Electronics And Instrumentation

8th Semester

Subject: Analytical Instrumentation
Subject code: BT 808

Unit-4

Mass Spectrometers

5.3 Ion Traps

Another ion storage device in rapid development is the ion trap. Although it has long been used by physicists. it was only much later that it was converted into a powerful GC detector . In this case, only high frequencies and no magnetic field are necessary to create a cage for the ions in a closed quadrupole field. The ions are ejected several times per second from the trap, hitting the detector sequentially. The first commercial version had a limited mass range of 600 amu and low resolution, but quite convincing detection capabilities. The mass range has since been dramatically increased (up to 40 000 amu), although the resolution and particularly the mass accuracy is still fairly poor. In recent versions, an additional scan ramp is used to evaluate the ion population of the trap for optimization of the residence time. However, high-resolution experiments using electrospray have now been described [I281 and the detection capabilities have been steadily improved by optimizing the ion transfer into the trap. A modern version that is used as a detector for HPLC is shown in Figure .

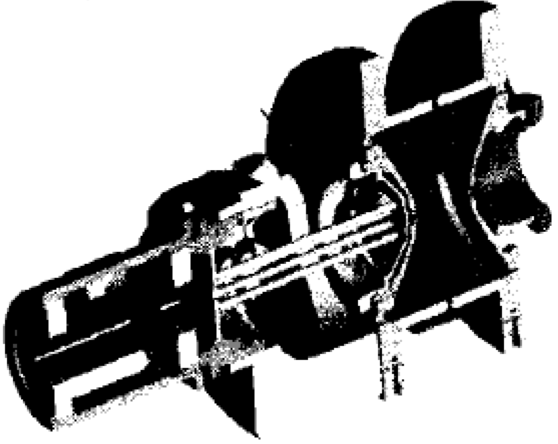

Figure . Cut view of the LCQDeca (Thermoquest)

A weak point is still quantitative reproducibility. The storage capability is limited because when many ions are stored, coulomb repulsion destroys the performance of the trap. Therefore, software has been developed to monitor the number of ions in the trap and adjust the storage time accordingly to avoid unwanted ion - molecule reactions. Ion traps are the analyzer of choice in all cases where structure elucidation is the major application and several commercial versions from different verndors are on the market today.

5.4 Isotope Mass Spectrometer

The reliable determination of isotope ratios of elements normally needs specialized instrumentation. The ion sources depend on the type of element or molecule; for many elements the thermal ionization source has been employed, but for others and for small molecules, EI can be used as well. Although conventional analyzers can be used in such instruments, for precise determination, simultaneous detection of more than one ion beam is necessary and the instruments must be optimized for this purpose. Isotope ratio mass spectrometry (IRMS) is a specialized technique designed for precise determination of isotope ratios such as 12C/13C, 'H/2H in organic compounds.
The analysis requires the separation of compounds by GC, combustion of the compound to small molecules such as CO2 and H20, ionization and accurate measurement of the signals due to the isotopically pure fragments. The analyzers allow simultaneous detection of the signals at low levels with high precision by using several Faraday cups (Fig.).

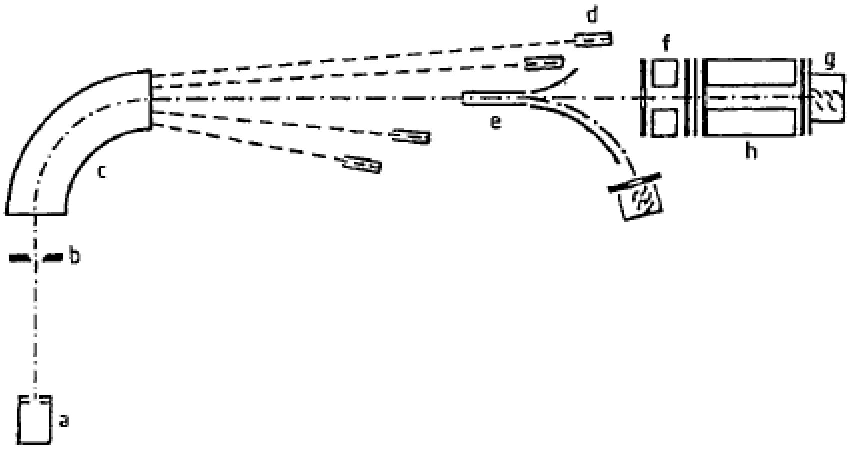

Figure . Isotope mass spectrometer with variable faraday cups and a quadrupole mass filter for MSlMS experiments where a deceleration lens is necessary between the analyzers a) Ion source; b) Aperture slit; c) Magnet; d) Variable Faraday cups; e) Center slit: fl Deceleration lenses; g) Counter-SEM; h) Quadrupole mass filter

