

CHAPTER 5

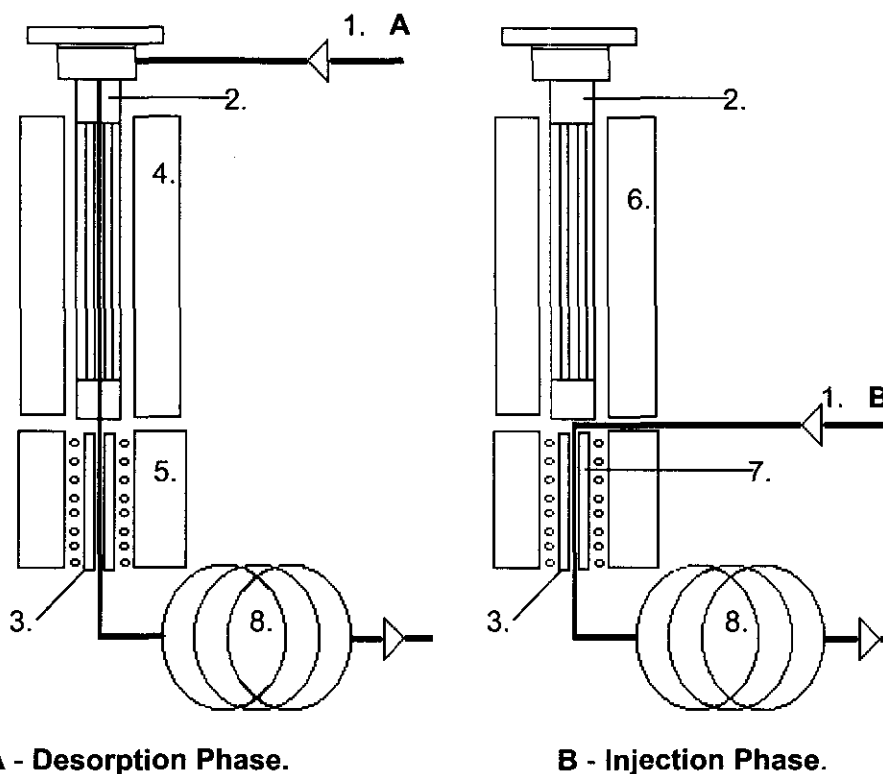
INSTRUMENTATION

5.1 THERMAL DESORPTION – CRYOGENIC TRAPPING UNIT (TCT)

Volatile compounds, which have been pre-concentrated on ad/absorbents, need to be quantitatively transferred as a narrow injection band onto the GC capillary column.

One method for achieving this is by using a thermal desorption cold trap injector. A ChromPack 4020 desorption unit was used in our study, Figure 5.1[116]. A glass tube, either empty or packed with sorbent, is placed in the desorption oven, where it is heated while the carrier gas transfers the volatiles from the tube onto a cold trap.

The cold trap consists of a fused silica capillary, 30cm long with an internal diameter of 0.53mm, which is coated with a thick film of stationary phase to increase its capacity. During desorption, the cold trap is cooled and maintained at sub-ambient temperatures ranging from 0°C to -100°C by using liquid nitrogen. Upon completion of desorption the cooling flow is stopped. A metal capillary tube, which surrounds the fused silica cold trap is heated ohmically. This ensures a ballistic temperature increase from, for example -100°C to 250°C within 1 minute. Within that time, the carrier gas transfers the contents of the cold trap and refocuses it onto the GC capillary column, which is at a lower temperature. Figure 5.1 shows the 2 main phases, namely desorption and injection, in the TCT - CP 4020 [116].



A - Desorption Phase.

B - Injection Phase.

1. **A** High purity Helium carrier gas flow during the **desorbtion** phase.
1. **B** High purity Helium carrier gas flow during the **injection** phase.
2. Glass tube containing ab-/ad-sorbent.
3. Fused Silica cold trap.
4. Heated desorbtion oven.
5. Liquid Nitrogen-cooled chamber.
6. Ambient desorbtion oven.
7. Ballistically heated fused silica cold trap.
8. Gas chromatograph.

Figure 5.1. The 2 main phases in the TCT 4020 thermal desorption unit.

5.2 GAS CHROMATOGRAPH (GC)

A GC consists of a carrier gas supply, an inlet, an oven containing a capillary column and a detector, as depicted in figure 5.5. The carrier gas (mobile phase) must be inert and of high purity. Typical gases used are nitrogen, helium or hydrogen. The choice of the gas used depends on the speed of analysis required and the detector used. In our experiments, helium was used as it is recommended for use with mass spectrometric detection [117]. The flow rate of the carrier gas should be chosen to

ensure the maximum number of chromatographic plates in the column, which in turn determines the degree of separation or resolution between the compounds [118,119].

