	0.02	0.99995	7.76
1,1,1-Trichloroethane	0.01	0.01	1.00000	3.64
Carbon tetrachloride	0.02	0.01	0.99985	0.32
Benzene	0.2	0.01	0.99995	8.08
Trichloroethylene	0.02	0.02	1.00000	2.24
cis-1,3-Dichloropropene	NA	0.03	0.99965	18.92
Trans-1,3-Dichloropropene	NA	0.03	0.99960	18.92
Toluene	0.2	0.01	0.99990	19.28
1,2-Dibromoethane	NA	0.02	0.99995	3.96
Perchloroethylene	0.01	0.01	1.00000	1.36
Chlorobenzene	0.1	0.01	0.99990	11.88
Ethylbenzene	0.6	0.02	0.99985	18.88
m/p-Xylene	0.6	0.03	0.99975	25.84
Styrene	0.1	0.04	0.99920	16.40
o-Xylene	0.1	0.02	0.99980	11.24
m-Dichlorobenzene	0.2	0.20	0.99905	9.37
p-Dichlorobenzene	0.2	0.30	0.99885	20.64
o-Dichlorobenzene	0.1	0.30	0.99554	17.64
Freon12	NA	NA		
Freon113	NA	0.02	0.99979	0.73
1,2-Dichloropropane	NA	0.02	0.99998	3.92
Bromomethane	NA	0.03	0.99923	8.40

NA: Not available

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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 Cryogenic Concentration 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 MLD058.MTH is used for normal operation. Other methods include IDLE58.MTH for system standby, BAKEOUT58.MTH for conditioning/bakeout of the system. They are used in automated sequences along with method MLD058.

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 Method - MLD058.MTH

```
Star Chromatography Workstation - Method Listing Thu Mar 08 13:28:30 2001
Method: MLD058.mth
********************************************************************************
**********************
    3800 GC
**********************
Module Address: 44
 Front Valve Oven
-----------------
      Oven Power: On
     Temperature: 50 C
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
            4.00 min: On
            7.00 min: Off
            8.00 min: Off
           11.00 min: Off
           11.01 min: Off
           16.00 min: Off
     Valve 2: Sample Preconcentration Trap Valve
             Initial: SPT Desorb
            0.01 min: SPT Desorb
            4.00 min: SPT Trap
            7.00 min: SPT Trap
            8.00 min: SPT Desorb
           11.00 min: SPT Desorb
           11.01 min: SPT Desorb
           16.00 min: SPT Desorb
     Valve 3: Sample Preconcentration Trap Valve
             Initial: SPT Desorb
            0.01 min: SPT Desorb
            4.00 min: SPT Desorb
            7.00 min: SPT Desorb
            8.00 min: SPT Desorb
           11.00 min: SPT Trap
           11.01 min: SPT Trap
           16.00 min: SPT Desorb
     Valve 4: Series Bypass Valve
             Initial: Series
            0.01 min: Series
            4.00 min: Series
```

```
            7.00 min: Series
            8.00 min: Series
           11.01 min: Series
           16.00 min: Series
     Valve 5: Event A Valve
             Initial: Off
            0.01 min: Off
            4.00 min: Off
            7.00 min: Off
            8.00 min: Off
           11.00 min: On
           11.01 min: Off
           16.00 min: Off
     Valve 6: Event B Valve
             Initial: Off
            0.01 min: Off
            4.00 min: Off
            7.00 min: Off
            8.00 min: Off
           11.00 min: Off
           11.01 min: Off
           16.00 min: Off
     Valve 7: Event C Valve
             Initial: Off
            0.01 min: Off
            4.00 min: Off
            7.00 min: Off
            8.00 min: Off
           11.00 min: Off
           11.01 min: Off
           16.00 min: Off
 Front Injector Type 1079
-------------------------
            Oven Power: On
               Coolant: On
     Enable Coolant at: 250 C
       Coolant Timeout: 30.00 min
     Temp    Rate      Hold     Total
      (C)   (C/min)   (min)     (min)
     ---------------------------------
      -30       0      8.10      8.10
      250     200     36.40     45.90
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      5.00      5.00
```

```
      -30     200      4.95     11.10
      250     200     33.40     45.90
  Rear Injector Type 1041
-------------------------
     Temperature: 150 C
  Rear Injector EFC Type 3
-------------------------
     Flow    Rate      Hold     Total
 (ml/min) (ml/min/min) (min)    (min)
 ------------------------------------
      2.0     0.0     45.90     45.90
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     45.90     45.90
Output Port A
--------------
      Time    Signal   Attenuation
      (min)   Source
      ----------------------------
    Initial    Front          1
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 : 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
Integration Parameters  Address 44  Channel Front
-----------------------------------------------
Subtract Blank Baseline     : No
Initial S/N Ratio           : 5
Initial Peak Width          : 4 sec
Initial Tangent Height %    : 10%
```

Varian Star Workstation Method - MLD058.MTH

```
Monitor Noise               : Before every run
Measurement Type            : Peak Area
Initial Peak Reject Value   : 1000    counts
Report Unidentified Peaks   : Yes
Report Missing Peaks        : No
Calibration Setup       Address 44  Channel Front
-----------------------------------------------
Calculation Type            : % (No Calibration)
Number of Calibration Levels: 1
Curve Origin                : Force
Curve Fit                   : Linear
Weighted Regression         : (None)
Replicate Treatment         : Average Calibration Replicates
    Averaging Weight        :  50% (applied to new replicates)
Replicate Tolerance         : Add replicates within tolerance of 0.5%
    Out-of-Tolerance Action : No Action
Calibration Range Tolerance :      10.0%
    Out-of-Tolerance Action : No Action
Verification Setup      Address 44  Channel Front
-----------------------------------------------
Deviation Tolerance         : 100.0%
    Out-of-Tolerance Action : No Action
Peak Table  Address 44  Channel Front
---------------------------------
Reference Peaks Time Windows:Width:0.10 min. Retention Time 2.0%
Other Peaks Time Windows    :Width:0.10 min. Retention Time 2.0%
            Peak Table Empty
Time Events Table   Address 44  Channel Front
-----------------------------------------
            Time Events Table Empty
Report Format: Module 3800 Address 44 Channel Front
-------------------------------------------------
Title                     :
Print Chromatogram        :  No
Print Results             :  No
Convert Results to ASCII?:  Off
Calibration Block Reports
Print Report              :  No
Convert Report to ASCII?  :  Off
Print Copies              :  1
```

