Determination of Xylenes in Gasoline

(Fundamentals of Analytica Chemistry, eight edition
Ewing's Analytical Instrumentation Handbook)

I. Introduction

Gas liquid chromatography (GC) is a popular, powerful and easy to use analytical tool. Mixtures to be analyzed are injected into an inert gas stream (Helium in our instrument) and swept into a tube packed with a solid support coated with a resolving liquid phase. Absorptive interaction between components in the gas stream and the coating leads to a differential separation of the components of the mixture, which are then swept in order through a detector flow cell. One of the weaknesses of gas chromatography is its requirement for volatile compounds, but its major problem is the lack of definite proof of the nature of the detected compounds as they are separated. For most GC detectors, identification is based on retention time on the column. Since many compounds may possess the same retention time, we are left in doubt about the nature and purity of the compounds in the separated peak.

The mass spectrometer (MS) takes injected material, ionizes it in a high vacuum, propels and focuses these ions and their fragmentation product through a magnetic mass analyzer, and then collects and measures the amount of each selected ion in a detector. A MS is an excellent tool for identifying the structure of a single compound but is less useful for studying mixtures.

The combination of the two components into a single GC/MS system forms an instrument capable of separating mixtures into their individual components, identifying, and then providing quantitative and qualitative information on the amounts and chemical structure of each compound. The GC/MS system possesses weaknesses of both components. It requires volatile components, and because of this requirement, has some molecular weight limit.

In this experiment you are going to use the GC/MS to study the components of gasoline sample, specifically you are going to look for different isomers of xylene. Conventional gasoline consists mostly of aliphatic hydrocarbons obtained by the fractional distillation of petroleum, enhanced with iso-octane or the aromatic hydrocarbons toluene and benzene to increase its octane rating. Small quantities of various additives are common, for purposes such as tuning engine performance or reducing harmful exhaust emissions. Some mixtures also contain significant quantities of ethanol as a partial alternative fuel. The amount of certain hazardous compounds, such as carcinogens e.g. benzene, is regulated and their concentration in gasoline is very low.

Oxygenated fuel is conventional gasoline that has been blended with oxygenates to achieve a certain concentration of oxygen in the fuel by weight. Reformulated gasoline (RFG) is a formulation of gasoline that has lower amounts of certain chemical compounds that contribute to the formation of ozone and air toxins. It does not evaporate as readily as conventional gasoline during the summer months. It may contain oxygenates, which increase the combustion efficiency of gasoline and reduce carbon monoxide emissions. The law also specifies that RFG contain oxygen (2 percent by weight). Ethanol is the two most commonly used substance that adds oxygen to gasoline. The addition of oxygenated compounds compensates for the reduction in aromatic and olefinic compounds by increasing the octane number. Oil companies decide which substance to use to meet the law's requirements. The Houston-Galveston-Brazoria area is required by the Clean Air Act Amendments of 1990 to use RFG. This eight-county area includes Brazoria, Chambers, Fort Bend, Galveston, Harris, Liberty, Montgomery, and Waller counties.

In this experiment we will be looking for xylenes in a gasoline sample collected from a random gasoline station in the area using GC/MS. Xylenes is a collective term for a mixture of *m*-, *o*-, and *p*-isomers of xylene. These isomers differ only in placement of two methyl groups on a benzene ring. Technical and commercial grades of xylenes often contain substantial amounts of ethylbenzene (10-50%), and perhaps minor amounts of other solvents as well. Mixtures of xylenes and ethylbenzene are occasionally termed mixed xylenes. Most mixed xylenes are used to blend gasoline, but they are also used in the paint and coatings industry. *m*-xylene is used to produce isophthalic acid, which is used in polyesters; *o*-xylene is used to produce phthalic anhyride, which is used in plasticizers; *p*-xylene is used to produce terephthalic acid and dimethyl terephtalate, both of which are used to produce polyesters. *o*-xylene and *p*-xylene are used in vitamin and pharmaceutical synthesis, and to produce insecticides. Ethylbenzene is used to produce styrene.

II. Gas Chromatography Mass Spectrometry (GC/MS)

Gas chromatography (GC) is one of the most widely used techniques for qualitative and quantitative analysis. It involves repeated distribution or partitioning of analytes between two different phases, mobile gaseous phase and liquid or solid stationary phase held in a column. In gas-liquid chromatography (GLC) a liquid substance serves as a stationary phase and its name is usually shortened to gas chromatography (GC). GLC is based on partitioning of the analyte between a gaseous mobile phase and a liquid phase immobilized on the surface of an inert solid packing or on the walls of capillary tubing. Gas-solid chromatography (GSC) is based on solid stationery phase in which retention of analytes occurs because of physical adsorption. In performing the chromatographic separation, the sample is vaporized and injected onto the head of chromatographic column. Elution is brought about by the flow of an inert gaseous mobile phase. A schematic of a gas chromatographic system with a mass spectrometer detector is shown in Figure 1. The basic gas chromatograph consist of the carrier gas (mobile phase) supply, the inlet or injector, the column, the detector and the data system (not shown in the Figure 1).

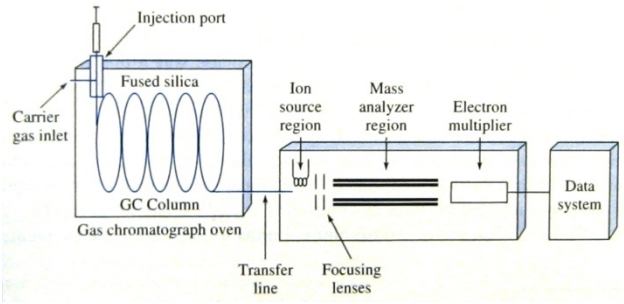


Figure 1. GC/MS schematic
source Fundamentals of Analytical Chemistry by Skoog.