With such instruments, an abundance sensitivity greater than lo-' was obtained for 230Th/232Thr atios .To obtain the highest precision, further precautions must be taken with sample handling, instrumental parameters, and electronics to minimize the noise levels. This makes the procedure highly complicated, and only a few laboratories in the world are able to perform such precise measurements. An example **is** the correction of the Avogadro number, based on isotope mass spectrometry with silicon isotopes.

5.5 Accelerator Mass Spectrometry(AMS)

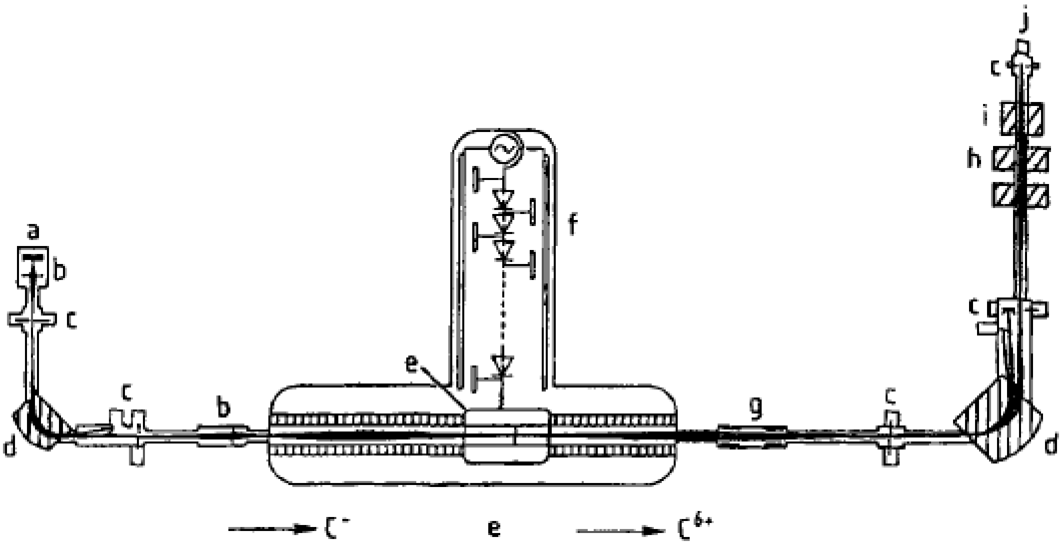

Figure. Accelerator mass spectrometry a) Ion source; b) Lens: c) Slits: **d)** Beam bending magnet; e) Stripper foil charged to 2.5~10' V; f) High voltage source; g) Electrostatic lens; h) Magnetic lens; i) Velocity filter; j) Ion detector)

Accelerator mass spectrometry (Fig.) is designed for the most precise atom counting of cosmogenic radionuclides such as "'Be, *I4C,* "A1, Si, and %I. It can measure these elements with unparalleled detection power in, for example, polar ice cores, deep sea sediments, or wood. The nuclide I4C is used in the geosciences for dating of organic matter. The ions from the source (different sources may be used) are selected with a 90" magnet, accelerated toward the stripper foil, and converted into highly charged positive ions. These ions are focused again into a magnetic sector and detected within a gas-filled chamber by means of secondary ions produced there. The differentiation of, for example, I4C6+ and N7+ is possible, since both species penetrate into the chamber with a different depth. The detector is designed to identify species of nearly the same mass and velocity but different charges with very high selectivity