Varian Star Workstation Method - IDLE58.MTH

```
Star Chromatography Workstation - Method Listing   Thu Mar 08 13:28:30 2001
Method: idle58.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
     Valve 2: Sample Preconcentration Trap Valve
              Initial: SPT Desorb
     Valve 3: Sample Preconcentration Trap Valve
              Initial: SPT Desorb
     Valve 4: Series Bypass Valve
              Initial: Series
     Valve 5: Event A Valve
              Initial: Off
     Valve 6: Event B Valve
              Initial: Off
     Valve 7: Event C Valve
              Initial: 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)
     --------------------------------
      200       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 Method - IDLE58.MTH

```
-------------------------
      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
--------------
      Time    Signal   Attenuation
      (min)   Source
      ---------------------------
    Initial    Front          1
Output Port B
--------------
      Time    Signal   Attenuation
      (min)   Source
      ---------------------------
    Initial    Front          1
Output Port C
--------------
      Time    Signal   Attenuation
      (min)   Source
      ---------------------------
    Initial    Front          1
Data Acquisition
----------------
           Monitor Length : 64 bunched points (6.4 sec)
       Front FID/TSD Scale: 1 Volts
```

Varian Star Workstation Method - IDLE58.MTH

```
      Middle FID/TSD Scale: 1 Volts
        Rear FID/TSD Scale: 1 Volts
Integration Parameters  Address 44  Channel Front
-------------------------------------------
Subtract Blank Baseline     : No
Initial S/N Ratio           : 5
Initial Peak Width          : 4 sec
Initial Tangent Height %    : 10%
Monitor Noise               : Before every run
Measurement Type            : Peak Area
Initial Peak Reject Value   : 1000    counts
Report Unidentified Peaks   : Yes
Report Missing Peaks        : No
Calibration Setup       Address 44  Channel Front
-------------------------------------------
Calculation Type            : % (No Calibration)
Number of Calibration Levels: 1
Curve Origin                : Force
Curve Fit                   : Linear
Weighted Regression         : (None)
Replicate Treatment         : Average Calibration Replicates
    Averaging Weight        :  50% (applied to new replicates)
Replicate Tolerance         : Add replicates within tolerance of 0.5%
    Out-of-Tolerance Action : No Action
Calibration Range Tolerance :      10.0%
    Out-of-Tolerance Action : No Action
Verification Setup      Address 44  Channel Front
-------------------------------------------
Deviation Tolerance         : 100.0%
    Out-of-Tolerance Action : No Action

Peak Table  Address 44  Channel Front
---------------------------------
Reference Peaks Time Windows:Width:0.10 min. Retention Time 2.0%
Other Peaks Time Windows    :Width:0.10 min. Retention Time 2.0%
            Peak Table Empty
Time Events Table   Address 44  Channel Front
----------------------------------------
            Time Events Table Empty
Report Format: Module 3800 Address 44 Channel Front
-------------------------------------------------
Title                    :
Print Chromatogram       :  No
Print Results            :  No
Calibration Block Reports
Print Report             :  No
Convert Report to ASCII? :  Off
Print Copies             :  1
```

Varian Star Workstation Method - BAKEOUT58.MTH

```
Star Chromatography Workstation - Method Listing   Thu Jun 07 12:26:38 2001
Method: bakeout58.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: On
             0.01 min: Off
             0.02 min: Off
     Valve 2: Sample Preconcentration Trap Valve
              Initial: SPT Desorb
             0.01 min: SPT Desorb
             0.02 min: SPT Desorb
     Valve 3: Sample Preconcentration Trap Valve
              Initial: SPT Desorb
             0.01 min: SPT Desorb
             0.02 min: SPT Desorb
     Valve 4: Series Bypass Valve
              Initial: Series
             0.01 min: Series
             0.02 min: Series
     Valve 5: Event A Valve
              Initial: Off
             0.01 min: On
             0.02 min: Off
     Valve 6: Event B Valve
              Initial: Off
             0.01 min: Off
             0.02 min: Off
     Valve 7: Event C Valve
              Initial: Off
             0.01 min: Off
             0.02 min: Off
 Front Injector Type 1079
------------------------
            Oven Power: On
               Coolant: On
     Enable Coolant at: 250 C
     Temp    Rate      Hold     Total
      (C)   (C/min)   (min)     (min)
```

```
     --------------------------------
      200       0     15.00     15.00
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)
     --------------------------------
      200       0     15.00     15.00
  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      0.10      0.10
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     50.00     50.00
 Front FID Detector
-------------------
      Oven Power: Off
     Temperature: 50 C
     Electronics: Off
   Time Constant: Fast
      Time    Range  Autozero
      (min)
      ----------------------
    Initial    12     yes
Output Port A
--------------
      Time    Signal   Attenuation
      (min)   Source
      ---------------------------
    Initial    Front          1
Output Port B
--------------
      (min)   Source
      ---------------------------
```

Varian Star Workstation Method - BAKEOUT58.MTH

