

CREATING A TRACE MS METHODS FILE USING XCALIBER 1.4

Set up the instrument to look qualitatively for the presence of the target pesticides.

You will want to qualitatively determine if you have any of the compound present in your samples. The best way to do this is to compare GC-MS total ion chromatograms (TIC) for neat (undiluted) standards (no greater than XXXX concentration); the solvents; and one of your extracts.

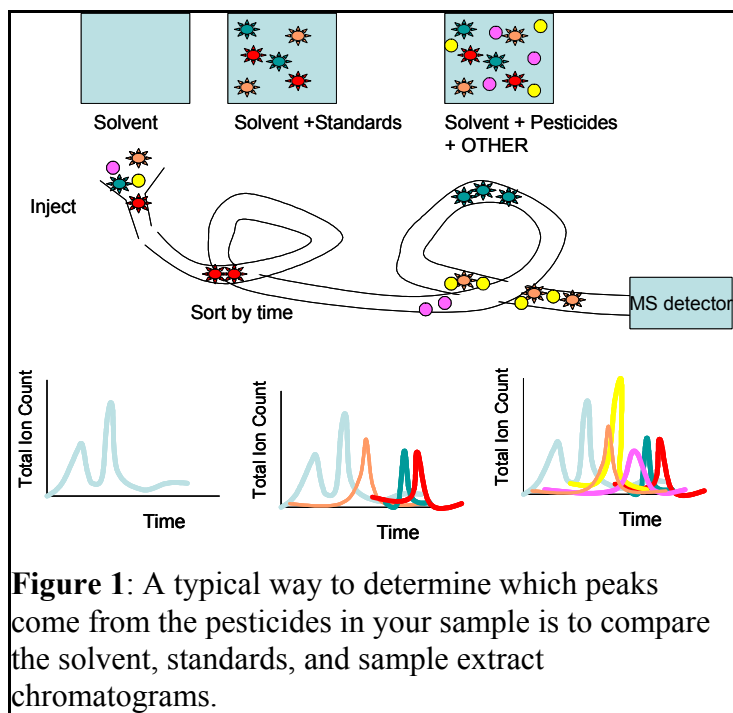


Figure 1: A typical way to determine which peaks come from the pesticides in your sample is to compare the solvent, standards, and sample extract chromatograms.

The solvent chromatogram should allow you to determine if you have some sort of background contaminate (for example phthalate from plastic containers) and to determine the level of the background ions contributed from the solvent. The neat standard TIC chromatogram allows you to determine under which conditions you can separate out all of your standards and at which time your standards should elute. This will allow you to tentatively determine if you have peaks at times associated with the pesticide standards in your own extract and if you have additional peaks for other compounds.

In the Figure 1 the solvent TIC shows a set of early peaks associated with the solvent. When we examine the TIC for the standards we

find new peaks with distinct times associated with the three different standard pesticides. When we compare to the sample extract we see the three standards and several other unknowns.

In each of the experiments we ran the GCMS at similar operating conditions (a METHOD FILE). In order to avoid setting up the method file over and over we place all of the information regarding using a total ion count, the temperature, etc. into a METHODS file and then in a SEQUENCE file we specify which samples are where in the autosampler, the method with which they are to be analyzed and the raw data file that the information is to be sent (Figure 2).

For this first set of experiments we ask the MS to survey all the ions coming off in a chromatographic peak. This is known as a FULL SCAN ACQUISITION (Figures 3 and 4). This allows us to track all possible ions that could be generated by all possible pesticides so that we can confirm our chromatographic peak identification.

