

Figure 9.14 Argon ICP torch used as an ionization source for ICPMS. (From Ewing, used with permission.)

cone with a small orifice in its center, called the sampling cone. The gas that enters through the orifice expands into an evacuated region. The central portion passes through another metal cone, the skimmer cone, into the evacuated mass analyzer. Singly charged positive ions are formed from most elements, metallic and nonmetallic. The ICP has a high ionization efficiency, which approaches 100% for most of the elements in the periodic table. The mass spectra are very simple and elements are easily identified from the m/z values and the isotope ratios observed. Background ions from the solvent and from the argon gas used to form the plasma are usually observed. Such ions include Ar^+ , ArH^+ , ArO^+ , and polyatomic ions from water and the mineral acids used to dissolve most samples.

9.2.3. Mass Analyzers

The mass analyzer is at the core of the mass spectrometer. Its function is to differentiate among ions according to their mass-to-charge ratio. There are a variety of mass analyzer designs. *Magnetic sector* mass analyzers and *quadrupole* mass analyzers are scanning instruments; only ions of a given mass-to-charge ratio pass through the analyzer at a given time. The m/z range is scanned over time. Other mass analyzers allow simultaneous transmission of all ions; these include *time-of-flight (TOF)*, *ion trap*, and *ion cyclotron resonance* mass analyzers as well as *dispersive magnetic* mass analyzers. Tandem mass spectrometers are instruments with several mass analyzers in sequence; these allow the selection of one ion in the first analyzer (the precursor ion) and the analysis of fragmentation or decomposition of that ion into product ions in the second analyzer.

9.2.3.1. Magnetic and Electric Sector Instruments

The principle of operation of a simple single-focusing magnetic sector mass analyzer was described briefly in Section 9.1. An ion moving through a magnetic field B will follow a circular path with radius r [Eq. (9.6)]. Changing B as a function of time allows ions of different m/z values to pass through the fixed radius flight tube sequentially. This scanning magnetic sector sorts ions according to their masses, assuming that all ions have a $+1$ charge and the same kinetic energy. A schematic of a 90° sector instrument is shown in Fig. 9.15. A variety of other magnetic mass spectrometers are shown in Fig. 9.16; some of these will be discussed later. The sector can have any apex angle, but 60° and 90° are common. It can be demonstrated that a divergent beam of ions of a given m/z will be brought to a focus by passing through a sector shaped magnetic field, as shown by the three ion paths in Fig. 9.15.

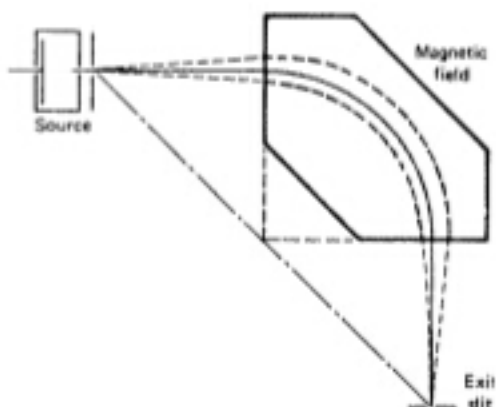


Figure 9.15 A 90° magnetic sector mass spectrometer. (From Ewing, used with permission.)

A dispersive magnetic sector mass analyzer does not use a flight tube with a fixed radius. Since all ions with the same kinetic energy but different values of m/z will follow paths with different radii, advantage can be taken of this. The ions will emerge from the magnetic field at different positions and can be detected with a position-sensitive detector such as a photoplate or an array detector. Examples of dispersive magnetic sector systems are shown in Fig. 9.16(c) and (d).