The mobile phase gas in gas chromatography is called carrier gas and must be chemically inert. It does not interact with molecules of the analyte, its only function is to carry the components of the sample from the inlet port through the column to the detector. The most commonly used mobile phase in GC is helium although nitrogen, argon and hydrogen are also used. The flow rates are controlled by a two-stage pressure regulator at the gas cylinder. Inlet pressures usually range from 10 to 80 psi greater than room pressure. It is assumed that if the inlet pressure is kept constant the flow rate will also be constant. Depending on the chromatographic column, typical flow rates are in the range 25 to 100 mL/min with packed columns and 1 to 25 mL/min for capillary column.

Sample injection is a critical step in GC. The inlet system must be well designed to facilitate the injection of the sample onto the head of the column without degradation of the column performance and without discrimination of sample components. In order to minimize the band spreading and to obtain the best resolution rapid injection of the suitable size of the sample is required; slow injection or oversized (too concentrated) sample cause band spreading and poor resolution. The sample size depends on the dimensions of the columns and on the sensitivity of the detector. For ordinary packed analytical columns sample sizes range from a few tenths of a microliter to 20 μL. Capillary columns need much less sample, 0.01 – 1 μL. Apart from the column requirement the sample size should not exceed the linear dynamic range of the detector. Typically, calibrated microliter syringes are used to inject liquid samples through a rubber or silicone diaphragm, or septum into a heated sample port located at the head of the column. The temperature of the injection port is usually kept at about 50°C greater than the boiling point of the least volatile component of the sample. This ensures flash vaporization of the liquid sample, and the carrier gas sweeps the vaporized sample onto the stationary phase. Due to the high sample capacity, the introduction of the sample into packed columns is usually problem-free. This is quite different with open tubular (capillary) columns, in which the sample capacity and carrier gas flow rates are much lower. In this case, usually a split injection is used. It involves injecting a liquid sample into a heated injection port, vaporizing the sample in the injection inlet, and splitting the vaporized sample into two parts so that small fraction of the vaporized sample enters the column and the major portion is vented to waste.

Gas chromatographic columns. Three types of columns can be used in gas chromatography packed, capillary, and megabore columns. For most current applications packed columns have been replaced by the more efficient and faster capillary columns. Recently, the 530-μm capillaries (called also megabore columns) have appeared. The 530-μm refers to the internal diameter. The most widely used capillary columns are fused-silica open tubular columns (FSOT columns) with internal diameters of 0.1 and 0.35 mm and the length from 15 to 100 m. Fused-silica capillaries are drawn from purified silica that contains minimal amounts of metal oxides. The tubes are strengthen by an outside protective polyimide coating, which is applied as the capillary tubing is being drawn. The columns prepared in this way are flexible and can be bent into coils with diameters of a few inches. The internal surface of the silica is usually treated or silanized, depending on the techniques used to bind the stationary phase. Commonly used stationary phases are based on polydimethyl siloxanes which have a repetitive backbone that consists of two hydrocarbon chains per silicon atom. The general formula of polysiloxanes is shown in Figure 2. In the polydimethyl siloxane , the

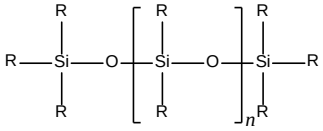
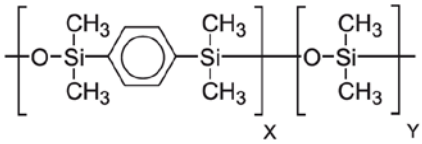


Figure 2. General structure of polydimethyl siloxanes.

—R groups are all —CH_3, giving a liquid that is relatively nonpolar. In the other polysiloxanes a fraction of the methyl groups are replaced by funcitional groups such as phenyl (—C_6H_6), cyanopropyl (—C_3H_6CN), or trifluoropropyl (—$C_3H_6CF_3$). The amount of substitution of the named group for methyl groups on the polysiloxane backbone is given by the percentage description in the name of the stationary phase. For example, 5% phenyl polydimethyl siloxane has a phenyl ring bonded to 5% by the number of the silicon atoms in the polymer. These substitutions increase the polarity of the stationary phase to various degrees.

The column is housed in a thermostated oven for a very precise temperature control, between 40 and 450°C stabilized to within 0.1°C. The optimum column temperature depends on the boiling point of the sample and the degree of separation required. A temperature slightly above the boiling point of the sample results in a reasonable elution time (2 to 30 mins). For samples with a broad boiling range, it is often desirable to employ temperature programming whereby the column temperature is increased either continuously or in steps as the separation proceeds.

The column used in our instrument is Varian FactorFour capillary Column. The stationary phase is equivalent to 5% phenyl, 95% dimethylpolysiloxane low bleed phase; the length and internal diameter are 30 meters and 0.25 mm respectively.



Detection systems. The commonly used detectors in gas chromatography are: the flame ionization detector (FID), the thermal conductivity detector (TCD), and electron capture detector (ECD). These detectors are considered universal because they are sensitive to almost every compound that elutes from the column and they give response signal which is proportional to the analyte concentration. However these detectors do not provide any structural information of an analyte and the compound identification has to proceed with the use of internal calibration based on retention times. One of the most powerful detectors which can provide definite identification of the separated compounds is the mass spectrometer. It measures a mass to charge ration (m/z) of ions that have been produced from the sample. However, most of the ions are singly charged (z = 1) and it is common to speak of measuring the mass of ions when mass-to-charge ratio is actually measured. The combination of the gas chromatography and mass spectrometry is known as GC/MS (Figure 1).

