**Electronics And Instrumentation**

**8th Semester**

**Subject: Analytical Instrumentation**
**Subject code: BT 808**

**Unit-4**

**Mass Spectrometers**

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## 4. Ion Generation

### 4.1 Thermal Ionization

Thermal ionization is a technique for elemental analysis that uses thermal energy to ionize elements. The sample is deposited on a ribbon which can be heated to very high temperature, and a second ribbon a few millimeters from the first is used to ionize the atoms in the gas phase. This ribbon is made from rhenium or tungsten, sometimes treated with carbon or thorium, depending on the nature of the element under investigation. Heavy metals such as lead, uranium, thorium, and others have been determined as positive ions in very different matrices such **as** geological samples, microelectronic chips, and ice cores from the antarctic, in conjunction with isotope dilution (IDMS) techniques. Iodine, bromine, chlorine, selenium, and **also** some heavy metals have been determined by using negative thermal ionization and IDMS. Thermal ionization with isotope dilution is considered one of the reference techniques allowing the most precise quantitative determination of elements.

### 4.2 Laser Desorption/Ionization

Lasers have been used in mass spectrometry for many years. Trace elements in biological samples can be determined by using laser microprobes (LAMMA, laser microprobe mass analyzer) or a combination of laser ablation with ICPMS. For the analysis of bulk materials, techniques such as resonance ionization mass spectrometry (RIMS) and laser ablation MS (LAMS) are employed. The desorption of organic substances from surfaces without destruction is difficult and the duration of ion production is short. Therefore, the mass limitation of this approach without a matrix is around 1000 amu. Recently, molecular ions of complete proteins with $M_r > 200\,000$ have been generated, which is mainly due to the use of appropriate matrices for matrix-assisted laser desorption/ionization. For sample preparation, the analytes are dissolved and crystallized in a matrix

on a target. The matrix for the first experiment using a UV laser for protein analysis was nicotinic acid , but the search for other matrices is continuing, since the nature of the matrix seems to be crucial. A similar approach with a metal powder (10 nm diameter) mixed with a liquid matrix (glycerol) to form a colloid gave comparable results . The crucial point is the absorption of the matrix, which protects the large molecules from the laser energy. Apparently, a variety of ions and radicals are formed initially from the matrix by photoionization and, in the dense expanding plume of desorbed material, protons become attached to the analyte molecules. These ions are then extracted in the TOF analyzer. The first lasers used were UV lasers tuned to the absorption of nicotinic acid, but later it was shown that IR lasers give similar spectra . Due to the pulsed ion generation, TOF instruments are the analyzers of choice, although recent attempts have used sector field instruments with simultaneous detectors. The signals obtained are rather broad, probably due to matrix - molecule adducts of the analytes, but the detection potential is very good. Since the accuracy of the mass measurement is ca. 1 x 1 0 ~ ’ - 5 ~ 1 0 ~y~ie,ld ing an error of ca. 100 - 500 amu at *M,* = 100 000, the precision of the technique is superior to other methods such as gel chromatography or centrifugation. Today, benchtop instruments are available with easy sample handling and short analysis times, making the technique suitable for biochemical laboratories. The development of delayed extraction has improved the resolution considerably and with post-source decay the detection of fragments has also become possible.

### 4.3 Electrospray

Electrospray was described in 1968 by DOLE and the ions were detected by ion mobility. FENN and coworkers , and, independently, ALEXANDRO eVt a readopted the idea as a means of creating ions for mass spectrometry and since then rapid development of this technique has occurred. The fundamental difference to thermospray is that the spray is formed by charging droplets to such an extent that they explode by coulomb repulsion into smaller and smaller droplets. The droplets are further decreased in size by collisions with gas and, finally, highly charged ions are liberated. The process in which ions are created from the droplets is still not clear and several partial models exist . The electrospray source is shown schematically in Figure. A capillary is held under high voltage (3 - *5* kV) at atmospheric pressure to generate a spray of charged droplets. To obtain a dry aerosol, either a heated steel capillary or a hot gas curtain is used in conjunction with collisions in the first vacuum stage. These collisions are necessary to decluster the ionic species. but may also be used to make fragments in a process equivalent to collision-induced dissociations for MS/MS experiments.