```
    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
```

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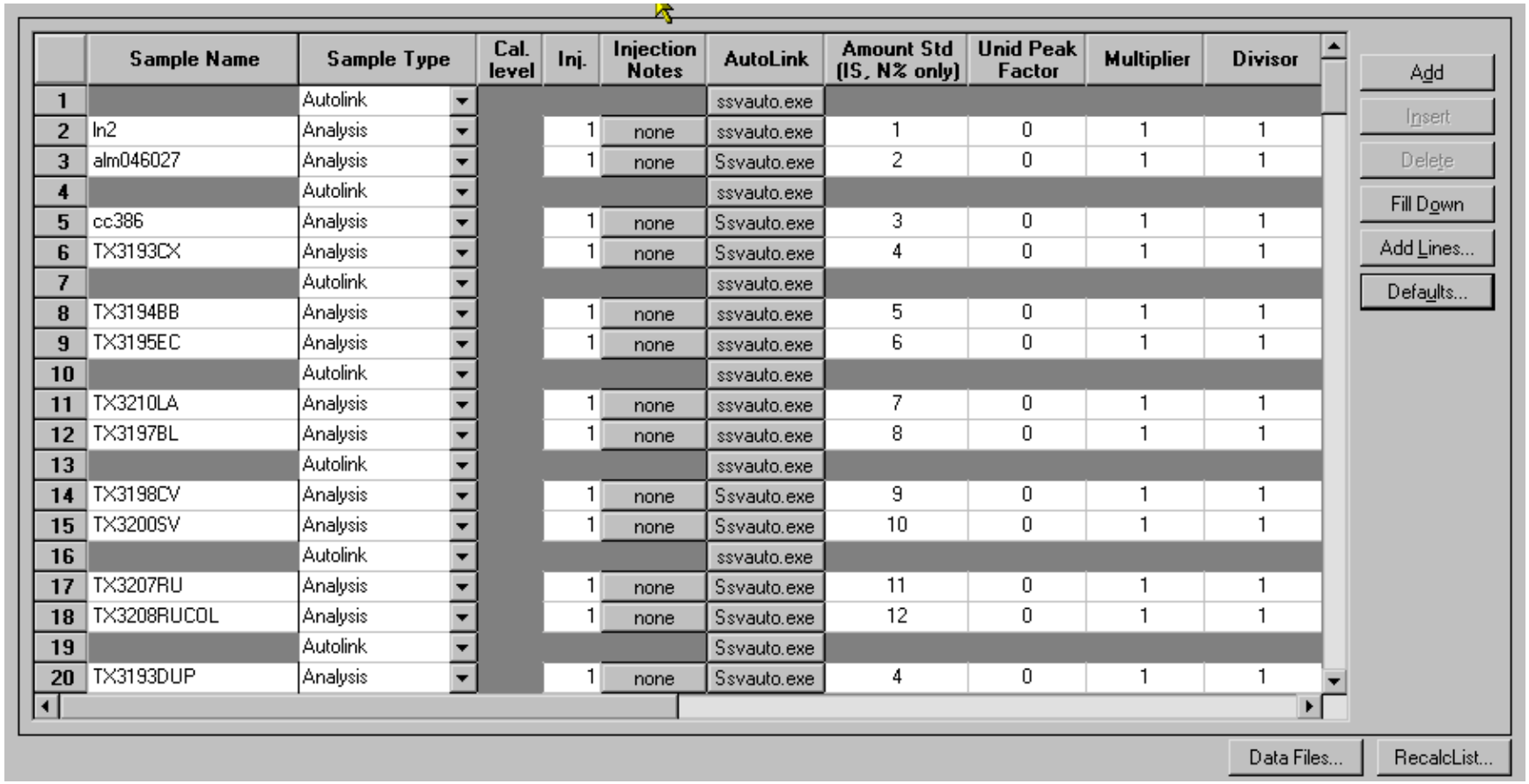
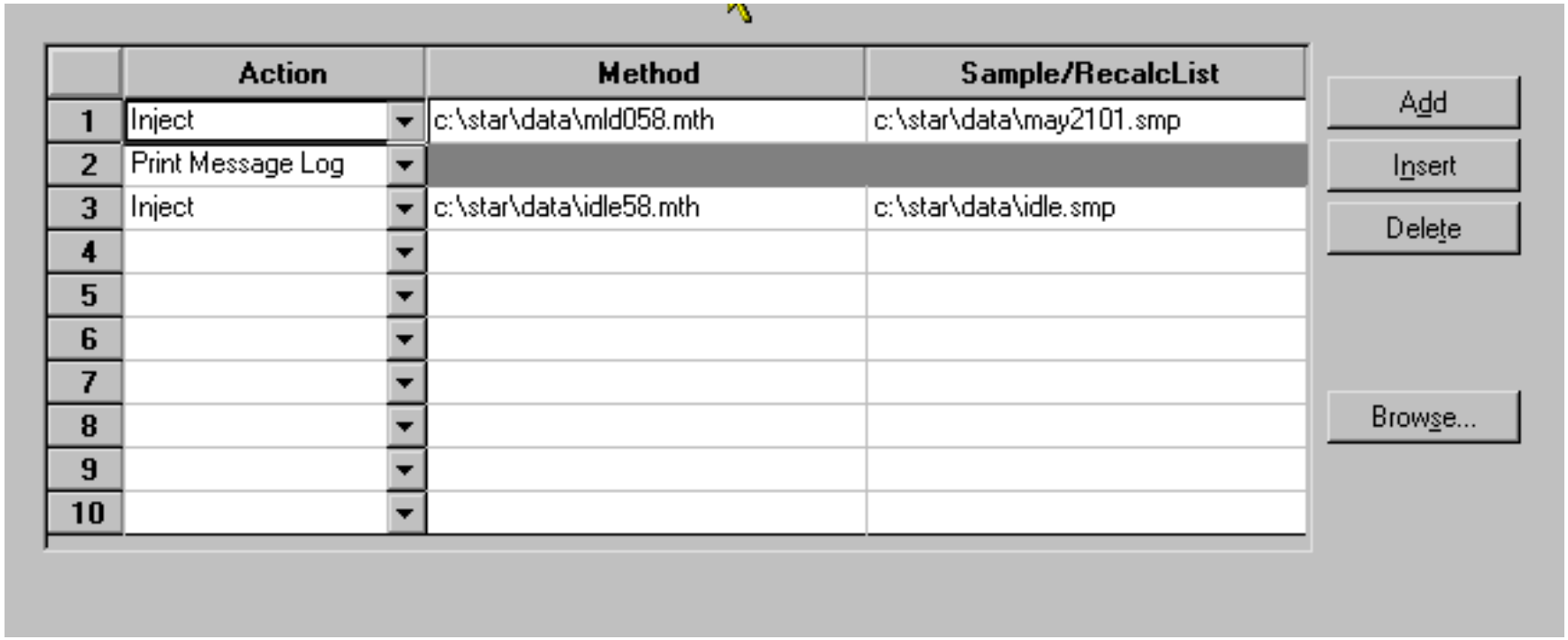
Varian Star GC Workstation Sample List - SAMPLE.SAM



	Sample Name	Sample Type	Cal. level	Inj.	Injection Notes	AutoLink	Amount Std (IS, N% only)	Unid Peak Factor	Multiplier	Divisor
1		Autolink				ssvauto.exe				
2	In2	Analysis		1	none	ssvauto.exe	1	0	1	1
3	alm046027	Analysis		1	none	Ssvauto.exe	2	0	1	1
4		Autolink				ssvauto.exe				
5	cc386	Analysis		1	none	Ssvauto.exe	3	0	1	1
6	TX3193CX	Analysis		1	none	Ssvauto.exe	4	0	1	1
7		Autolink				ssvauto.exe				
8	TX3194BB	Analysis		1	none	ssvauto.exe	5	0	1	1
9	TX3195EC	Analysis		1	none	ssvauto.exe	6	0	1	1
10		Autolink				ssvauto.exe				
11	TX3210LA	Analysis		1	none	ssvauto.exe	7	0	1	1
12	TX3197BL	Analysis		1	none	ssvauto.exe	8	0	1	1
13		Autolink				ssvauto.exe				
14	TX3198CV	Analysis		1	none	Ssvauto.exe	9	0	1	1
15	TX3200SV	Analysis		1	none	Ssvauto.exe	10	0	1	1
16		Autolink				ssvauto.exe				
17	TX3207RU	Analysis		1	none	Ssvauto.exe	11	0	1	1
18	TX3208RUCOL	Analysis		1	none	Ssvauto.exe	12	0	1	1
19		Autolink				Ssvauto.exe				
20	TX3193DUP	Analysis		1	none	Ssvauto.exe	4	0	1	1

Add
Insert
Delete
Fill Down
Add Lines...
Defaults...
Data Files...
RecalcList...

Varian Star GC Workstation Sample List - SAMPLE.SEQ



	Action	Method	Sample/RecalcList
1	Inject	c:\star\data\mld058.mth	c:\star\data\may2101.smp
2	Print Message Log		
3	Inject	c:\star\data\idle58.mth	c:\star\data\idle.smp
4			
5			
6			
7			
8			
9			
10			

Add
Insert
Delete
Browse...

Appendix IV: Hewlett-Packard GC/MS ChemStation

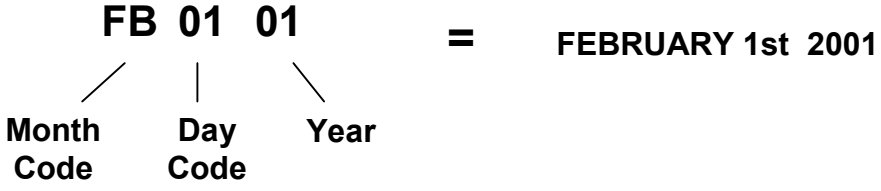
A Hewlett-Packard GC/MS ChemStation includes an Intel compatible PC, an Ethernet network adapter, a GPIB interface card, Microsoft 9.X or NT 4.0 operating system, and Hewlett-Packard Analytical MSD Productivity ChemStation Software, Version A.03.00 or B.03.00. The A software operates under Microsoft 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 MLD058.M is used for normal operation. Method IDLE.M is used for system standby. Both methods are used in automated sequences. Method MLD58.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. Although there are they are not used in this analysis, and are shown in lighter type. 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

Hewlett-Packard ChemStation Method - MLD058.M

