3.3. FIELD IONISATION

Field ionisation (FI) and field desorption (FD), which is discussed in Section 3.4, are two very closely related methods of ionisation which rely on essentially the same principle. We will deal with FI first and follow this with a discussion of FD, which corresponds to the historical sequence of their development.

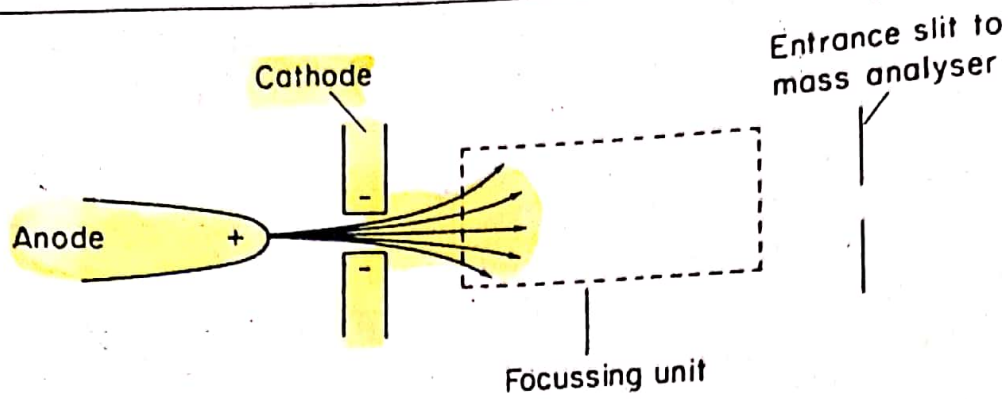A schematic diagram of an FI ion source is shown in Fig. 3.3a.

Fig. 3.3a. *Schematic diagram of a field ionisation ion source*

The most important components are the electrodes, an anode and a cathode, which are held at a potential difference of up to 10 kV and are sufficiently close together to develop a potential gradient of up to 10^8 V cm^{-1}.

SAQ 3.3a	Using the figures given above, calculate the distance between the electrodes.

When a sample molecule in the vapour phase impinges on the anode or comes very near to it, the potential gradient it experiences leads to an electron being transferred to the metal anode giving rise to the formation of a positive ion.

Π   What might you expect to happen to the positive ion when it is formed?

It is attracted towards the cathode and as this has a hole in it, some ions pass through.

SAQ 3.3b | These ions will have passed through a high potential difference. What effect will this have on them?

Most mass spectrometers are designed to analyse ions travelling at velocities attained by acceleration through potential differences of 4000 to 8000 volts. The ions leaving the cathode of the FI source will have passed through a potential difference of about 10 000 volts.

SAQ 3.3c | What must be done to these ions so that the mass spectrometer can analyse them?

The focussing device beyond the cathode has two functions. Firstly, it must retard the ions until they reach the correct velocity for analysis and secondly, it must focus the diverging beam of ions coming through the cathode into a coherent beam for mass analysis. We won't discuss the details of how these two feats are achieved.

The anode of the FI source is often termed the *emitter*, because molecules impinge upon it or come very close to it and are emitted as ions. The emitter is usually a sharp blade, a sharp tip or a wire. The efficiency of ion emission can be increased by a factor of about 10^3 by the technique of 'whiskering' the emitter. This will be described in more detail in the next section concerning the field desorption ion source.

Field ionisation usually produces molecular ions, $M^{\ddagger}$, but in some cases, quasi-molecular ions $(MH)^+$, are observed. Some samples produce both.

The quasi-molecular ions arise as a consequence of a high concentration of sample molecules existing near the anode, which gives rise to ion-molecule reactions. The formation of $M^{\ddagger}$ ions in some cases and $(MH)^+$ in others obviously introduces a degree of uncertainty into the determination of relative molecular masses of uncharacterised substances. This lowers the value of the technique somewhat. However, unlike CI, no higher adduct ions such as $(M + C_2H_5)^+$ are formed.

The FI method produces molecular ions with much lower internal energies than those produced by EI.