6. MS/MS Instrumentation

The combination of two or more analyzers, commonly known as MS/MS or tandem mass spectrometry, is a highly specific means of separating mixtures, studying fragmentation processes, and analyzing gas-phase reactions. The field is reviewed thoroughly in With the first analyzer, one ion is isolated from all the others. In the next, reactions of that ion are studied further. Fragments may be formed in unimolecular reactions from metastable ions, but generally fragmentation is induced by a variety of means. Collisions with gases in a collision chamber (CAD: collisionactivated decomposition), laser photodissociation can be employed to induce fission. Since MS/MS can be combined with chromatographic separation techniques, it has found a broad range of applications in analytical chemistry. Indeed, LC/MS interfaces such as thermospray or the API techniques depend largely on collision-induced dissociations and MSNS. Since they produce only molecular ions, little structural information is provided. With CAD and MUMS these details are obtainable. A recent review gives a fairly detailed discussion of the thermochemical aspects of the various fragmentation induction methods used in mass spectrometry .

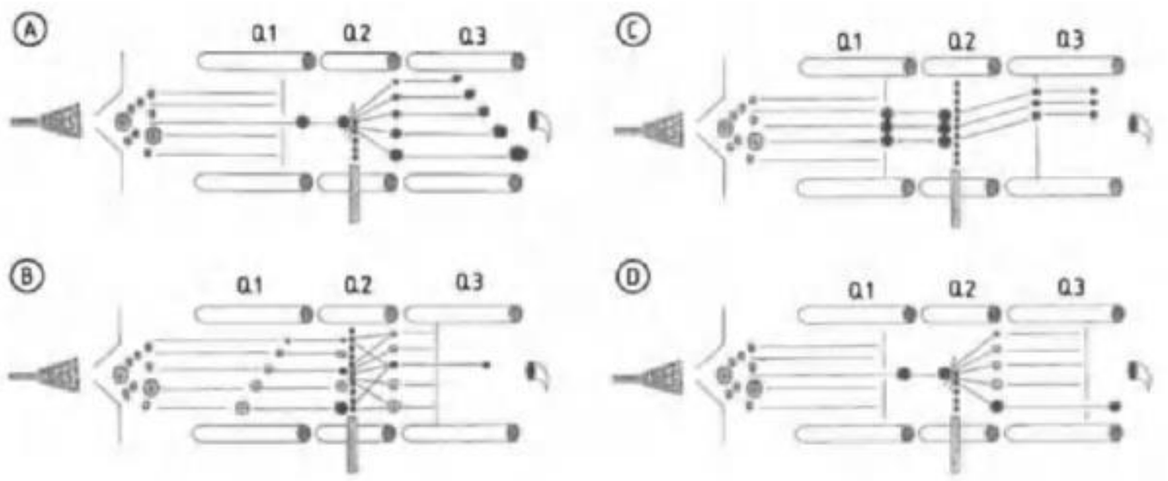

Figure . MS/MS experiments with the triple quadrupole MS A) Daughter scan; B) Parent scan; C) Neutral loss scan; D) Reaction monitoring QI, Q3: mass analyzers; Q2: collision cel

6.1 Triple Quadrupoles

Triple quadrupoles for analytical MSMS experiments have been built since the pioneering work of YOST and **ENKE** in 1978 and they have found applications in all areas of mass spectrometry. The first and the third quadrupole are MS-1 and MS-2, whereas the second in the middle is an RF-only quadrupole acting as collision cell. In the collision cell, the transmitted ions undergo low energy collisions with a gas. For the product ion scan (daughter scan), only one precursor (parent) is selected and the second analyzer scans for the product ions. For the precursor scan, the first quadrupole is scanned and only the selected product ion is recorded. In the neutral loss scan, both analyzers are scanned with the selected mass difference, and for reaction monitoring only one precursor and one product ion species is permitted to travel through MS-I and MS-2, respectively. In the meantime, instruments with different collision regions have been built. It was surprising that fragments are formed under the low energy regime in the collision cell. The fragment ion reactions are similar to those from high-energy collisions; exceptions include side-chain reactions of amino acids in peptides. The collision efficiency is quite high, particularly when the collision cell is an RFonly quadrupole or octapole with nearly 100% transmission. The resolution of both quadrupoles as MS-1 and MS-2 can be set independently allowing, for example, unit resolution for precursor and product ions. Many different experiments with scan functions similar to the linked scans have been made and the set up and computer control is quite straightforward. Above figure shows schematically the widely used MS/MS experiments. The triple quadrupole is the most common MSMS instrument today.