The basic components of the **mass spectrometer** are the pumping system, the interface to the gas chromatograph (inlet), the ion analyzer, the focusing lens, the ion detector, and the data system. Pumping systems providing high vacuum (10^{-5} Torr) are critical to the operation of mass spectrometer. Electrons and ionized compounds cannot exist long enough to reach the detector if they suffer collisions with air molecules in the analyzer.

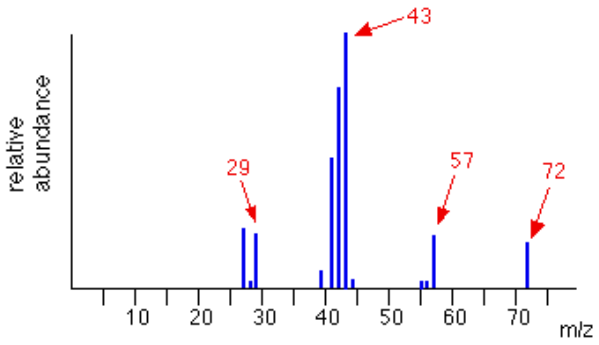


Figure 3. Simplified spectrum of pentane.
source: http://www.chemguide.co.uk/analysis/masspec/fragment.html

The effluent from the gas chromatograph is transferred to the mass spectrometer through the **inlet system**. The inlet has to interface between the atmospheric pressure of the GC system and the low pressure (10^{-5} to 10^{-8} torr) mass spectrometer system.

In the mass spectrometer, sample molecules enter an **ionization source**. A number of sources have been designed for mass spectrometer sample ionization: electron impact (EI), chemical ionization (CI), fast atom bombardment (FAB), and field ionization (FI), with the EI source being the most common.

The EI source exposes the sample from the gas chromatograph interface to a 70 eV electrons from the filaments. The sample molecules have an electron knocked off leaving behind a **molecular ion**

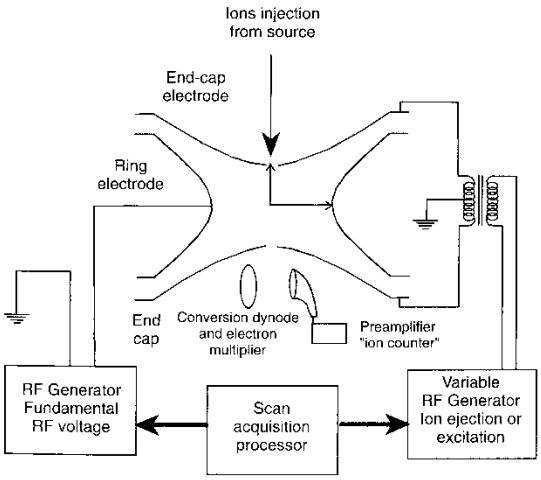


Figure 4. Ion trap with an RF voltage applied to the ring electrode, providing the fundamental frequency ν and its associated variable amplitude V.

with a positive charge M^+. The energy of 70 eV electron beam is high enough not only to ionize the sample molecules but also to break chemical bonds causing molecules to fragment.

$$\underset{70eV}{M} + e^- \rightarrow \underset{\text{molecular ion}}{M^+} + \underset{\sim 55eV}{e^-} + \underset{0.1eV}{e^-}$$

The fragments can also be ionized forming fragment ions. The uncharged molecules and fragments are pumped out of the ion source by vacuum pumps. The fragmentation pattern of the ions form at a given electron energy is characteristic of the ionized molecule. Every time a molecule of the same compound is ionized under the same conditions, it forms the same quantity and pattern of ions. The fragment pattern becomes a fingerprint that can be used to identify and quantitate the molecule being analyzed.

The next section of mass spectrometer is an **analyzer**. The analyzer serves to sort the ions according to their m/z values. The most common analyzers for GC/MS are the quadrupole mass filter and the ion trap. The former is probably more popular while the latter offers better resolution. The transfer line (Figure 1) connecting the GC and MS part is used to introduce the effluent from the GC into the ion trap. Once the sample is in the ion trap molecules of the sample are ionized with 70eV electrons furnished by heated filament at the top of the trap (Figure 4). A radiofrequency voltage is then applied to the ring electrode to trap all ions with masses equal or greater than a value which depend on the applied voltage. The ions in the trap will follow complex trajectories in the presence of a low helium pressure of about 0.01 Pa. A voltage of 125 DAC will confine all ions with masses equal or greater than 20 amu in the trap by forcing them into circular hyperbolic orbits. The analysis is performed by increasing the ring electrode radiofrequency voltage, which destabilizes the orbits of ions with increasing masses. The increase in the voltage cases the ions to increase the amplitude of their oscillations and they are eventually ejected through one of the endcap electrodes behind which stands an ion detector – a cascade dynode electron multiplier. The fragment ions striking the surface of the detector induce a cascade of ions within the detector body, amplifying the single-fragment signal enough for the data system to process.

