

INSTRUMENTAL LIMITS ON GCMS EXPERIMENTAL PARAMETERS

The GC-MS is a combination of two separate techniques: Gas Chromatography to separate out compounds based on boiling point (see GC module) and MS to a) identify unambiguously the compound you have separated (see MS module) and b) measure the amount of the compound.

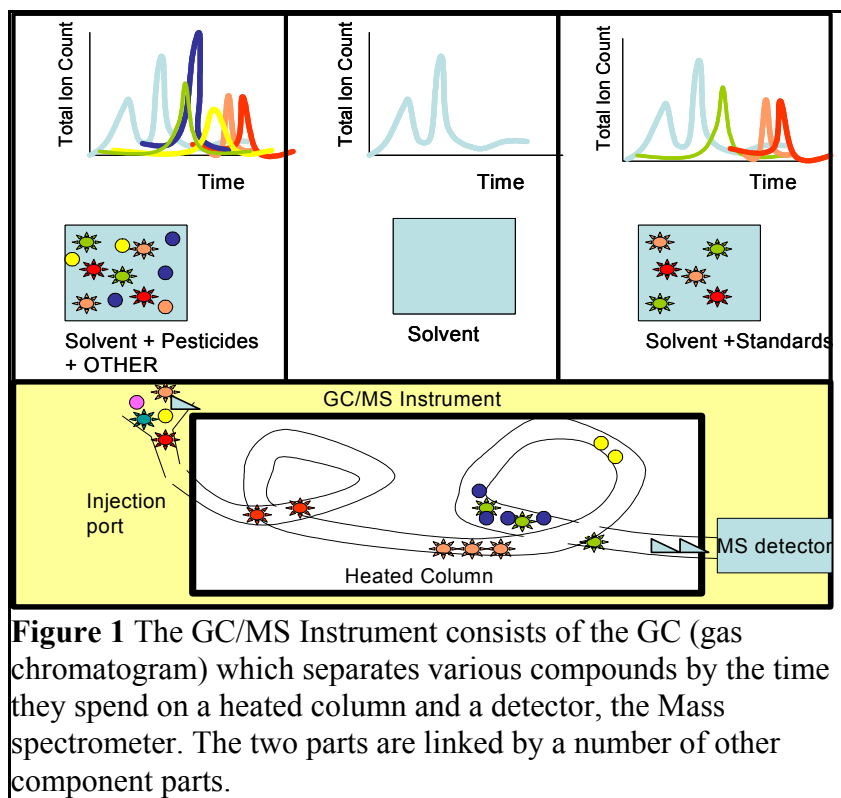


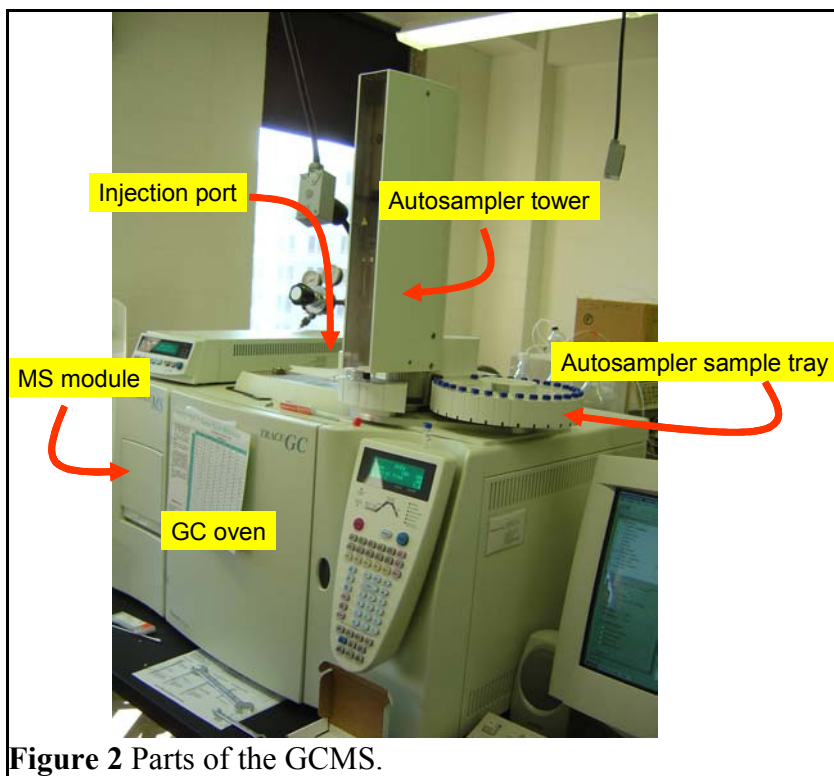
Figure 1 The GC/MS Instrument consists of the GC (gas chromatogram) which separates various compounds by the time they spend on a heated column and a detector, the Mass spectrometer. The two parts are linked by a number of other component parts.