```
TOPLEVEL PARAMETERS
-------------------
Method Information For: C:\HPCHEM\1\METHODS\MLD058.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 toxic analytes.
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: -10'C (On)             Maximum temp:  230 'C
   Initial time: 2.00 min               Equilibration time:  0.50 min
   Ramps:
      #  Rate  Final temp  Final time  CRYO (N2)
      1  6.00      200        1.00          Cryo:  On
      2   0.0(Off)                         Cryo fault:  On
   Post temp:  0 'C                        Cryo timeout:45.00min(On)
   Post time:  0.00 min                    Quick cryo cool:  On
   Run time:  38.00 min                    Ambient temp:  25 'C

FRONT INLET (HP PTV)               BACK INLET (SPLIT/SPLITLESS)
   Mode:  Splitless                   Mode:  Split
   Initial temp:  33 'C (Off)         Initial temp:  50 'C (Off)
   Cryo:  Off                         Pressure:  0.00 psi (Off)
   Cryo use temp:  25 'C              Total flow:  0.1 mL/min
   Cryo Timeout:  30.00 min (On)      Gas saver:  Off
   Cryo Fault:  On                    Gas type:  Helium
   Pressure:  0.07 psi (Off)
   Purge flow:  0.0 mL/min
   Purge time:  0.00 min
   Total flow:  3.1 mL/min
   Gas saver:  Off
   Gas type:  Helium
COLUMN 1                                COLUMN 2
   Capillary Column                        (not installed)
   Model Number:  J & W 1221564
   DB-VRX
   Max temperature:  260 'C
   Nominal length:  60.0 m
   Nominal diameter:  250.00 um
   Nominal film thickness:  1.40 um
```

```
   Inlet:  (unspecified)
   Outlet:  MSD
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
        Nanoliter Adapter           Off
        PostInj Solvent A Washes      0
        PostInj Solvent B Washes      0
        Viscosity Delay               0 seconds
        Plunger Speed              Fast
MS ACQUISITION PARAMETERS
General Information
------- -----------
Tune File                : ATUNE.U
Acquistion Mode          : Scan
MS Information
-- -----------
Solvent Delay            : 4.00 min
EM Absolute              : False
EM Offset                : 106
Resulting EM Voltage     : 1305.9
[Scan Parameters]
Low Mass                 : 33
High Mass                : 550
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)
34.00                    Off
END OF MS ACQUISITION PARAMETERS
END OF INSTRUMENT CONTROL PARAMETERS
-----------------------------------
DATA ANALYSIS PARAMETERS
-----------------------
Method Name: C:\HPCHEM\1\METHODS\MLD058.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    25
Integration Events: Meth Default
Report Type: Summary
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
Toxic analysis of ambient air.
Calibration Last Updated:
Reference Window: 0.50 Minutes
Non-Reference Window: 0.20 Minutes
Correlation Window: 0.05 minutes
Default Multiplier: 1.00
Default Sample Concentration: 0.00
Compound Information
--------------------
--------------------------------------------------------------------------------
```