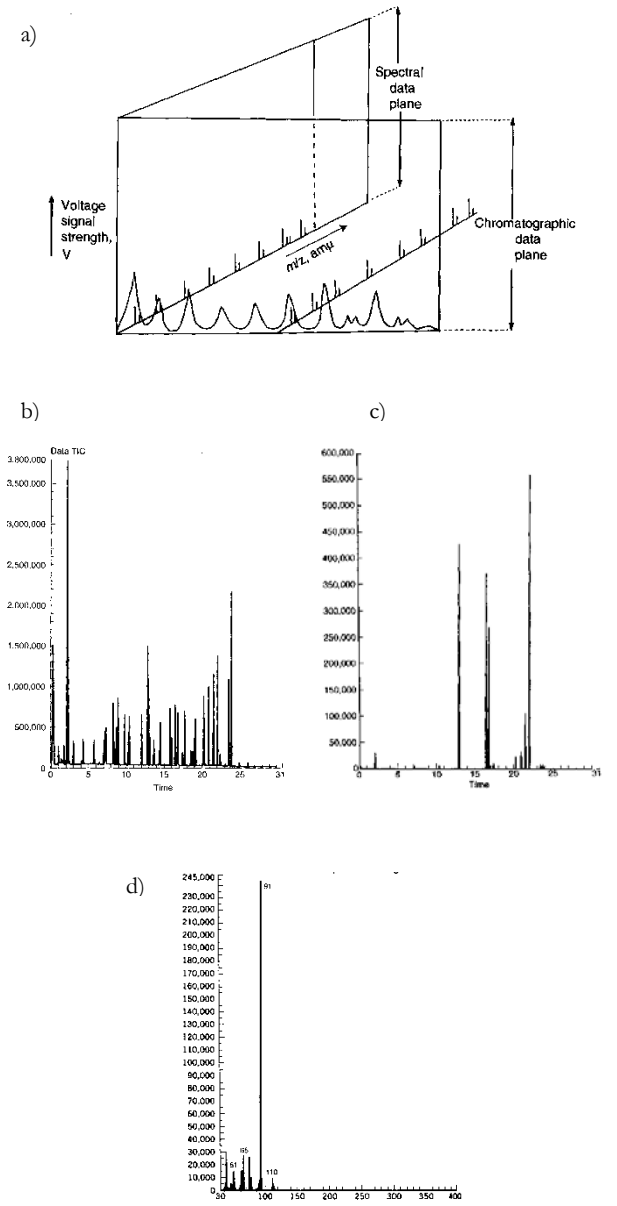


Figure 5. GC/MS data block (a), total-ion chromatogram (b), Single-ion chromatogram (c), and mass-fragment spectra (d).

III. Analysis of the GC/MS data

In GC/MS the mass spectrometer scans the masses repetitively during a chromatographic experiment. If the chromatographic run is 10 minutes and a scan is taken each second, 600 mass spectra are recorded. The resulting data are computer processed and we receive a three-dimensional block of data whose coordinates are: time, molecular mass (m/z), and ion concentration (Figure 5a). The data can be analyzed in several different ways. One way is to record the total current from all ions produced by the eluate. The resulting chromatogram is "reconstructed" by a computer from individual mass spectra recorded during a chromatography and is referred to as a total ion chromatogram (TIC). An example of TIC is shown in the chromatographic data plane in Figure 5b.

If we select a data cut at a single molecular mass, a single-ion chromatogram (SIC) is produced (Figure 5c) which represents the concentration of ions of the selected molecular mass present throughout the chromatographic run. Compounds that do not form an ion with this mass will not be present in the single-ion chromatogram. A SIC can also be produced by running the GC/MS in a fixed-mass mode in which the analyzer is set to look only at a given molecular mass (m/z) throughout the chromatographic run. Because the analyzer is continuously analyzing for only a single ion, the summed ion

yield is much higher and the detection limits for this ion are much lower

Selecting a data cut at a given time point in the three-dimensional block of data (spectral data plane in Figure 5d) will provide us with a display of ion concentration versus molecular mass called fragment spectra or simply mass spectra.

The mass spectrum of a molecule provides information about its structure. The fragmentation pattern under a given set of experimental conditions is a characteristic of this molecule and can be used to definitively identify the chemical nature of the chemical compound. Under the same conditions and in the same or similar instrument a given compound will always give the same fragment in the same ion concentration ratios.

Mass spectra first of all display the molecular ion (or parent ion) peak which is a radical cation M+. As a result of removing one electron from the molecule. In the spectrum for toluene, for example, the molecular ion peak is located at 92 m/e corresponding to its molecular mass. The molecular ion peak does not always appear or can be weak. The height of the molecular ion peak diminishes with branching and with increasing mass in a homologous series. Identifying the molecular ion can be difficult. A useful aid is the nitrogen rule: if the mass is an even number, the compound contains no nitrogen or an even number of nitrogens. Molecular ion peaks are also often preceded by M-1 or M-2 peak resulting from loss of a hydrogen radical or dihydrogen

The mass spectrum for toluene has around 30 signals (Figure 6 top). Several peaks can be rationalized in the fragmentation pattern shown in the bottom of Figure 6. More peaks are visible with m/e ratios larger than the molecular ion peak due to isotope distributions. The value of 92 in the toluene example corresponds to the monoisotopic mass of a molecule of toluene entirely composed of the most abundant isotopes (^{1}H and ^{12}C). The so-called M+1 peak corresponds to a fraction of the molecules with one higher isotope incorporated (^{2}H or ^{13}C) and the M+2 peak has two higher isotopes.

The fragmentation of the aromatic compounds generates a series of peaks having m/e = 77, 65, 63, etc, a pattern called "aromatic cluster". If the molecule contains a benzyl unit, the major cleavage will be to generate the benzyl carbocation, which rearranges to form the tropylium ion (a prominent peak and often is the base peak at m/e 91). The molecular ion, again, represents loss of an electron and the peaks above the molecular ion are due to isotopic abundance. The base peak in toluene is due to loss of a hydrogen atom to form the relatively stable benzyl cation. This is thought to undergo rearrangement to form the very stable tropylium cation, and this strong peak at m/e = 91 is very characteristic of compounds containing a benzyl unit. The frequently observed peak at m/e = 65 is due to the loss of neutral acetylene from the tropylium ion and the minor peaks below this arise from more complex fragmentation.

