M.Sc Inorganic Chemistry (Special-III) Elective Paper-1

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Course Title: Spectral Techniques in Inorganic Chemistry

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Common soft ionization techniques

- ElectroSpray Ionization (ESI)
- Desorption ESI (DESI, for solids)
- Matrix-Assisted Laser Desorption Ionization (MALDI) and
- Direct Analysis in Real Time (DART)

Note that ESI-MS even allows structural information relevant to solution phases to be obtained.

Among these soft ionization techniques, ESI method is routinely used, and will be discussed in detail.

ElectroSpray Ionization (ESI) technique

ElectroSpray Ionization can suppress fragmentation of molecules when they are ionized.

A solution that contains the species of interest is pumped rapidly through a stainless steel capillary needle, which is held at several kilovolts with respect to an electrode surrounding the needle.

The resulting charged spray is a very fine liquid aerosol, which then passes through a desolvating capillary, where evaporation of the solvent takes place.

The solution used is often water mixed with volatile organic solvents to promote evaporation, and other solvents that increase electrical conductivity and therefore decrease the initial droplet size.

Hard ionization technique

Techniques that fall into the hard ionization category include Electron Impact (EI), in which the gaseous sample interacts directly with a collimated beam of electrons (typically ca. 70 eV) to strip off an electron to leave the radical cation $M^{\cdot +}$ (usually called the molecular ion), which then breaks down into a mixture of neutral and positively charged fragments.

Alternatively, the sample molecule could capture an electron to give negatively charged ions.

In a softer variation of the technique, chemical ionization, the ionization of the sample is achieved via collision with ions of a reagent gas (often obtained by EI) instead of direct interaction with electrons.

EI sources are convenient to use and produce high ion currents, which results in high sensitivity. Although the technique is not good at determining accurate molecular mass, the large number of fragmentation peaks makes unambiguous sample identification much more likely.

For this reason, this technique is one of the main ones used to populate chemical fragmentation databases that are subsequently used in compound identification screening.

Mass analyzers

The role of the mass analyzer is to separate the complex mixture of ions generated by the ion source according to their mass-to-charge ratios. This is invariably achieved using an oscillating electric field.

Double-focusing mass analyzer

Double-focusing mass analyser accelerates (see Figure in next slide) the ions through a potential V of some thousands of volts and then passes the stream through two analyzers, one electrostatic and one magnetic, which bend the ion trajectories into circular paths of radius r.