The sample is introduced into the capillary column via the inlet. Samples are dissolved in an appropriate organic solvent and about 1 μL injected using a micro litre syringe. The sample is injected instantaneously so that, in conjunction with the high temperature of the inlet, e.g. 250°C, the volatilised components in the sample are focussed onto the cooler column, eg.40°C, as a narrow injection band. The inlet can be set-up for either split or splitless injection. When the sample is too concentrated or injected as a large volume, split injection is used at a preset split-ratio so that only a small proportion is actually transferred onto the column. When sample components are present in trace amounts the entire sample can be transferred onto the column in splitless injection, thereby improving detection limits [118].

The thermal desorption unit is used an alternative "inlet" for the desorbed components of the trap (see above).

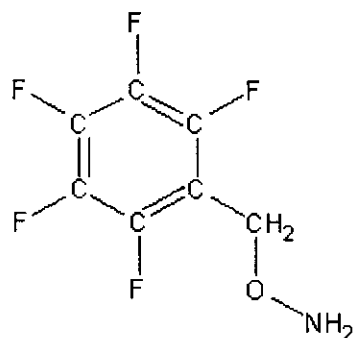
The capillary column used is 30m long and 0.25mm in internal diameter. It is coated on the inside with a thin film (0.25micron) of 95% polydimethylsiloxane and 5% methylphenylsiloxane stationary phase. We used a temperature program starting at 30°C held for 1 minute, ramped at 5°C per minute to 150°C then ramped again at 50°C to 280°C for 4 minutes. The last temperature ramp is used to remove silicone, released from the silicone traps during desorption, as well as other compounds still in the column. The eluted compounds then enter the detector.

Two kinds of detectors were used in our study. The Flame Ionisation Detector (FID) and a Mass Spectrometer (MS). They are discussed in detail below.

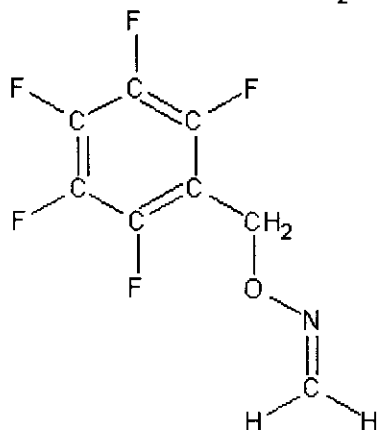
standards [122-124]. Figure 5.3 shows the estimation of the ECN contributions of PFBHA and the HCHO-Oxime. The ECN for the other aldehydes studied can be predicted in the same way. The calculation method used to determine the FID response for the HCHO-oxime and PFBHA are shown below.

Table 5.1. Contributions to the Effective Carbon Number (ECN) [120,122].

ATOM	TYPE	ECN CONTRIBUTION
C	Aliphatic	1
C	Aromatic	1
C	Olefinic	0.95
C	Acetylene	1.30
C	Carbonyl	0
C	Carboxyl	0
C	Nitrile	0.3
O	Ether	-1.0
O	Primary Alcohol	-0.5
O	Secondary Alcohol	-0.75
O	Tertiary Alcohol	-0.25
N	Amine	As for O in Alcohol
Cl	An olefinic C	+0.05
Cl	Aliphatic C with 2 Cl atoms	-0.12 per Cl



6 aromatic C - atoms	= 6 x 1
5 F - atoms	= 5 x 0.05
1 aliphatic C - atom	= 1 x 1
1 ether O - atom	= 1 x -1
1 primary amine	= 1 x -0.5
<u>sum total PFBHA</u>	<u>= 5.75</u>



6 aromatic C - atoms	= 6 x 1
5 F - atoms	= 5 x 0.05
1 aliphatic C - atom	= 1 x 1
1 ether O - atom	= 1 x -1
1 secondary amine	= 1 x -0.75
1 olefinic C - atom	= 1 x 0.95
<u>sum total OXIME</u>	<u>= 6.45</u>

Figure 5.3. Estimating Effective Carbon Numbers for PFBHA and the HCHO-Oxime.

Dodecane has 12 aliphatic carbon atoms, so similarly the ECN for dodecane(C12) is 12. Thus, assuming the FID response for C12 is 100%. Then the FID response, in terms of ECNs, for PFBHA and the HCHO-Oxime can be seen as a fraction of the FID response for C12. The FID response factor for C12 is given as

$$\frac{(\text{ECN C12})}{(\text{ECN C12})} \times \frac{(\text{C12 peak area})}{\text{amount C12 (ng)}}$$

The response for PFBHA can then be given as

$$\frac{(\text{ECN PFBHA})}{(\text{ECN C12})} \times \frac{(\text{C12 peak area})}{\text{amount C12 (ng)}}$$

The amount of PFBHA can then be determined by

$$\frac{(\text{PFBHA peak area}) / (\text{ECN PFBHA})}{(\text{ECN C12})} \times \frac{(\text{C12 peak area})}{\text{amount C12 (ng)}}$$

Similarly the HCHO-Oxime amount can be determined by

$$\frac{(\text{Oxime peak area}) / (\text{ECN Oxime})}{(\text{ECN C12})} \times \frac{(\text{C12 peak area})}{\text{amount C12 (ng)}}$$

The amount of aldehyde can then be calculated using elementary chemistry. The ratio between aldehyde and oxime formed is 1:1[50]. Since the ECNs for PFBHA and the HCHO-Oxime were estimated, the amounts calculated are not accurate.