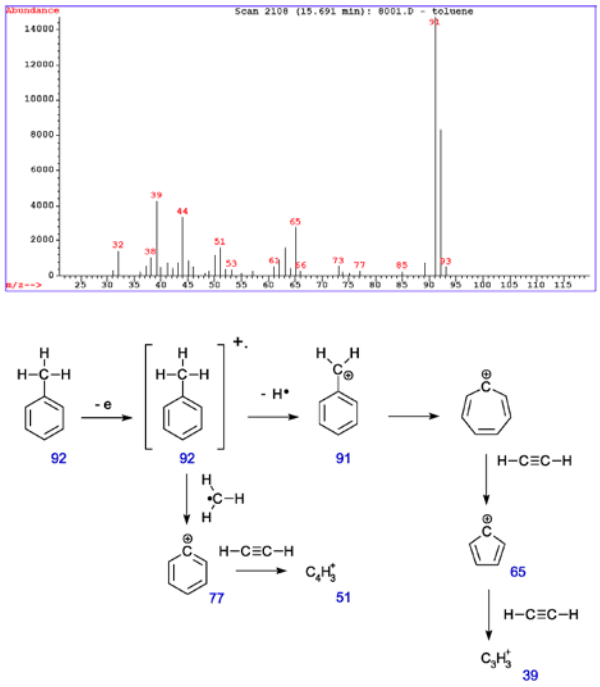


Figure 6. Mass spectrum of Toluene and possible fragmentation pattern.

http://en.wikipedia.org/wiki/Mass_spectrum_analysis

IV. Instrument operation

MS Workstation is a suite of applications for controlling chromatographs, collecting data from chromatograph detectors, and analyzing those data. The MS Workstation Toolbar provides quick and easy access to the MS Workstation applications. When activated, the MS Workstation Toolbar behaves very much like the Windows Taskbar. It docks on any of the four sides of the display screen and other Windows programs will not cover or go behind it when they are opened in full screen mode.

IV-A. Preparing a GC/MS acquisition method

Before injecting your sample, you need to make sure the current method has appropriate settings for your analysis. You can edit the default method, create a new method, or load a method previously saved using *Method Builder* (Figure 7). To open the method builder, click  in the MS Workstation toolbar. In order to activate a method click  on the toolbar go to the menu *File* and pick *Activate Method* to display the file selection dialog. Highlight the method *gasoline.mth* and click Open. The GC and MS portions of the method will be downloaded to the instrument.

As you step down through the Method Directory (left pane in Figure 7), the parameters associated with each section of the Method are displayed for editing in Parameters window. The navigation window (left pane) shows the overall structure of the Method, its sections, and subsections. The branches can be expanded by clicking on the plus sign or contracted by clicking on the minus sign to show the desired level of detail. The parameters window (right pane) shows the parameters for the highlighted item in the navigation window. Method parameters are viewed and edited in this window.

The GC control window contains sections (Flow/Pressure, Injector, and Column Oven). The Column Oven window contains the Column Oven Program. Use the Column Oven Program to specify the Stabilization Time of the Column Oven, and to specify its programmable temperature ramp.

Use the spreadsheet to build a temperature ramp program to heat and/or cool the Column Oven. For the gasoline method the first row of the spreadsheet contains the Initial Temperature (35°C) and Hold Time (2 min) for the Column Oven. The Column Oven will equilibrate to this setting, and stabilize for the specified Stabilization Time, when the method is activated, and will be restored to this setting when each chromatographic run is completed. Rows after the first row of the spreadsheet contain the programmed settings for each of the ramp segments. Each segment will ramp to the specified temperature at the specified rate (assuming the rate is achievable), and then hold the temperature for the specified time. (Note that the Rate in the first row is always blank and cannot be edited. Also note that the entire Total column cannot be edited.). Therefore, in the gasoline method after 2 mins of stabilization at 35°C the temperature will be ramped to 60°C at the rate of 2°C per minute (second row). Once the temperature of 60°C is reached the temperature is ramped faster at rate of 50°C per minute until it reaches 250°C and it is hold at this temperature for 6 minutes. The total time for this temperature program is 24.3 minutes.

Click the *MS Acquisition Method* in the *Method Directory* Pane to display the MS method in the parameters window. The table in the parameters window for the gasoline MS section consists of just one segment. This segment from 0.00 to 24.30 minutes is Electron Ionization with Automatic Gain Control (EI Auto) to acquire MS data over the m/z range 35-135.

Note: The default table for a new MS section consists of two segments. The first segment is a Filament/Multiplier Delay segment for the first three minutes (Ionization Mode = None). This segment will be acquired with the filament and multiplier turned off to protect the instrument until after the elution of the solvent peak. However, because our sample does not contain solvent this segment was deleted.

Now you can close the *Method Builder* window. If you made any changes to the method, you will be asked if you want to save the method. Do not save it.

