minute, with a narrower capillary outlet, providing smaller droplets and more efficient ionisation. Multiple sprayers (2-8) may be used in either technique: independent liquid streams are fed into the MS source and sampled sequentially into the mass analyser. This allows coupling of up to 8 LC systems into one mass spectrometer and the use of a standard reference solution for accurate mass measurement with high resolution instruments (to determine empirical formulae). ESI flow rates range from nL/min to about 200µL/min and response is dependent on the concentration of analyte rather than amount, allowing use of microbore and capillary columns, or even chip-based LC. With larger columns the best performance is obtained by splitting the flow via a simple T-piece. Capillary electrophoresis and electro-chromatography may also be linked to MS.

APCI is a development of ESI, in which the LC eluent is rapidly evaporated on passing through a nebuliser at high temperature. Ionisation is produced by corona discharge in the spray and solvent ions are produced that can react with the analytes in the gas phase (chemical ionisation). Higher flow rates of ml min^{-1} can be used and a greater degree of fragmentation takes place. APPI is a newer technique which is reported to have fewer matrix effects than ESI or APCI. LC eluent is sprayed with a nebulising gas into a heated probe, as in APCI, and a 'dopant' compound is vaporised and ionised by UV radiation, forming 'photo-ions'. The photo-ions initiate a cascade of ion-molecule reactions, forming ionised analyte.

ESI is generally most suitable for relatively polar molecules, across a wide range of molecular mass, while APCI and APPI are most suitable for small (less than 1000 Da) relatively non-polar molecules.

Mass analysers

The type of mass analyser defines the mass spectrometer. Thus there are sector instruments relying on magnetic and electric fields for *m/z* ion separation, quadrupole