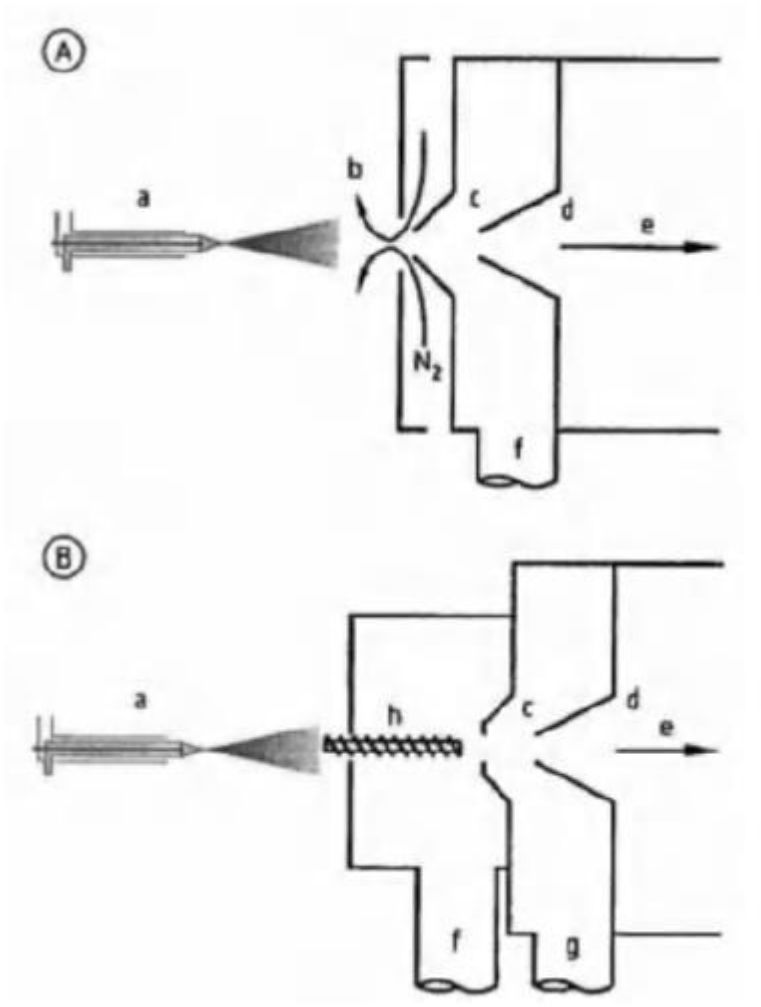


**Figure .** Electrospray ion source types **A)** Desolvation region with gas curtain; B) Desolvation region with heated capillary a) Sprayer with three concentric capillaries: the inner flow is the eluent from the separation (CZE, HPLC), the next flow is sheath liquid such **as** methanol or isopropanol to enhance desolvation, and the outer flow is sheath gas, normally **ni**trogen; **b)** Gas curtain; c) Nozzle; d) Skimmer; e) To ion optics and analyzer; f) To roughing pump; g) To turbomolecular pump; h) Heated capillary

For quadrupole mass spectrometers, the ions from the first stage are extracted and pass directly into the mass spectrometer through a skimmer. For sector field mass spectrometers, a second vacuum stage is required to minimize high-energy collisions in the acceleration region, which could destroy the ions. The main advantage of electrospray is that even molecules with very high molecular mass can be detected at low *dz* values, because the ions are highly charged (charges of up to 100 have been observed). Thus, the use of inexpensive quadrupole instruments is possible

## 5. Analyzers

### 5.1 Quadrupoles

Quadrupoles are the most successful concept from a broad range of so-called dynamic mass spectrometers. They differ from static analyzers in that they use a high-frequency voltage to disperse the ions. In a quadrupole four poles (rods) form a hyperbolic field through which the ions travel with low kinetic energies. The superposition of high frequency and a variable d.c. voltage enables the quadrupole to separate the ions according to their mass. The regions of stability and instability are shown in Figure . The coefficients *a* and *q* are derived from the Matthieu equations. They are functions of the d.c. voltage *U* and the a. c. voltage *V,* COSWF~o.r **a** fixed frequency, m is proportional to both *U* and *V,* and when the ratio *dq = 2U/V0* is held constant, the masses follow stable paths and **a** spectrum may be recorded.