However, they are sufficient for our purpose which is merely to have an indication of the amounts involved.

5.4 THE MASS SPECTROMETER (MS)

The MS can be divided into three sections, all of which are under a vacuum of at least 10^{-5} Torr. Compounds eluting from the GC are ionised in the ion source and then accelerated by a potential difference to pass through various focussing lenses towards the mass analyser and finally towards an electron multiplier [119,125,126]. Detection limits for MS detectors are typically 1 ng for Total Ion Monitoring and 1 pg for Selected Ion Monitoring [126].

Electron Impact (EI) ionisation is used by both the quadrupole and ion trap mass analysers that were used in our study. A hot tungsten or rhenium filament produces

electrons with an energy of 70eV, which is in excess of the energy required to ionise a molecule (~10eV). These high-energy electrons also provide enough energy to cause the ionised molecule (M^+) to undergo significant fragmentation, unique to every compound. After the bombardment of electrons, the ions are accelerated by a potential of 5-15V towards the centre of the mass analyser [119,125,126].

The quadrupole is a mass analyser or rather a "mass filter", see figure 5.4 [119,125]. Four cylindrical metal rods are arranged in pairs in parallel beside each other. One pair is connected to the positive terminal of a dc potential, and the other pair to the negative dc potential. In addition, to each pair of rods, a variable Radio-Frequency (RF) ac potential, 180° out of phase, has been applied.

The ions have a constant velocity as they enter the quadrupole, in the z- direction, parallel to the metal rods (x and y-axes). As a result of the dc and RF voltages (V_{dc} and V_{rf}) applied to the rods, the ions acquire complex oscillations in the x and y directions. Ions are deflected, by these oscillations, towards the rods, neutralised and carried away.

For a given set of conditions (V_{dc} and V_{rf}), only ions of a single m/z ratio will have a stable oscillation and will be able to traverse the length of the quadrupole, without striking the rods. These ions will enter the electron multiplier detector. Mass scanning is achieved by varying each of the RF and dc frequencies while keeping their ratios constant [119,125,126].

Total Ion Chromatograms (TIC) are produced when the compounds eluting from the GC are scanned every 10 seconds, from the lowest mass to the highest mass within a selected mass range, usually m/z ratio 40 to 400. Compounds analysed by GC-EI-MS, normally have a single charge ($z=1$), so the m/z ratio is the same as their actual mass (m) [125].

To improve sensitivity, Selected Ion Monitoring (SIM) can be used. In this case the quadrupole scans only for certain selected masses. This way more time is allocated

to the m/z ratio of interest whereas with Total Ion monitoring only a fraction of time is allocated to the detection of that m/z ratio.