The importance of this technique for routine analysis and research in compound development is that many, many samples are run. This is most easily done with an autosampler. The instrument consists therefore of the following main parts:

- 1) autosampler
- 2) Interface from autosampler to the GC (sample inlet port)
- 3) GC
- 4) Interface of GC to the MS
- 5) Ionization source of the MS
- 6) Detection module of the MS

Each component part requires the operator to understand the physical and chemical limits which apply to each part in order to avoid setting parameters which shorten the lifetime of the

instrument and/or cause catastrophic instrument damage. the component can sustain and the



AUTOSAMPLER

The autosampler tower contains the syringe which is used to transfer samples from the vials to the injection port on the GC. The autosampler tower should never be moved manually and should only be moved by instructions from the computer.

INTERFACE TO THE GC (SAMPLE INLET PORT)

The sample inlet port can have several different features designed to optimize the amount of sample that reaches the

chromatographic column to be separated and, later, detected. The **cold on-column** injector is designed for very labile species. It allows these species to be injected directly onto the column so that no material is lost in the purging of the injector. A **split** injector allows the volume of sample to be decreased in order to avoid overloading the column with total mass of the compounds to be measured. The injector we will use is the **Programmable Temperature Vaporizer (PTV)**. This injector can also be operated in the split mode. This allows for liquid introduction at 35 °C where the liquid containing solvent and pesticide will reside at the top of the column in the injector. A slow controlled heating of the injector acts as a microdistillation unit to boil off, through time, the various components before they hit the column. This often aids in avoiding sample degradation.

GAS CHROMATOGRAPHIC COLUMN OVEN

The ultra-fast oven allows temperature of the oven (and hence, the column) to be raised and cooled rapidly. The rate of heating generally is faster at lower temperatures. For most methods one should **NOT** pass 50 °C/min. At very rapid temperature variation the method will not be repeatable and the retention time may shift from run to run.

Cooling is necessary to go from run to run and adds time to the total method. The oven takes approximately 4 minutes to cool.

The maximum temperature that should be applied to the column is set by the chemical identity of the solid phase and the bonded polymer liquid phase. In general, the maximum

temperature that should be used for the oven is

MS interface

Temperature should match that of the end of the GC column.

MS SOURCE

The source lifetime is dependent upon its use. The energy of the source depends upon the operating voltage and current. Because the most efficient delivery of energy to most compounds for ionization and fragmentation occurs at 70 eV we are limited in the total current that we can apply to the ionizing filament. The maximum current used should be 350 μA . 70 eV gives the highest electron energy in a region where small fluctuations in the source current does not greatly change the electron energy (flat profile). The highest source current one wants to work with is 250 μA . The larger the source current the shorter the lifetime of the source. The higher the source energy the more fragments are generated - resulting in multiple peaks of high intensity.

As electrons boil off the filament they collide with molecules exiting the gas chromatographic column. The high energy electrons are sufficiently energetic that they exit bonding electrons entirely out of the molecule, leaving behind positively charged ions. Hence we typically use EI+ monitoring (of positive ions).