```
 1)  Freon 12                                        ( )
Ret. Time   5.34 min., Extract & Integrate from   5.14 to   5.54 min.
Signal       Rel Resp.   Pct. Unc.(abs)    Integration
Tgt   85.00                                *** METH DEFAULT ***
Q1    87.00     40.00       20.0          *** METH DEFAULT ***
Q2   101.00     10.00       10.0          *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            0.750        49123
Qualifier Peak Analysis ON
Curve Fit: Linear
--------------------------------------------------------------------------------
 2)  VinCl                                          ( )
Ret. Time   7.06 min., Extract & Integrate from   6.86 to   7.26 min.
Signal       Rel Resp.   Pct. Unc.(abs)    Integration
Tgt   62.00                                *** METH DEFAULT ***
Q1    64.00     50.00       20.0          *** METH DEFAULT ***
Q2    61.00     10.00       10.0          *** METH DEFAULT ***
Q3    60.00     10.00       10.0          *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            0.270         4914
Qualifier Peak Analysis ON
Curve Fit: Linear
--------------------------------------------------------------------------------
 3)  Buta                                           ( )
Ret. Time   7.57 min., Extract & Integrate from   7.37 to   7.77 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt   54.10                                *** METH DEFAULT ***
Q1    39.10     93.30       20.0          *** METH DEFAULT ***
Q2    53.10     68.70       20.0          *** METH DEFAULT ***
Q3    51.10     29.00       20.0          *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            0.840        10312
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
--------------------------------------------------------------------------------
 4)  CH3Br                                          ( )
Ret. Time   8.53 min., Extract & Integrate from   8.33 to   8.73 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt   93.90                                *** METH DEFAULT ***
Q1    95.90     97.20       20.0          *** METH DEFAULT ***
Q2    92.90     20.60       20.0          *** METH DEFAULT ***
Q3    80.90     13.20       20.0          *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            2.100        44985
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
--------------------------------------------------------------------------------
 5)  Freon 11                                       ( )
Ret. Time  10.91 min., Extract & Integrate from  10.71 to  11.11 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt  100.90                                *** METH DEFAULT ***
Q1   102.90     64.80       20.0          *** METH DEFAULT ***
Q2   104.90     10.30       20.0          *** METH DEFAULT ***
Q3    66.00     11.90       20.0          *** METH DEFAULT ***
```

```
Lvl ID   Conc (ppb)  Response
1            2.000       139366
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
-------------------------------------------------------------------------------
 6)  Isoprene                                    ( )
Ret. Time  11.95 min., Extract & Integrate from  11.75 to  12.15 min.

Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt   67.10                                *** METH DEFAULT ***
Q1    53.10     61.30       20.0           *** METH DEFAULT ***
Q2    39.10     37.40       20.0           *** METH DEFAULT ***
Q3    68.10     72.10       20.0           *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            0.730        45419
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
-------------------------------------------------------------------------------
 7)  DCM                                         ( )
Ret. Time  12.76 min., Extract & Integrate from  12.56 to  12.96 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt   49.00                                *** METH DEFAULT ***
Q1    84.00     89.40       20.0           *** METH DEFAULT ***
Q2    85.90     56.50       20.0           *** METH DEFAULT ***
Q3    51.00     31.30       20.0           *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            2.800        72869

Qualifier Peak Analysis ON
Curve Fit: Avg. RF
-------------------------------------------------------------------------------
 8)  Freon 113                                   ( )
Ret. Time  12.95 min., Extract & Integrate from  12.75 to  13.15 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt  100.90                                *** METH DEFAULT ***
Q1   150.90     89.60       20.0           *** METH DEFAULT ***
Q2    85.00     40.90       20.0           *** METH DEFAULT ***
Q3   102.90     66.30       20.0           *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            0.210        13315
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
-------------------------------------------------------------------------------
 9)  CHCl3                                       ( )
Ret. Time  16.45 min., Extract & Integrate from  16.25 to  16.65 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt   82.90                                *** METH DEFAULT ***
Q1    84.90     64.70       20.0           *** METH DEFAULT ***
Q2    47.00     18.20       20.0           *** METH DEFAULT ***
Q3    86.90     10.40       20.0           *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            0.240        14318
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
```

```
------------------------------------------------------------------------
10)  EDC                                          ( )
Ret. Time  17.72 min., Extract & Integrate from  17.52 to  17.92 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt   62.00                                *** METH DEFAULT ***
Q1    49.00     26.90       20.0          *** METH DEFAULT ***
Q2    64.00     32.70       20.0          *** METH DEFAULT ***
Q3    63.00     15.90       20.0          *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            1.940        74767
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
------------------------------------------------------------------------
11)  TCEA                                         ( )
Ret. Time  17.90 min., Extract & Integrate from  17.70 to  18.10 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt   97.00                                *** METH DEFAULT ***
Q1    98.90     66.30       20.0          *** METH DEFAULT ***
Q2    61.00     37.70       20.0          *** METH DEFAULT ***
Q3    63.00     11.00       20.0          *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            0.910        55382
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
------------------------------------------------------------------------
12)  CCl4                                         ( )
Ret. Time  18.61 min., Extract & Integrate from  18.41 to  18.81 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt  116.90                                *** METH DEFAULT ***
Q1   118.90     91.00       20.0          *** METH DEFAULT ***
Q2   120.90     31.50       20.0          *** METH DEFAULT ***
Q3    82.00     21.90       20.0          *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            0.080         5830
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
------------------------------------------------------------------------
13)  Benzene                                      ( )
Ret. Time  18.71 min., Extract & Integrate from  18.51 to  18.91 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt   78.00                                *** METH DEFAULT ***
Q1    77.00     22.80       20.0          *** METH DEFAULT ***
Q2    52.10     14.90       20.0          *** METH DEFAULT ***
Q3    51.00     14.50       20.0          *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            2.020       180498
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
------------------------------------------------------------------------
14)  DCP                                          ( )
Ret. Time  19.87 min., Extract & Integrate from  19.67 to  20.07 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt   63.00                                *** METH DEFAULT ***
Q1    62.00     70.30       20.0          *** METH DEFAULT ***
```

```
Q2    76.00     41.00       20.0           *** METH DEFAULT ***
Q3    65.00     31.30       20.0           *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            0.980        48008
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
---------------------------------------------------------------------------
15)  TCE                                          ( )
Ret. Time  20.00 min., Extract & Integrate from  19.80 to  20.20 min.

Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt  129.90                                *** METH DEFAULT ***
Q1   131.90     98.00       20.0           *** METH DEFAULT ***
Q2    94.90     98.00       20.0           *** METH DEFAULT ***
Q3    60.00     35.00       20.0           *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            0.560        22494
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
---------------------------------------------------------------------------
16)  c-DClprpene                                  ( )
Ret. Time  22.30 min., Extract & Integrate from  22.10 to  22.50 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt   75.00                                *** METH DEFAULT ***
Q1    39.00     39.60       20.0           *** METH DEFAULT ***
Q2    77.00     30.80       20.0           *** METH DEFAULT ***
Q3   109.90     22.80       20.0           *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            4.730       210127
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
---------------------------------------------------------------------------
17)  t-DClprpene                                  ( )
Ret. Time  21.41 min., Extract & Integrate from  21.21 to  21.61 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt   75.00                                *** METH DEFAULT ***
Q1    39.10     39.50       20.0           *** METH DEFAULT ***
Q2    77.00     33.00       20.0           *** METH DEFAULT ***
Q3   109.90     24.50       20.0           *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            4.730       200970
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
---------------------------------------------------------------------------
18)  Toluene                                      ( )
Ret. Time  22.99 min., Extract & Integrate from  22.79 to  23.19 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt   91.00                                *** METH DEFAULT ***
Q1    92.00     67.30       20.0           *** METH DEFAULT ***
Q2    65.00     22.40       20.0           *** METH DEFAULT ***
Q3    63.00     16.70       20.0           *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            4.820       544391
Qualifier Peak Analysis ON
```

```
Curve Fit: Avg. RF
---------------------------------------------------------------------------
19)  EDB                                          ( )
Ret. Time  24.09 min., Extract & Integrate from  23.89 to  24.29 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt  106.90                                *** METH DEFAULT ***
Q1   108.90     93.90       20.0           *** METH DEFAULT ***
Q2    81.00      5.90       20.0           *** METH DEFAULT ***
Q3    92.90      5.90       20.0           *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            0.990        43139
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
---------------------------------------------------------------------------
20)  PERC                                         ( )
Ret. Time  24.49 min., Extract & Integrate from  24.29 to  24.69 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt  164.00                                *** METH DEFAULT ***
Q1   128.80     75.00       20.0           *** METH DEFAULT ***
Q2    93.90     39.30       20.0           *** METH DEFAULT ***
Q3   166.00    110.00       20.0           *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            0.340        14640

Qualifier Peak Analysis ON
Curve Fit: Avg. RF
---------------------------------------------------------------------------
21)  ClBenz                                       ( )
Ret. Time  25.92 min., Extract & Integrate from  25.72 to  26.12 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt  112.00                                *** METH DEFAULT ***
Q1    77.00     57.30       20.0           *** METH DEFAULT ***
Q2   114.00     32.90       20.0           *** METH DEFAULT ***
Q3    51.00     17.50       20.0           *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            2.970       253409
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
---------------------------------------------------------------------------
22)  EtBenz                                       ( )
Ret. Time  26.39 min., Extract & Integrate from  26.19 to  26.59 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt   91.00                                *** METH DEFAULT ***
Q1   106.10     32.30       20.0           *** METH DEFAULT ***
Q2    77.00      8.50       20.0           *** METH DEFAULT ***
Q3    51.00      8.50       20.0           *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            4.720      1037392
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
---------------------------------------------------------------------------
23)  m/p-Xylene                                   ( )
Ret. Time  26.82 min., Extract & Integrate from  26.62 to  27.02 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
```

```
Tgt   91.00                                   *** METH DEFAULT ***
Q1   106.00     49.60       20.0              *** METH DEFAULT ***
Q2    77.00     13.40       20.0              *** METH DEFAULT ***
Q3    51.00      9.00       20.0              *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            6.460       515816
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
---------------------------------------------------------------------------
24)  Styrene                                      ( )
Ret. Time  27.53 min., Extract & Integrate from  27.33 to  27.73 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt  104.00                                   *** METH DEFAULT ***
Q1   103.00     47.10       20.0              *** METH DEFAULT ***
Q2    78.00     39.60       20.0              *** METH DEFAULT ***
Q3    51.00     20.90       20.0              *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            4.100       322355
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
---------------------------------------------------------------------------
25)  o-Xylene                                     ( )
Ret. Time  27.68 min., Extract & Integrate from  27.48 to  27.88 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt   91.00                                   *** METH DEFAULT ***
Q1   106.00     47.90       20.0              *** METH DEFAULT ***
Q2    77.00     12.10       20.0              *** METH DEFAULT ***
Q3    51.10      9.00       20.0              *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            2.810       305334
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
---------------------------------------------------------------------------
26)  m-DCB                                        ( )
Ret. Time  31.40 min., Extract & Integrate from  31.20 to  31.60 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt  145.90                                   *** METH DEFAULT ***
Q1   147.90     62.90       20.0              *** METH DEFAULT ***
Q2   111.00     39.60       20.0              *** METH DEFAULT ***
Q3    75.00     27.90       20.0              *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            3.770       217322
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
---------------------------------------------------------------------------
27)  p-DCB                                        ( )
Ret. Time  31.56 min., Extract & Integrate from  31.36 to  31.76 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt  145.90                                   *** METH DEFAULT ***
Q1   147.90     63.20       20.0              *** METH DEFAULT ***
Q2   111.00     39.00       20.0              *** METH DEFAULT ***
Q3    75.00     31.90       20.0              *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1            5.160       289816
```

```
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
-------------------------------------------------------------------------
28)  o-DCB                                        ( )
Ret. Time  32.36 min., Extract & Integrate from  32.16 to  32.56 min.
Signal       Rel Resp.   Pct. Unc.(rel)    Integration
Tgt  145.90                                *** METH DEFAULT ***
Q1   147.90     63.00       20.0           *** METH DEFAULT ***
Q2   111.00     40.80       20.0           *** METH DEFAULT ***
Q3    75.00     28.40       20.0           *** METH DEFAULT ***
Lvl ID   Conc (ppb)  Response
1           4.410       196068
Qualifier Peak Analysis ON
Curve Fit: Avg. RF
-------------------------------------------------------------------