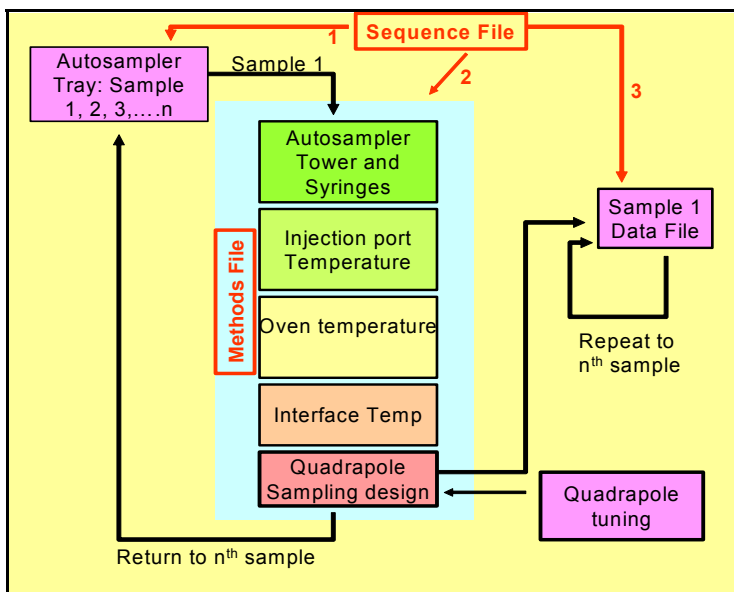


Figure 2 A sequence file specifies the samples and sample order, the Methods File to be used, and the data files in which to store the data. The Methods file is “independent” of the sequence file and can be set up and used repetitively to create identical experiments on a wide number of samples.

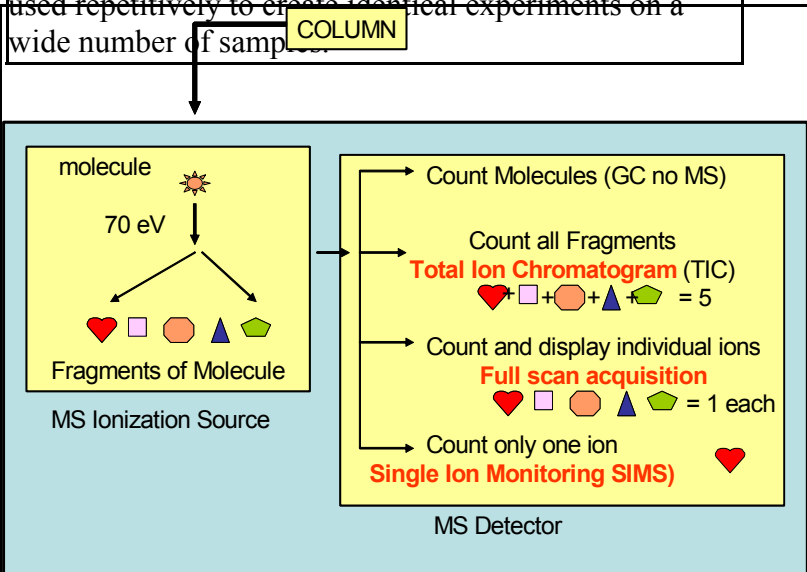
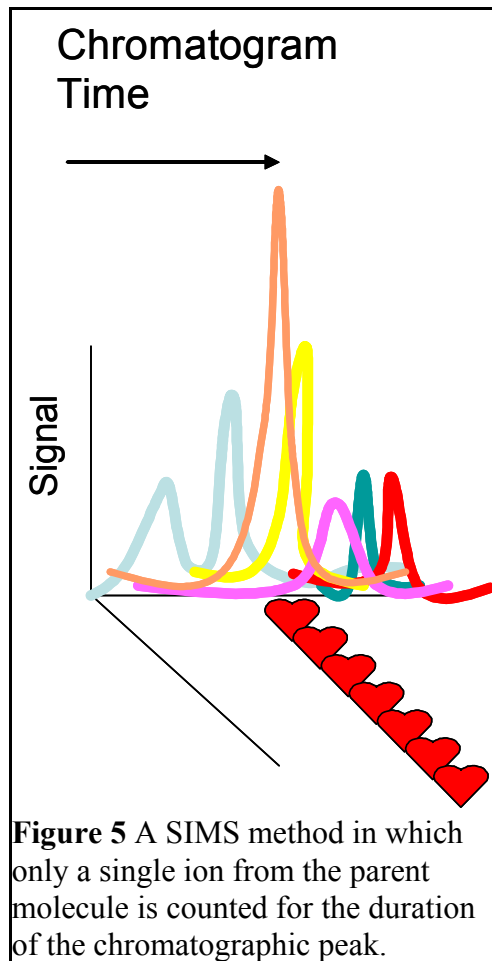
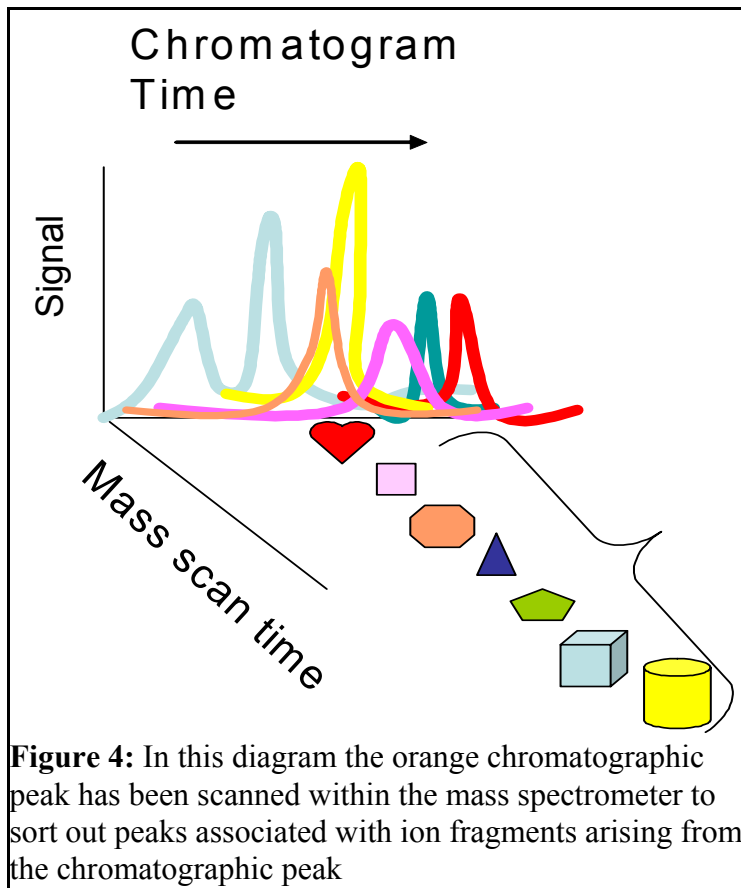