SAQ 3.3d	What is the consequence of this as far as the mass spectrum is concerned?

SAQ 3.3d

Although there is less fragmentation than in EI mass spectra, FI spectra usually show some fragment ions and these can be structurally informative. This is well illustrated by a comparison of the EI and FI spectra of xanthosine (Fig. 3.3b). The FI spectrum of xanthosine shows a much enhanced $M^{\ddagger}$ peak, but the structurally significant ions at m/z 152 and 133 are also present.
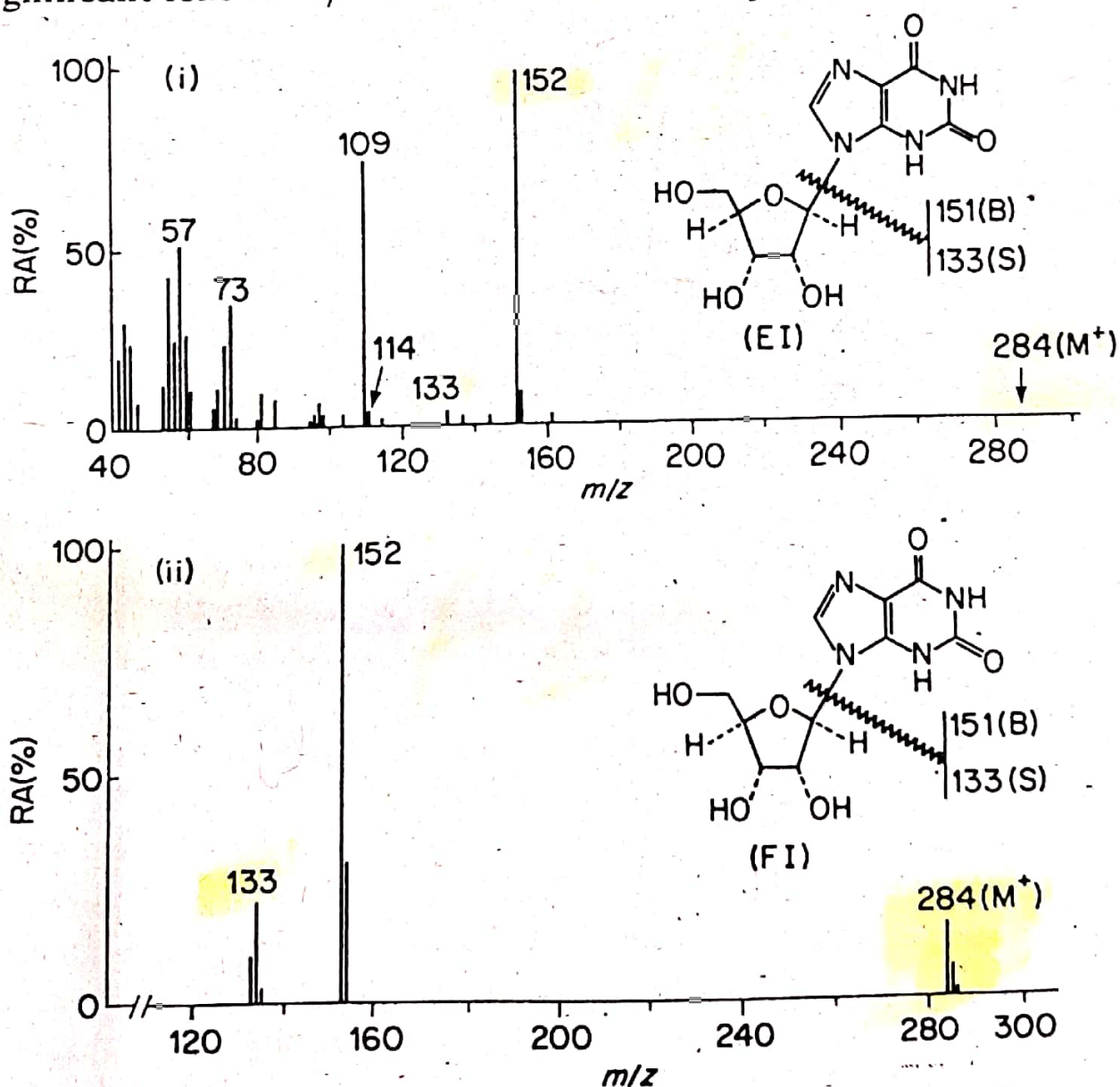

Fig. 3.3b. *Mass spectrum of xanthsosine, (i) using EI and (ii) using FI*

SAQ 3.3e	List any advantages and disadvantages of FI over EI or CI and any limitations of the technique.