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

Hewlett-Packard ChemStation Method - IDLE.M

```
TOPLEVEL PARAMETERS
-------------------
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 the analysis of ambient air for toxic analytes.
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:  230 'C
   Initial time:  2.00 min              Equilibration time:  0.50 min
   Ramps:
      #  Rate  Final temp  Final time  CRYO (N2)
      1  7.00      200        0.00          Cryo:  Off
      2   0.0(Off)                         Cryo fault:  On
   Post temp:  0 'C                        Cryo timeout:45.00min(On)
   Post time:  0.00 min                    Quick cryo cool:  Off
   Run time:  16.29 min                    Ambient temp:  25 'C
FRONT INLET (HP PTV)                BACK INLET (SPLIT/SPLITLESS)
   Mode:  Split                          Mode:  Split
   Initial temp:  50 'C (Off)            Initial temp:  50 'C (Off)
   Cryo:  Off                            Pressure:  0.00 psi (Off)
   Cryo use temp:  25 'C                 Total flow:  0.1 mL/min
   Cryo Timeout:  30.00 min (On)         Gas saver:  Off
   Cryo Fault:  On                       Gas type:  Helium
   Pressure:  0.00 psi (Off)
   Total flow:  45.0 mL/min
   Gas saver:  Off
   Gas type:  Helium
COLUMN 1                                 COLUMN 2
   Capillary Column                         (not installed)
   Model Number:  J & W 1221564
   DB-VRX
   Max temperature:  260 'C
   Nominal length:  60.0 m
   Nominal diameter:  250.00 um
   Nominal film thickness:  1.40 um
   Inlet:  (unspecified)
   Outlet:  MSD
FRONT DETECTOR (NO DET)                  BACK DETECTOR (NO DET)
```

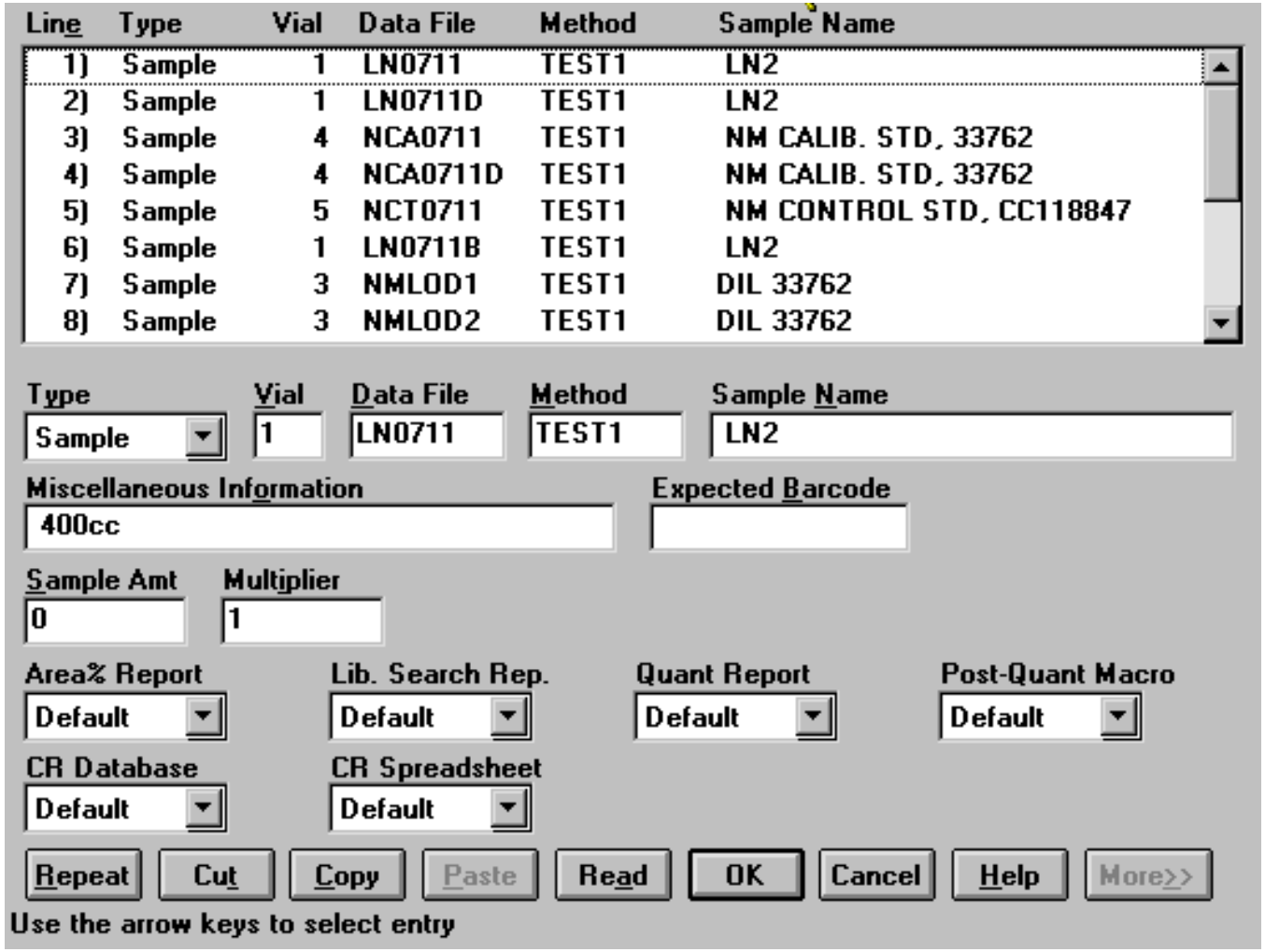
Hewlett-Packard ChemStation Method - IDLE.M

```
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
        Nanoliter Adapter           Off
        PostInj Solvent A Washes      0
        PostInj Solvent B Washes      0
        Viscosity Delay               0 seconds
        Plunger Speed              Fast
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     : 1305.9
[Scan Parameters]
Low Mass                 : 35
High Mass                : 550
Threshold                : 150
Sample #                 : 2       A/D Samples    4
[MSZones]
MS Quad                  : 150 C   maximum 200 C
MS Source                : 230 C   maximum 250 C
END OF MS ACQUISITION PARAMETERS
```

Hewlett-Packard ChemStation Method - IDLE.M

```
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:  Yes
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
----------------------------
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
------------------------------
```

Hewlett-Packard ChemStation Method - SAMPLE.S



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Appendix V: MLD058 Standard and Control Concentrations