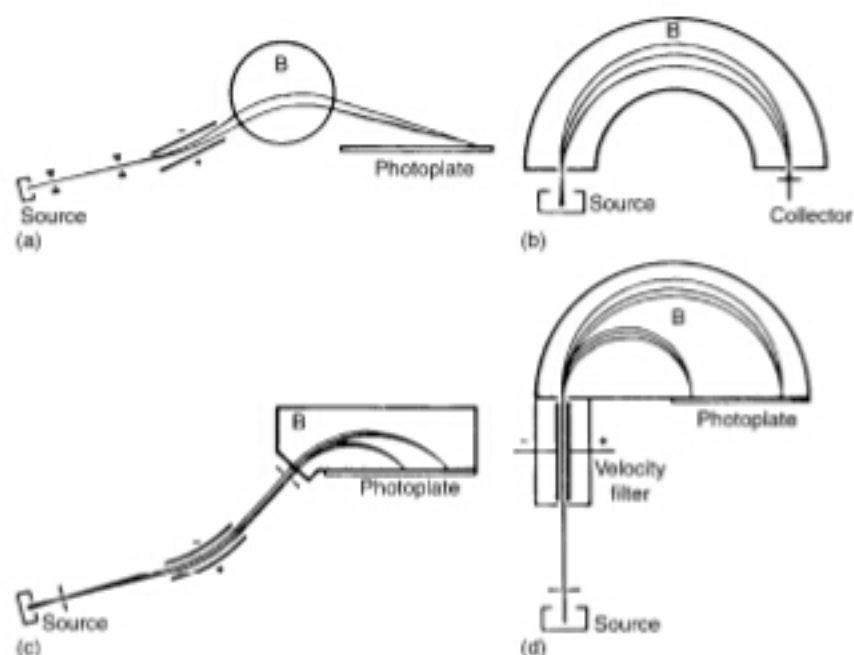


Figure 9.16 Early mass spectrometer designs. (a) Aston, 1919; (b) Dempster, 1918; (c) Mattauch-Herzog, 1935; (d) Bainbridge, 1933. In each case, B signifies the magnetic field. Spectrometers (c) and (d) are dispersive mass spectrometers; (c) the Mattauch-Herzog design is also a double sector instrument, using an electric sector before the magnetic field.

A single-focusing instrument such as the system shown in Fig. 9.16(b) has the disadvantage that ions emerging from the ion source do not all have exactly the same velocity. This is due to several factors. The ions are formed from molecules that have a Boltzmann distribution of energies to begin with. The ion source has small variations in its electric field gradient, causing ions formed in different regions of the source to experience different acceleration. Also, when fragmentation occurs, kinetic energy is released. This results in a distribution of velocities and adversely affects the resolution of the instrument by broadening the signal at the detector.

However, ions in a radial electrostatic field also follow a circular trajectory. The electrostatic field is an *electric sector* and separates ions by kinetic energy, not by mass (Fig. 9.17). The ion beam from the source can be made much more homogeneous with respect to velocities of the ions if the beam is passed through an electric sector before being sent to the mass analyzer. The electric sector acts as an energy filter; only ions with a very narrow kinetic energy distribution will pass through.

Most magnetic sector instruments today combine both an electric sector and a magnetic sector. Such instruments are called double-focusing mass spectrometers. One common commercial double-focusing design is the Nier–Johnson design (Fig. 9.18), introduced in 1953; a second common design using two sectors is the Mattauch–Herzog dispersive design, shown in Fig. 9.16(c).

Mass ranges for magnetic sector instruments are in the m/z 1–1400 range for single-focusing instruments and m/z 5000–10,000 for double-focusing instruments. Very high mass resolution, up to 100,000, is possible using double-focusing instruments.

9.2.3.2. Time of Flight (TOF) Analyzer

A TOF analyzer does not use an external force to separate ions of different m/z values. Instead, pulses of ions are accelerated into an evacuated field free region called a drift tube. If all ions have the same kinetic energy, then the velocity of an ion depends on its mass-to-charge ratio, or on its mass, if all ions have the same charge. Lighter ions will travel faster along the drift tube than heavier ions and are detected first. The process is shown schematically in Fig. 9.19.

A schematic TOF mass spectrometer is shown in Fig. 9.20. The drift tube in a TOF system is approximately 1–2 m in length. Pulses of ions are produced from the sample using pulses of electrons, secondary ions, or laser pulses (e.g., MALDI). Ion pulses are produced with frequencies of 10–50 kHz. The ions are accelerated into the drift tube by a pulsed electric field, called the ion-extraction field, because it extracts (or draws out) ions into the field-free region. Accelerating voltages up to 30 kV and extraction pulse frequencies of 5–20 kHz are used.

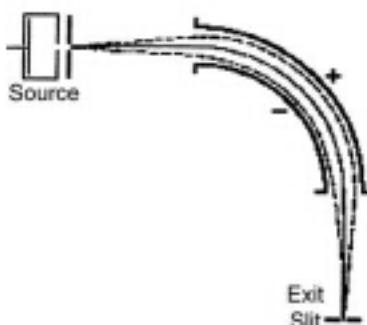


Figure 9.17 A cylindrical electrostatic-sector energy filter. (From Ewing, used with permission.)

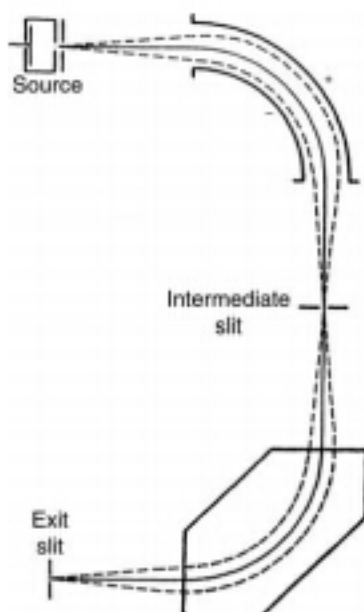


Figure 9.18 A Nier-Johnson double focus mass spectrometer. (From Ewing, used with permission.)

