

### 3 Mass spectrometry

Mass spectrometry is an incredibly important analytical technique for the identification of molecules by way of measuring their mass-to-charge ratios,  $m/z$ , in the ionized state. It is particularly useful for the detection and analysis of traces of macromolecules down to less than 1 pg ( $10^{-12}$  g). The general design of a mass spectrometer comprises sample injector, sample ionizer, mass analyzer and ion detector (Fig. 3.1). First the sample is injected into the ionizer which ionizes sample molecules. Then sample ions are analyzed and detected. To prevent collisions with gas molecules, sample ionizer, mass analyzer and ion detector are generally operated in vacuum.



**Fig. 3.1** General design of a mass spectrometer

The ion separation power of mass spectrometers is described by the resolution,  $R$ , defined as:

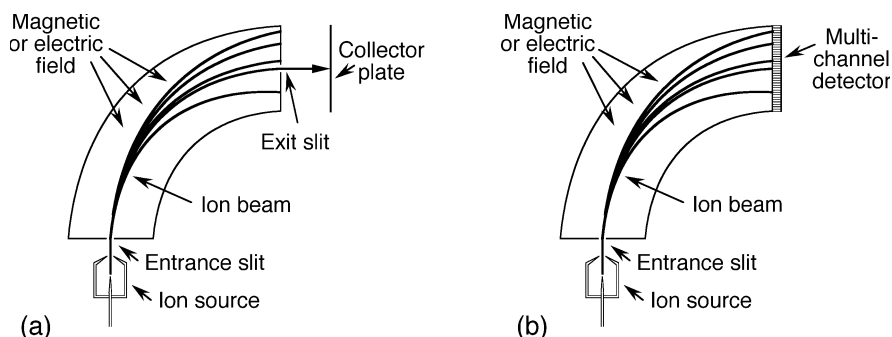
$$R = \frac{m}{\Delta m} \quad , \quad (3.1)$$

where  $m$  and  $\Delta m$  are the ion mass and mass difference between two resolvable peaks in the mass spectrum, respectively.  $R$  typically ranges between 100 and 500,000.

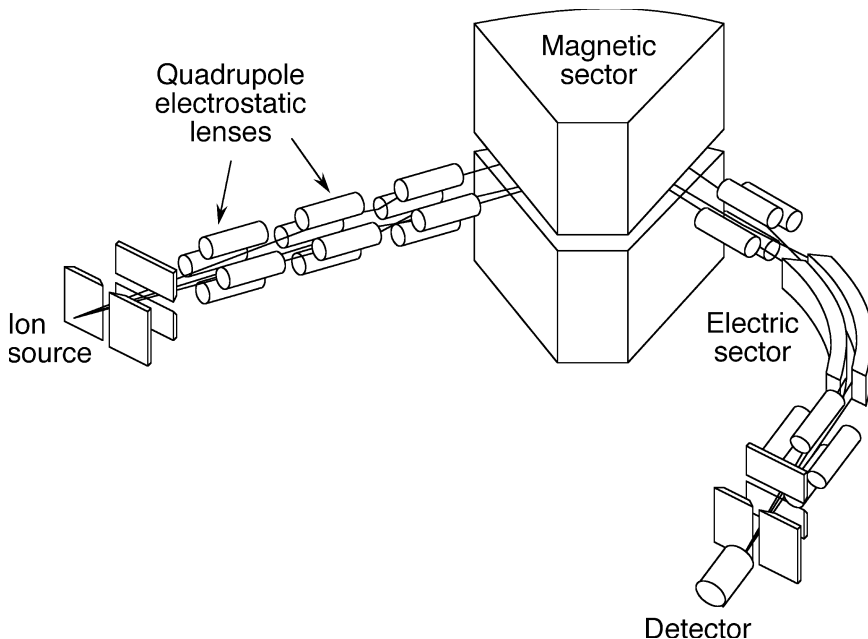
#### 3.1 Principles of operation and types of spectrometers

According to their mass analyzer designs, there are five important types of mass spectrometers (MS): (a) magnetic and/or electric sector MS (Figs. 3.2 and 3.3), (b) quadrupole MS (Fig. 3.4), (c) ion trap MS (Fig. 3.5), (d) time-of-flight MS (Figs. 3.6–3.9), and (e) Fourier transform MS (Fig. 3.10). Time-of-flight mass spectrometers (TOFs) often are less expensive than other types of mass spectrometers and have, compared to quadrupole MS and many sector MS, the advantage of recording the masses of all ions injected into the analyzer without scanning, contributing to a high sensitivity. TOFs usually have a smaller mass range and resolving power than Fourier transform mass spectrometers (FTMS).

### 3.1.1 Sector mass spectrometer



**Fig. 3.2** Single magnetic or electric sector mass spectrometer with a single channel (a) and multichannel (b) detector, respectively. Ions leaving the ion source are accelerated and passed through the sector in which the electric or magnetic field is applied perpendicular to the direction of the ion movement. The field bends the ion flight path and causes ions with different  $m/z$  to travel on different paths. In scanning mass analyzers (a) the electric or magnetic field strength is varied and only one mass detected at a time. In non-scanning mass analyzers (b) all masses are recorded simultaneously within a limited mass range with the help of a multichannel detector



**Fig. 3.3** Advanced virtual image ion optics with high transmission in a benchtop single-sector mass spectrometer (GCmateII from JEOL Ltd., Tokyo; Matsuda et al., 1974; Matsuda, 1976, 1981)