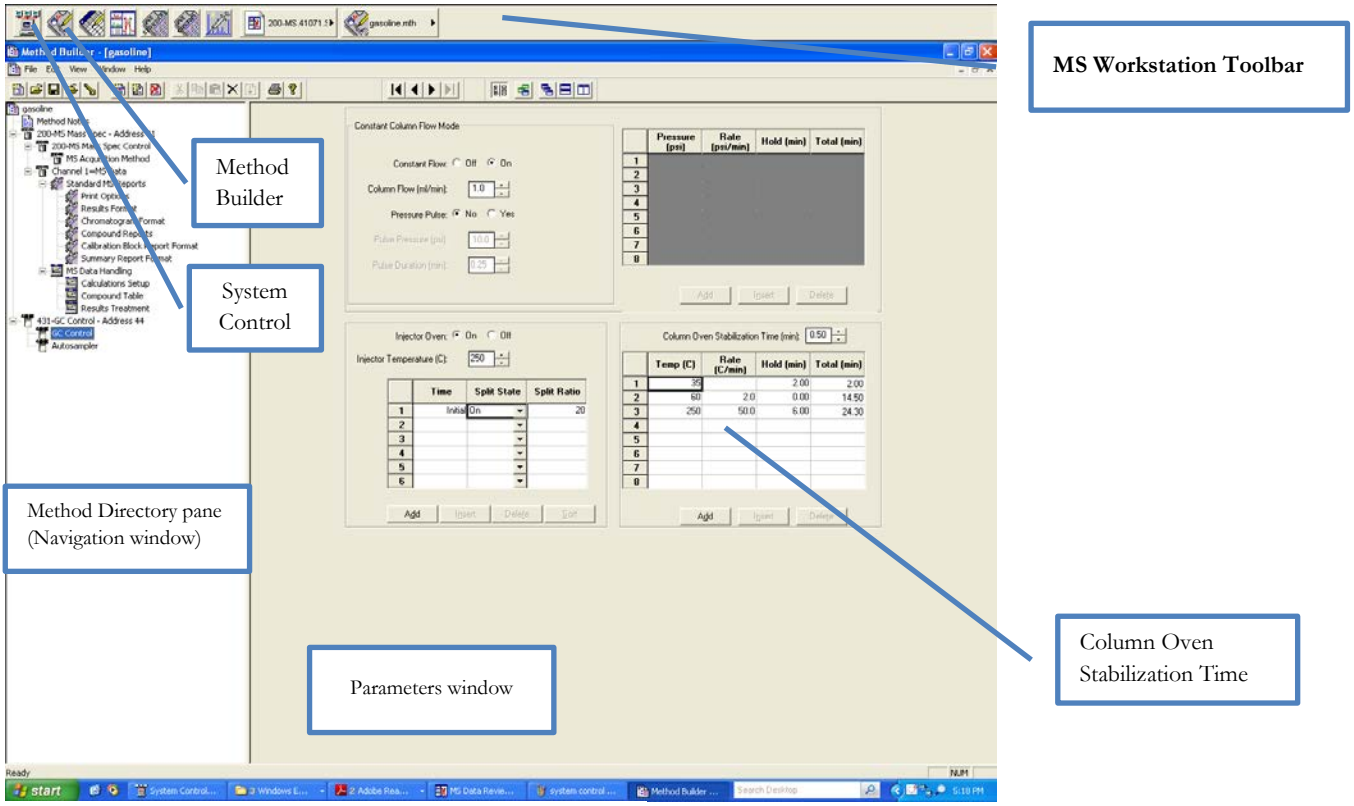


Figure 7. Method Builder window

Figure 8. System Control Window.

IV-B. Starting the acquisition

If the System Control is not open, start the application by clicking first icon from the left on the Workstation Toolbar. You should see three windows inside the System Control Window (Figure 8): Instrument 1 Status; 431-GC.44; and 200-MS.41. If you cannot see 431-GC or 200-MS windows click on the corresponding icon in the Instrument 1 Status window.

1. Click on the *Inject* → *Inject Single Sample* option. The **Instrument 1 Parameters** dialog box should appear. Enter your name or initials in the Operator field and Click the OK button. The **Inject Single Sample** dialog (**Error! Reference source not found.**) should appear. The active method is displayed in the field **Inject the Sample using the Method**. Type in a name for your sample in the **Data File Names** field by clicking on the **Data Files….** button to open the **Data File Generation** dialog (Figure 10). In this dialog, you can choose a directory where you want to save the data file and select the symbols for the labels you want to be added as extensions to the file name. After you making the file name selections, click the Inject button in the lower left of the **Inject Single Sample** dialog. Verify in the **Control and Status** area of the **200-MS.41** window (Figure 8) that the status is "Ready" and "No Faults" light is green. You may also check the status of the GC module in the **431-GC Operation** section of the **431-GC.44** window (Figure 8). While the GC injector and column temperatures are being adjusted to those set in the method, the status will be *Equilibrating*. When the GC has equilibrated and stabilized, the Ready and No-Fault lights should turn green and the Status Indicator in the **System Control Toolbar** should read *Waiting for Injection of Sample* in yellow.
2. *Injecting the sample*. Rinse the microliter syringe in the solution and expel air bubbles by carefully pumping the syringe plunger up and down several times. Each small tick mark on the syringe corresponds to **0.2** µL. Pull the syringe up to the **2** µL mark to create an upper air gap. Place the needle in the solution and draw the plunger up to the **2.2** µL mark. Finally, remove the syringe from the solution and draw the plunger up a further **2** µL until the plunger reaches **4.2** µL. You can now see exactly how much sample solution is in the syringe. There should be approximately **2** µL of air above the sample and **0.2** µL of sample in the barrel of the syringe then **2** µL of air below the sample. The syringe needle