Ions are separated in the drift tube according to their velocities. The velocity of an ion, v , can be expressed as:

$$v = \sqrt{\frac{2zV}{m}} \quad (9.10)$$

where V is the accelerating voltage. If L is the length of the field-free drift tube and t is the time from acceleration to detection of the ion (i.e., the flight time of the ion in the tube),

$$v = \frac{L}{t} \quad (9.11)$$

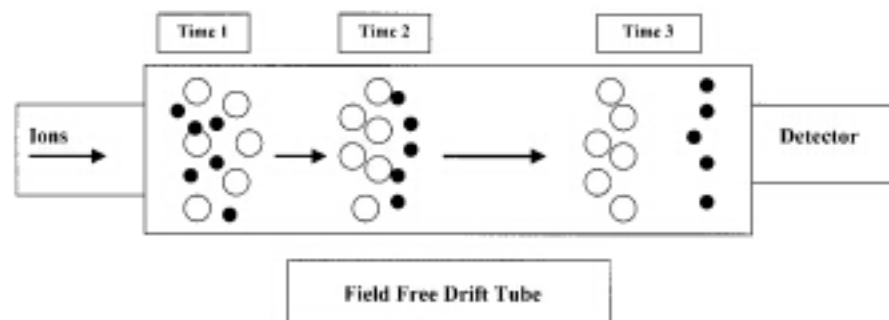


Figure 9.19 A pulse of ions of two different m/z values enters the field free drift tube of a TOF mass spectrometer at time 1. The large white circles have $m/z >$ than the small dark circles. As they travel down the tube, the lighter ions move faster, and by time 3, have been separated from the heavier ions.

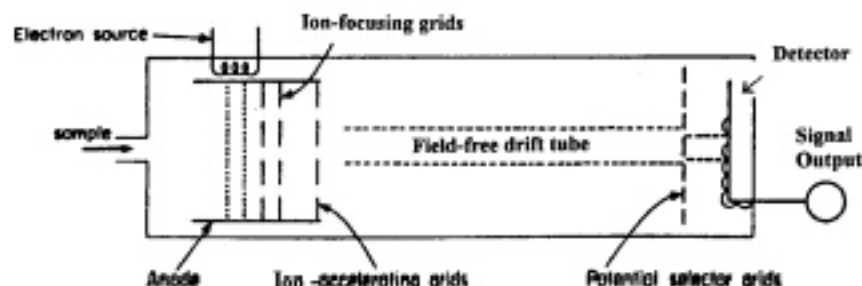


Figure 9.20 Schematic TOF mass spectrometer.

and the equation that describes ion separation is:

$$\frac{m}{z} = \frac{2Vt^2}{L^2} \quad (9.12)$$

The flight time, t , of an ion is:

$$t = L\sqrt{\frac{m}{2zV}} \quad (9.13)$$

Eq. (9.13) can be used to calculate the difference in flight time between ions of two different masses. Actual time separations of adjacent masses can be as short as a few nanoseconds, with typical flight times in microseconds.

TOF instruments were first developed in the 1950s, but fell out of use because of the inherent low resolution of the straight drift tube design (as in Fig. 9.20). The drift tube length and flight time are fixed, so resolution depends on the accelerating pulse. Ion pulses must be kept short to avoid overlap of one pulse with the next, which would cause mass overlap and decrease resolution. Interest in TOF instruments resurfaced in the 1990s with the introduction of MALDI and rapid data acquisition methods. The simultaneous transmission of all ions and the rapid flight time means that the detector can capture the entire mass spectral range almost instantaneously.

The resolution of a TOF analyzer can be enhanced by the use of an ion mirror, called a **reflectron**. The reflectron is used to reverse the direction in which the ions are traveling and to energy-focus the ions to improve resolution. The reflectron's electrostatic field allows faster ions to penetrate more deeply than slower ions of the same m/z value. The faster ions follow a longer path before they are turned around, so that ions with the same m/z value but differing velocities end up traveling exactly the same distance and arrive at the detector together. The use of a curved field reflectron permits the focusing of ions over a broad mass range to collect an entire mass spectrum from a single laser shot. In a reflectron TOF, the ion source and the detector are at the same end of the spectrometer; the reflectron is at the opposite end from the ion source. The ions traverse the drift tube twice, moving from the ion source to the reflectron and then back to the detector. A schematic of a commercial reflectron TOF mass analyzer is shown in Fig. 9.21.

The mass range of commercial TOF instruments is up to 10,000 Da. Resolution depends on the type of TOF and ranges from 1000 for instruments designed as dedicated detectors for GC (GC-TOFMS) to 20,000 for reflectron instruments. One limitation to the use of a conventional reflectron instrument is a loss in sensitivity; about 10% of the ions are lost with a conventional wire grid reflectron.