3.4. FIELD DESORPTION

The problems that none of the previous methods of ionisation have been able to overcome are how to deal with thermally unstable or involatile compounds. Field desorption (FD) is the first of two techniques we shall discuss which addresses these problems.

∏   If you had to begin designing an ion source to deal with these types of compounds, what fundamental principle would you attempt to use? I don't want you to think in detail about ion sources, just about physical principles.

If vaporising the sample is a problem, it might be overcome if we could produce ions directly from the solid state. This is what field desorption does. It operates on the same principle as FI in that it uses an emitter held at a high temperature with respect to a cathode. But, the sample is placed on the surface of the emitter in the solid state and ions are desorbed directly from the solid towards the cathode.

The anode is first prepared by covering it with a carbon coating in the form of microneedles or 'whiskers', about 0.001 cm in length. This enlarges the surface area for coating with the sample and also increases ionisation efficiency. Whiskering is something of an art, which needs a skilled operator to get good results. The sample is applied in the form of a solution and the solvent subsequently removed by evaporation.

Π   Coating the sample onto the emitter must obviously be done in the laboratory, outside the ion source of the mass spectrometer. How do you think the emitter might be introduced into the source?

If the emitter is attached to a direct insertion probe similar to that described in Section 2.2, this can be inserted into the ion source *via* a vacuum lock.