Figure 3 The mass spectrometer detector can be operated in a variety of modes to optimize the counting of the compound eluted from the column and fragmented in the ionization source. The most common methods are total ion chromatogram which sums and counts all ions, full scan acquisition which displays a mass spectra for each peak and single ion monitoring (SIMS) which counts only a single ion.



In a SIMS experiment (Figure 3 and 5) the goal is to increase the detection limit by spending more time looking at the ions of interest rather than “wasting” time looking at all of the possible ions that could be generated in the ionization source.

A type mass can consists of monitoring between 100 and 400 masses by counting at each of those masses for between 1 and 4 ms. This results in 1 full scan every approximately 0.422 seconds or 2.3 full scans per second. A typical GC peak width is about 5 s, therefore one can accomplish

$$\left[\frac{4.2 \text{ mass scans}}{s} \right] \left[\frac{5s}{\text{chromatographic peak}} \right] = \frac{\sim 10 \text{ mass scans}}{\text{chromatographic peak}}$$

Thus each ion has been measured 10 times when using a full mass scan. In contrast in a SIMS

method the in is measured for a total of 5 s. The relative intensity of the signal expected is

$$\frac{\text{Signal}_{sSIMS}}{\text{Signal}_{Fullscan}} = \left(\frac{5s}{(1ms)(10measurements)} \right) \left(\frac{10^3 ms}{s} \right) = 500$$

By sitting at a single mass for the entire GC peak width you can increase the sensitivity of the peak by at least 500 fold which will lower the detection limit into the ppt range.