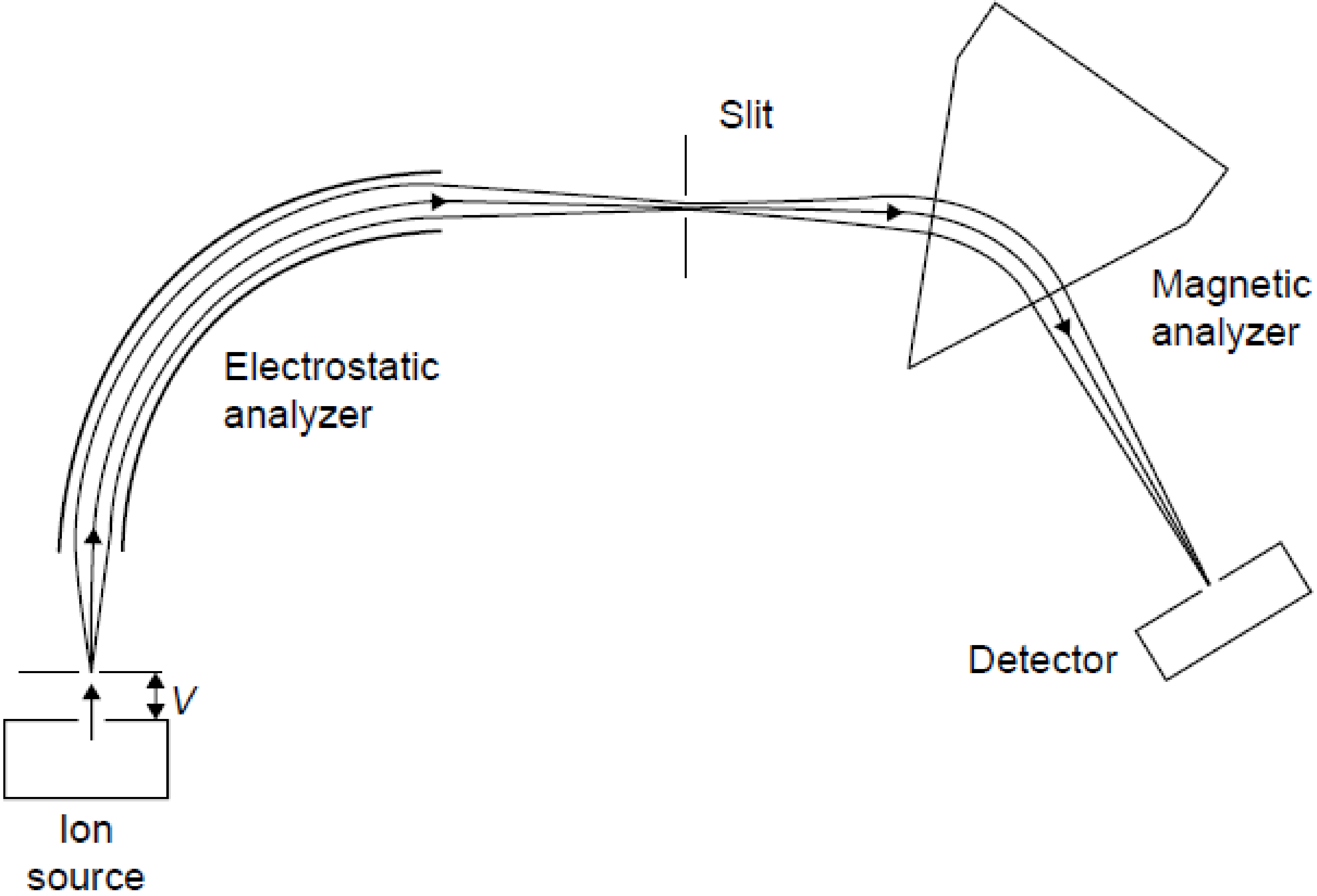

Figure: Schematic diagram of a double-focusing mass spectrometer.

If the electrostatic analyzer is positioned before the magnetic analyzer then the instrument is described as having a ‘forward geometry’; a reverse geometry’ instrument is one in which the ordering of the analyzers has been switched.

The electrostatic analyzer has the effect of limiting the range of kinetic energies of the ion mixture reaching the magnetic sector, since ions with too high or too low kinetic energies will strike the analyzer plates and not pass through.

After passing through a focusing slit, the ion stream enters a magnetic field, B, where the radius of their path on their way to the detector can be described by the equation

$$r^2 = \frac{2Vm}{B^2 q}$$

where $q = z \times e$, i.e. the ionic charge z multiplied by the elementary charge e. Systematically varying the magnetic field and/or the accelerating voltage therefore influences the direction of the departing ions, so those that share similar m/z ratios are focused on the detector in turn.

The detector is typically an electron multiplier or a Daly detector, which creates cascades of electrons (i.e. a current) in numbers directly proportional to the number of ions that strike it. The resulting spectrum is simply a plot of ion current against mass-to-charge ratio.

Time-Of-Flight (TOF) analyzer

In this analyzer the ion stream is accelerated by an electric field through a linear flight tube. All ions move with almost exactly the same kinetic energy, but as the velocities of the different ions are dictated by *m/z* they can be recorded individually as a function of time.

A variation on this set-up is the reflectron, or ion mirror (as shown in Figure).