Field desorption is the 'softest' of the ionisation techniques to be discussed in this section. Generally it only produces molecular ions and/or quasi-molecular ions with virtually no fragmentation. An example of this is shown in Fig. 3.4a, which compares the EI, CI, and FD spectra of the anti-inflammatry compound, dihydrocortisone ($M_r = 364$) which has the structure.
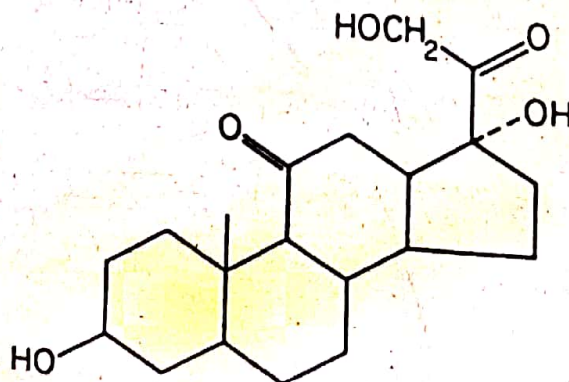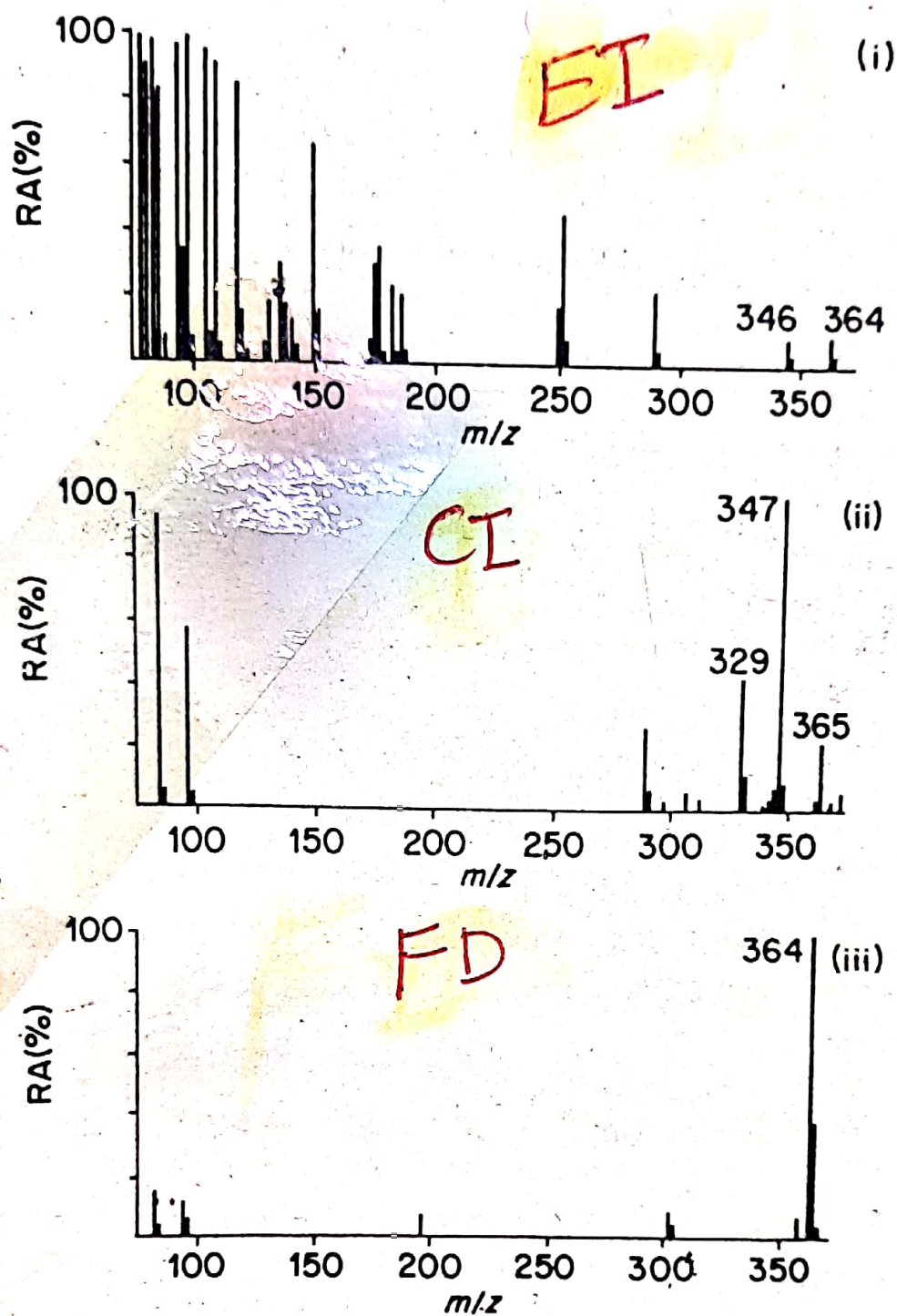
Fig. 3.4a. *Mass spectra of dihydrocortisone obtained by (i) EI; (ii) CI and (iii) FD ionisation*

SAQ 3.4a

What is the consequence of not producing fragment ions?

There is a further drawback with FD which is related to the persistance of the spectrum. With an EI ion source, the small amount of sample introduced (usually, about 1 mg via an AGHIS or septum inlet or 1 μg on a probe) is usually sufficient to produce many hundreds of mass spectra and as long as sample remains in the instrument, the mass spectrum is produced. This process may go on for an hour or more. Although, in practice, one wouldn't usually need that length of time, it is not uncommon to spend 15 min or so adjusting the instrument to give the best conditions for that particular sample (this is referred to as tuning the instrument) and recording the spectrum.

In the case of FD, some samples will not give persistant spectra. As soon as the emitter is switched on ions are formed, but the ion current very quickly decays to nothing. This gives hardly any time for tuning before recording the spectrum. Thus the spectrum may not be recorded under the most favourable instrumental conditions. Nevertheless, FD has proved to be a very useful technique for obtaining spectra of thermally unstable or involatile compounds. As an example of this, the FD mass spectrum of polystyrene shows ions up to m/z 11 000.

| SAQ 3.4b | List the advantages and shortcomings of the FD technique. |