Compound Name	Abbr. [1]	NIST (Standard) ALM046027 ppbv	NIST (Standard) ALM029258 ppbv	Scott-Marin (Control) CC386 ppbv [2]	Scott-Marin (Control) CC386 ppbv [3]	Scott-Marin (Control) CC386 ppbv [4]
1,3-Butadiene	Buta	0.84	1.10	1.20	1.10	ni
1,2-Dibromoethane	EDB	0.99	0.49	ni	0.30	ni
1,2-Dichloroethane	EDC	1.94	2.00	1.55	2.00	ni
1,2-Dichloropropane	DCP	ni	0.98	ni	ni	ni
1,1,1-Trichloroethane	TCEA	0.91	1.06	0.74	0.80	0.75
cis-1,3-Dichloropropene	c-DClprpene	4.73	ni	ni	ni	ni
trans-1,3-Dichloropropene	t-DClprpene	4.73	ni	ni	ni	ni
Benzene	Benz	2.02	5.20	3.45	3.50	ni
Bromomethane	CHBr3	ni	2.20	ni	ni	ni
Carbon tetrachloride	CCl4	0.08	0.19	0.14	0.15	0.14
Chlorobenzene	ClBenz	2.97	5.20	2.42	2.50	2.36
Chloroform	CHCL3	0.24	0.61	0.15	0.15	0.15
Dichloromethane	DCM	2.80	2.00	2.03	2.00	2.09
Ethylbenzene	EtBenz	4.72	5.10	1.97	3.00	1.98
Trichlorofluoromethane	Freon 11	2.00	1.18	ni	ni	ni
Dichlorodifluoromethane	Freon 12	0.75	0.49	ni	ni	ni
1,1,2-Trichloro-1,2,2-Trifluoroethane	Freon 113	ni	0.21	ni	ni	ni
2-Methyl-1,3-butadiene	Isoprene	0.73	2.10	2.41	0.70	ni
m/p-Xylene	m/p-Xyl	5.58	10.20	6.84	5.00	6.72
m-Dichlorobenzene	m-DCB	3.77	10.00	3.14	3.00	2.90
o-Dichlorobenzene	o-DCB	4.41	10.10	2.84	3.00	2.53
p-Dichlorobenzene	p-DCB	5.16	ni	3.00	3.00	2.76
o-Xylene	o-Xyl	2.81	5.10	2.44	2.50	2.39

Appendix V: MLD058 Standard and Control Concentrations

Compound Name	Abbr. [1]	NIST (Standard) ALM046027 ppbv	NIST (Standard) ALM029258 ppbv	Scott-Marin (Control) CC386 ppbv [2]	Scott-Marin (Control) CC386 ppbv [3]	Scott-Marin (Control) CC386 ppbv [4]
Perchloroethylene	PERC	0.34	0.31	0.24	0.25	0.25
Styrene	Sty	4.10	4.80	5.51	3.00	3.88
Toluene	Tol	4.82	5.20	2.37	2.50	2.19
1,1,2-Trichloroethylene	TCE	0.56	0.95	0.34	0.35	0.32
Vinyl Chloride	VinCl	0.27	1.64	0.82	0.70	ni

(1) Abbr. = Abbreviation – sometimes used in lieu of the full name in the analytical software

(2) Control concentrations as determined by Method MLD058, “Standard Operating Procedure for the Determination of Aromatic and Halogenated Compounds in Ambient Air by Capillary Column Gas Chromatography/Mass Spectrometry”

(3) Uncertified concentrations as received from the manufacturer (Scott-Marin, Inc.; 6531 Box Springs Boulevard, Riverside, CA 92507-0725)

(4) Control concentrations as determined by Method MLD052, “Standard Operating Procedure for the Determination of Volatile Aromatic and Halogenated Compounds in Ambient Air by Capillary Column Gas Chromatography with Photoionization and Electron Capture Detectors”, and Method MLD057, “Standard Operating Procedure for the Determination of 1,3-Butadiene and Benzene in Ambient Air by Capillary Column Gas Chromatography with Photoionization Detector”

na Not applicable for this compound

ni Not included in the mixture

Appendix VI - Revision History

Revision Number	Approval Date	Comments
1.00	January 2, 2000	Initial SOP
2.00	May 15, 2002	This Revision

#A05

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:	Steve Madden	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 MLD058 Revision Number 2.0	May 15, 2002

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. 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. Table 2, page 24, lists the NIST Standards associated with this SOP. Appendix V, page 89, lists the concentrations of the NIST 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). This system is described in SOP MLD074, "Standard Operating Procedure for Preparation of Calibration and Control Standards Using a Gas Mixer/Dilution Apparatus."

The sentence "~~Table 2, page 24, lists the NIST Standards associated with this SOP. Appendix V, page 89, lists the concentrations of the NIST Standards associated with this SOP.~~" Is deleted.

Section 5.3, page 7, states

5.3 A control standard mixture, or mixtures, containing all analytes of interest at concentrations within the calibration range of the GC System. Table 2, page 24, lists the Control Standards associated with this SOP. Appendix V, page 89, lists the concentrations of the Control Standards associated with this SOP.

ARB modification to Section 5.3, page 7, states

5.3 A control standard mixture, or mixtures, containing all analytes of interest at concentrations within the calibration range of the GC 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). This system is described in SOP MLD074, "Standard Operating Procedure for Preparation of Calibration and Control Standards Using a Gas Mixer/Dilution Apparatus."*

The sentence ". ~~Table 2, page 24, lists the Control Standards associated with this SOP. Appendix V, page 89, lists the concentrations of the Control Standards associated with this SOP.~~" Is deleted.

Table 2, page 24

This table is deleted.

Table "Appendix V: MLD058 Standard and Control Concentrations", page 89

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 tothe 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

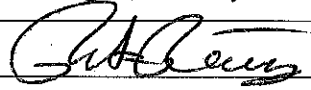
Section 5. Justification for Deviation(s)
(provide explanation of why modification(s) to existing ARB document is necessary)

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. The mixer/diluter system make the use of these higher concentrations feasible.

The deletions of Table 2, page 24, and Appendix V, page 89, are a 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:		8/20/15
Addendum Number	A05 MLD 058.2	

Completed form must be scanned/emailed or mailed to:

Mr. Patrick Rainey
1927 13th Street, P.O. Box 2815
Sacramento, California 95811
prainey@arb.ca.gov