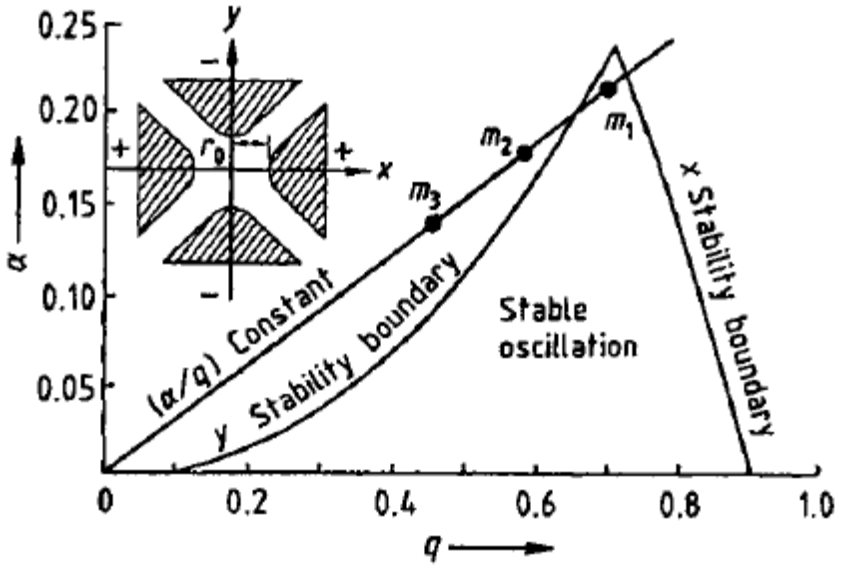


**Figure .** Quadrupole stability diagram indicating the conditions for stable and unstable oscillations

Although mathematical treatment of the separation process is complicated, the operation of such a spectrometer is simple. They have quickly become established in GUMS systems, since they can be very compact, easy to handle, and less expensive than other instruments. In addition, computer control is simple. This advantage became even more significant with the development of triple quadrupole instruments .

## 5.2 Time-of-Flight (TOF) Mass Spectrometer

A few years ago, time-of-flight instruments were used almost exclusively for surface analysis. Then, the development of plasma desorption and laser desorptiodionization changed the situation dramatically. It is now conceivable that in the future TOF analyzers may become routine analyzers. The mass analysis is based on the fact that after uniform acceleration in the ion source, small ions arrive earlier at the detector than heavy ions. This is because all particles acquire the same energy resulting in different velocities. If the acceleration voltage is *V,* the energy is eV**.** For an analyzer of length *L,* the time to travel to the detector is

$$t = \sqrt{\left(\frac{m}{z}\right)\left(\frac{1}{2eV}\right)}L$$

and, solved for *m/z*

$$\frac{m}{z} = \frac{2eVt^2}{L^2}$$

The detectors, normally multichannel arrays, are capable of resolving the resulting small differences in time. Almost every ion leaving the source can be recorded, giving TOF instruments excellent sensitivity. To enhance resolution, a reflector device can be added to the linear flight tube. This reflectron focuses the ion beam on the detector, compensating for the initial energy spread of the ions, because the faster ions penetrate more deeply into the reflector than the slower ions and thus have **a** somewhat longer path to the detector. Resolutions in the range of 5000- 10000 have been obtained and ions with *m/z* > I00000 have been recorded. Alternatively, the reflector can be used to determine the sequence of biopolymers by means of laser desorption MS. Many metastable ions dissociate after acceleration, and fragments can be generated by collisions (psd, post-source decay) . These normally arrive simultaneously with the precursor ions, since no field is present to induce separation. If the voltage of the reflectron is then changed stepwise, such ions can be separated prior to arrival at the detector since their masses are different. Recently orthogonal injection of ions into the TOF instrument was used to interface electrospray and electron impact sources, also giving excellent performance . The acquisition speed of the TOF instruments renders them excellent detectors for rapid separations, such as microCE. An impressive example has been published recently and in Figure spectra of such a combination are shown.