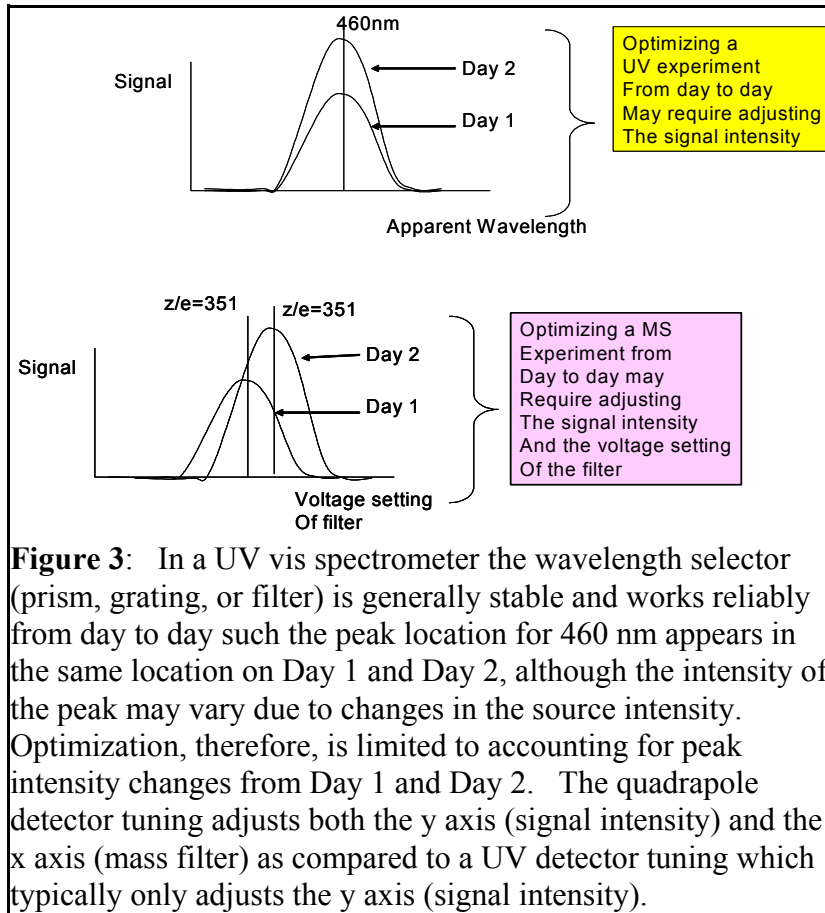
MS DETECTOR- Calibration

In many instruments we generally do not worry about “finding” the standard as that part of the operation of the instrument is highly stable and reproducible.

As an analogy we generally expect that when we turn on a spectrophotometer and place a cutoff color filter in place that we will isolate the same set of visible wavelengths regardless of the day or time (Figure 3). In a UV vis spectrometer the wavelength selector (prism, grating, or filter) is generally stable and works reliably from day to day such the peak location for 460 nm appears in the same location on Day 1 and Day 2, although the intensity of the peak may vary due to changes in the source intensity. Optimization, therefore, is limited to accounting for peak intensity changes from Day 1 and Day 2.

In a mass spectrometer the location of the peak associated with a particular mass is varies from day1 to day 2 (Figure 3) The quadrapole mass spec uses electronic algorithms to set voltages at the inlet lens and at the four (quad) electrodes. The voltage experienced by the molecule is never exactly that that the operator believes is applied by the algorithm because the electrodes can become coated, altered, burned, or pitted. Because we do not generally attempt to open up the high vacuum compartment to clean the four electrodes in the quadrapole detector we must anticipate resetting the “x” or “mass” axis on a regular basis. As a result the “filter” is not always the same from day to day or week to week. The quadrapole detector tuning adjusts both the y axis (signal intensity) and the x axis (mass filter) as compared to a UV detector tuning which typically only adjusts the y axis (signal intensity).

The MS detector, like that of most instruments, does need to have the signal optimized.



This is done, again, by an algorithm which tweaks the voltages applied to the quadrapole.

This tweaking is called “tuning” and should be done on a regular basis. You will not be asked to tune the instrument, because tuning of this particular instrument can only be accomplished while using the software program that internally links to the hardware meaning that the program can not successfully be parameterized off line.