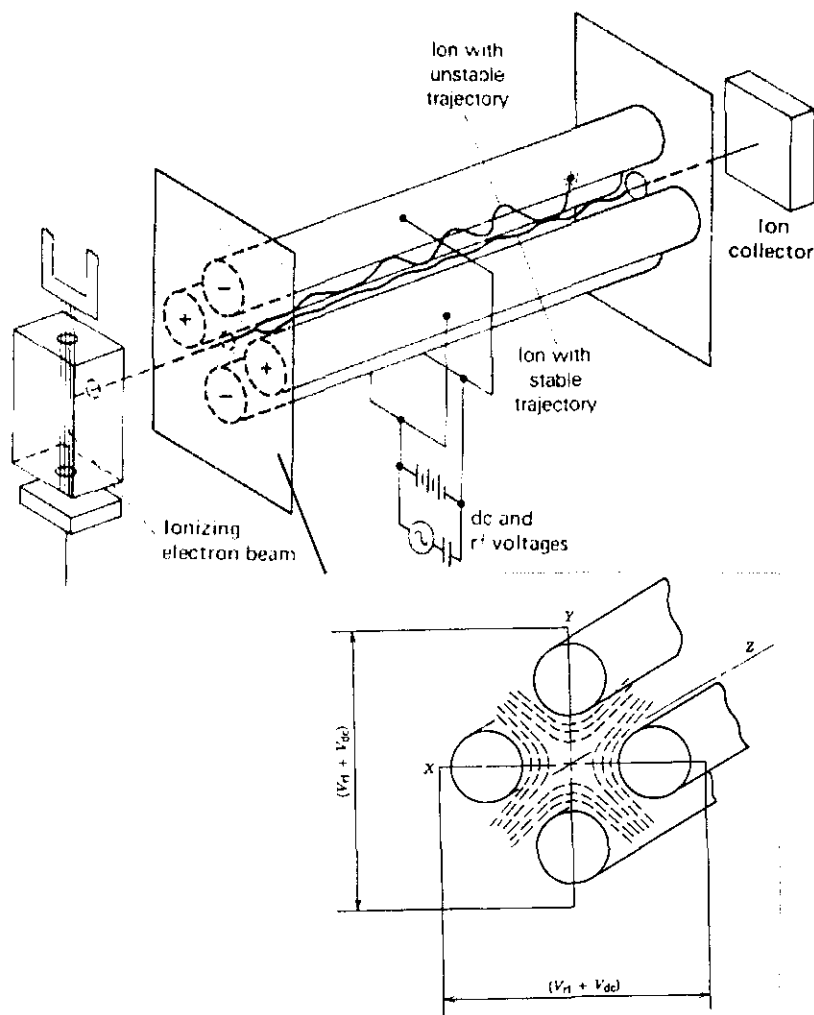


Figure 5.4. A Quadrupole Mass Spectrometer[125,126].

An ion trap (ITD) is the spherical configuration of the linear quadrupole, depicted in figure 5.5 [125]. In this case, the RF voltage is applied to a central doughnut-shaped ring electrode, which is enclosed on both ends with cap electrodes. Ions from the ion source enter the enclosure through a grid in the top end-cap. Unlike the linear quadrupole, ions are "trapped" temporarily within the ITD until they are sorted according to m/z ratios. The ions with appropriate m/z ratios are in a stable orbit

within the enclosure. As the electric field is scanned, the heavier ions are stabilized in their orbit while the lighter ones become unstable, collide with the wall of the ring electrode and leave the trap through the bottom end-cap. These emitted ions move towards the electron multiplier detector [119,125,126].

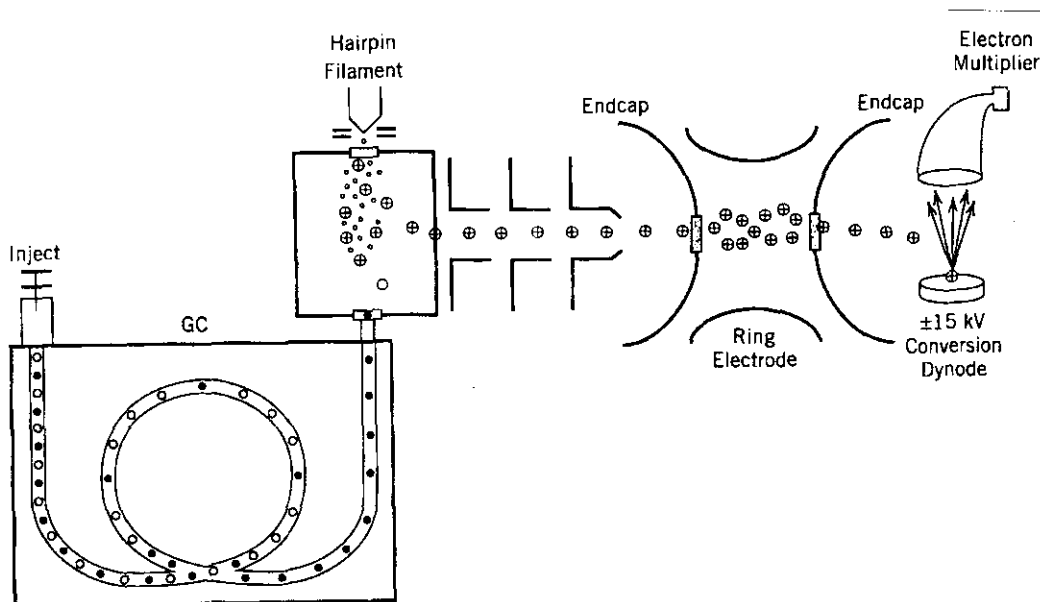


Figure 5.5. A Gas Chromatograph (GC) coupled to an Ion Trap Detector (ITD), having an external ion source [125].

The continuous-dynode electron multiplier is a glass trumpet-shaped device, which has been coated with lead on the inside. A potential difference of 1.8-2kV is applied across the length of the trumpet. The positive ions emitted from the mass analyser, enter the detector and strike the lead surface. Upon this impact, electrons are ejected, which in turn impact the surface and eject more electrons, this continues in a "zigzag" path until the tapered end of the trumpet is reached, which is connected to the amplifier. From here the data is acquired, converted and controlled by electronics, the output is sent to a data acquisition system on a computer [126].