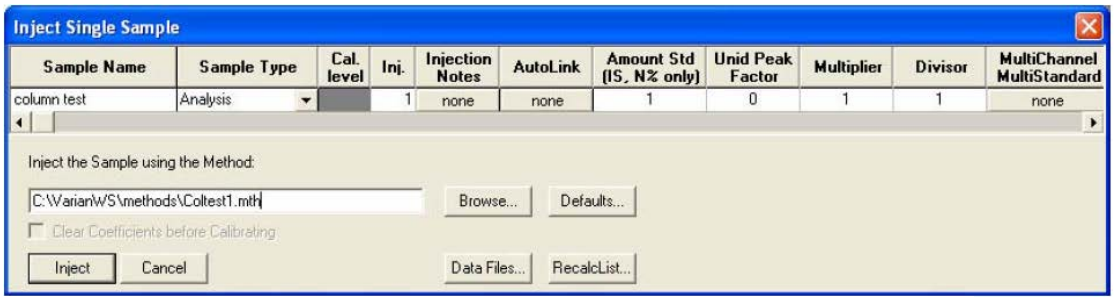


Figure 9. Inject Single Sample Dialog.

should be left in the injector for 2-3 seconds before depressing the plunger. Inject the sample using an even, consistent injection speed. The optimum speed is about 1 µL/second. Once you have injected the sample, press down on the automatic start switch on the GC injector to start the acquisition and you will observe the acquisition of your data has begun. Please ask the TA or Lab Coordinator if you need help injecting the sample.

IV-C. Monitoring Data Acquisition in Progress from System Control

The chromatogram appears in the display window, there are no peaks observed at first. Examine the features of the 200-MS Module during the run. Note that the Status Indicator in System Control now indicates Running. In the Control and Status region, note the progress of the Runtime indicator. In the MS Method region, note the information associated with Segment 1. Now observe the Data

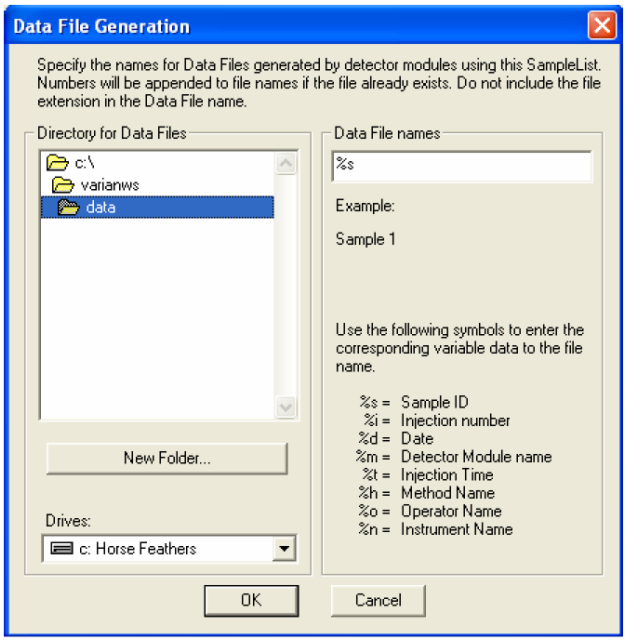
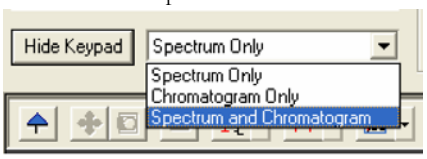


Figure 10. Data File Generation Dialog.

File name, Scan Number, Ion Time, and Ion Count in the Operating Conditions region. Click on the Hide Keypad button to get a full-screen display of the chromatogram. Click on the Show Keypad button to display the keypad again.

Time Select button in the Chromatogram toolbar. This button allows you to display the mass spectrum of a particular peak in the chromatogram. You may also click and drag in the chromatogram display to expand a given area for careful examination. You may look at both the Spectrum and Chromatogram by selecting that option from the drop-down list box.



IV-D. Data analysis

Open the MS Data Review application by clicking the MS Data Review button on the MS Workstation Toolbar. The Plot Chromatograms and Spectra window will appear on the screen (Figure 10). A data file can be viewed by clicking on it in the directory tree in the file selection pane. To select more than one file click on the file name while holding ctrl key. The chromatogram and spectra pane can be expanded to cover the whole screen by clicking on the Show/Hide Selection pane icon. The selection pane can be restored to its original size by clicking on the icon again. Notice that there are two toolbars in this display. The one on top is referred to as the MS Data Review toolbar. The lower toolbar is called the Chromatogram toolbar. If you are not yet familiar with the options in the Chromatogram toolbar, explore some of these features by holding the mouse cursor over each button and observing the tooltip descriptions.

Select the Click and Drag Action button on the Chromatogram toolbar and select Zoom Chromatogram or hold down the "z" key then click and drag the mouse within the Chromatogram display to expand the display around a window in the chromatogram. The new time range is applied to all chromatograms in the Chromatograms Window, while the specified intensity range is applied to the

selected plot. You may also click and drag under the time axis to zoom the time range without affecting the intensity axis of the display. You can use the Full Scale button to restore the full scale on both axes.

Click on the first peak in the chromatogram. The mass spectrum of the scan you selected is now displayed along with the chromatogram.

Running a Library Search on a Single Spectrum. Click on the Search button and select Library Search Active Spectrum. The results are displayed in the Library Search a Spectrum window. The active mass spectrum is compared with the high-quality spectra from the database and the best matches are displayed. This greatly help with identification; however, the quality of the match will depend on the quality of your mass spectra and might not always give you a reasonable answer. Use common sense.

Printing Spectra and Chromatograms. Spectrum and Chromatogram Reports can be printed by selecting File> Print. The Make Reports dialog opens. This dialog can also be displayed by right clicking in the Spectrum or Chromatogram panes or click the Print icon in the Toolbar.