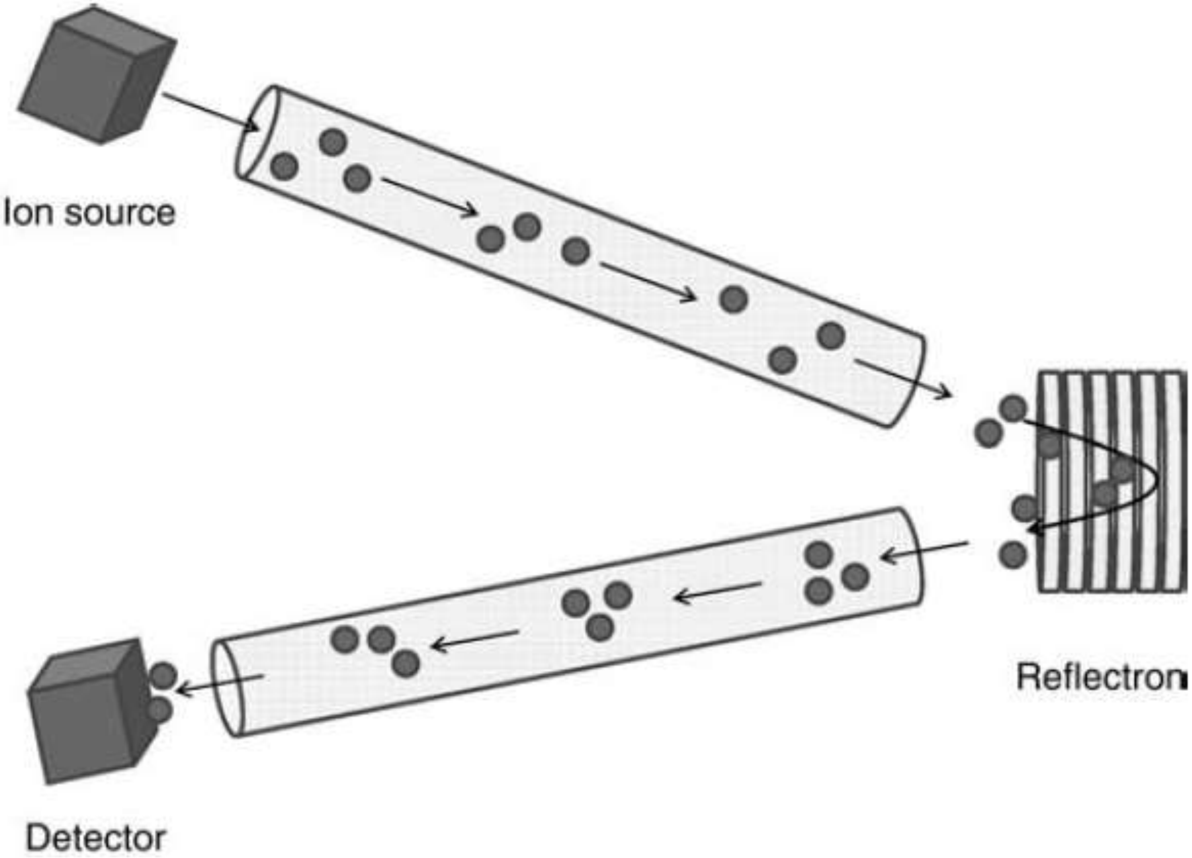

Figure: Schematic diagram of a time-of-flight reflectron mass analyzer.

Here, a series of concentric ring electrodes apply a stepwise increase in voltage, and the extent to which the ions can penetrate these rings depends on their subtle variations in kinetic energy.

The net effect of the reflectron is to bring the slow- and fast-moving ions with the same values of *m/z* together, so that when they are reflected back to the detector, which is located at a distance twice that achieved in a standard TOF analyzer, they are registered together.

Time resolution is really critical for this mass analyzer, so it has benefited from improvements in electronics and fast time-resolved digital data collection systems.

Channel-plate detectors also offer superior time resolution over the more traditional electron multiplier setup.

TOF was first put forward commercially in the 1960s, and has recently enjoyed a resurgence in interest, largely due to the development of new pulsed laser ionization sources (such as MALDI) that promote vaporization with minimal fragmentation.