V. Experimental procedure

This experiment focuses on the use of GC/MS in analysis of xylenes in gasoline. The acquisition method (detailed in section IV-A) has been set up for you before class. Follow the instructions given in section IV-B for the injection of a sample carefully. Addition of too much sample will result in the unsuccessful separation of the components in gasoline, and you will have to run the samples again.

1. Pipet 5 mL of gasoline into a fresh vial.
2. Inject 0.2 µL of gasoline sample into the gas chromatograph using a microliter syringe.
3. Add 0.1 mL of *o*-xylene to the gasoline sample, mix well and inject 0.2 µL.

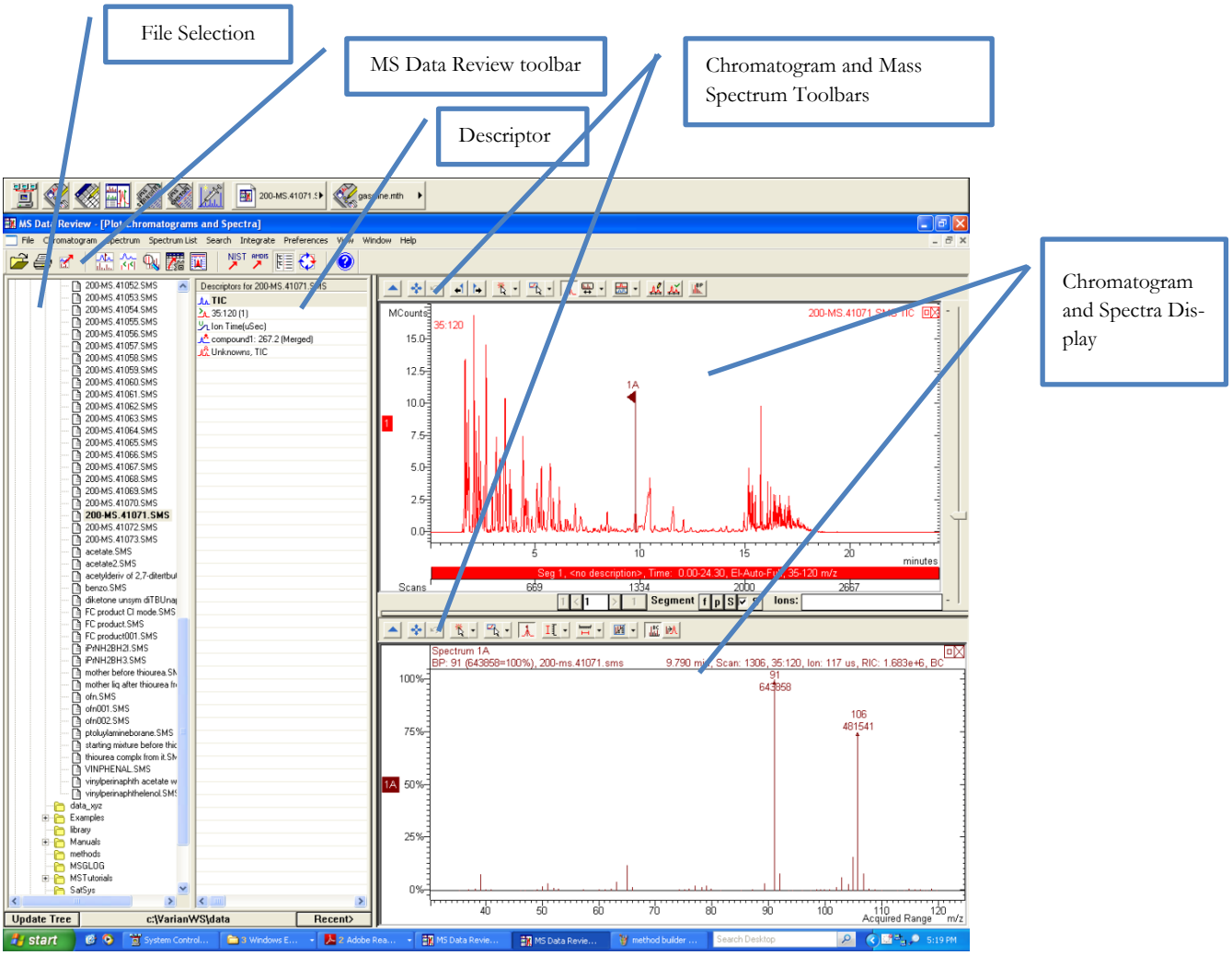


Figure 11. MS Data Review window

4. Add 0.1 mL of *p*-xylene to the gasoline sample containing already *o*-xylene, mix well and inject 0.2 μL.
5. Add 0.1 ml of *m*-xylene to the gasoline solution containing *o*- and *p*-xylenes, mix well and inject 0.2 μL.

VI. Discussion

1. Open the results for the gasoline in the MS Data Review. Looking at the MS spectra of corresponding peak in a chromatogram can you determine whether xylenes are present in the gasoline sample? You will need to search the database for reference MS spectra of xylenes in order to know what you are looking for.
2. Compare the chromatograms obtained for gasoline and gasoline spiked with xylenes. Do you see any extra peaks in the spiked gasoline samples? This would be the case if the gasoline sample did not contain the compound you added. Otherwise you should see an existing peak growing, because the retention time of the added compound is the same as the retention time of a compound already present in the gasoline.
3. Are identical (or almost identical) retention times a definite proof that two compounds are the same?
4. Describe the fragmentation pattern of xylenes.
5. If you already performed Raman experiment which of the two techniques in your opinion is more suitable for analysis of xylene isomers in gasoline sample. If you have not performed the Raman experiment, please answer this question in the lab report for Raman experiment.