Electronics And Instrumentation

8th Semester

Subject: Analytical Instrumentation
Subject code: BT 808

Unit-4

Mass Spectrometers

1. Introduction

A mass spectrometer can be defined as any instrument capable of producing ions from neutral species and which provides a means of determining the mass of those ions, based on the mass-to-charge ratio *(dz*w,h ere **2** is the number of elemental charges) and/or the number of ions. Therefore, a mass spectrometer has an ion source, an analyzer, and a detector. All further details are largely dependent on the purpose of the mass spectrometric experiment. Historically, mass spectroscopy was developed to separate atoms and to determine the masses of isotopes accurately . The predecessor of magnetic sector field mass spectrometers was built in 1918 by DEMPSTER. Later, some of the first instruments for the analysis of molecules were used by analytical chemists in refineries to determine hydrocarbons (the first article in the first issue of the journal *Analytical Chemistry* dealt with mass spectrometry of **a** mixture of hydrocarbons). Combinations of infrared and mass spectroscopy were reported shortly afterwards **.**

Today, mass spectrometers may be used to determine the isotopic distribution of an element, the elemental or molecular composition of a sample, or the structure of a compound or its molecular mass. They also make it possible to study the kinetics and thermodynamics of gasphase processes or the interactions at phase boundaries. Mass spectrometers can also serve to accurately determine physical laws and natural constants. In recent years, mass spectrometry has become one of the key technologies in proteome and genome research because of the rapid development of new components-from the ion sources to the detector- and inter gration into the World Wide Web has also helped to make this possible.

2. General Techniques and Definitions

2.1 Resolution

Generally, resolution is defined by $R = m/Am$, where m is the mass under consideration. This can be separated from a mass $m + Am$, assuming a peak overlap of 10 %. The equation can be used either to calculate the resolution

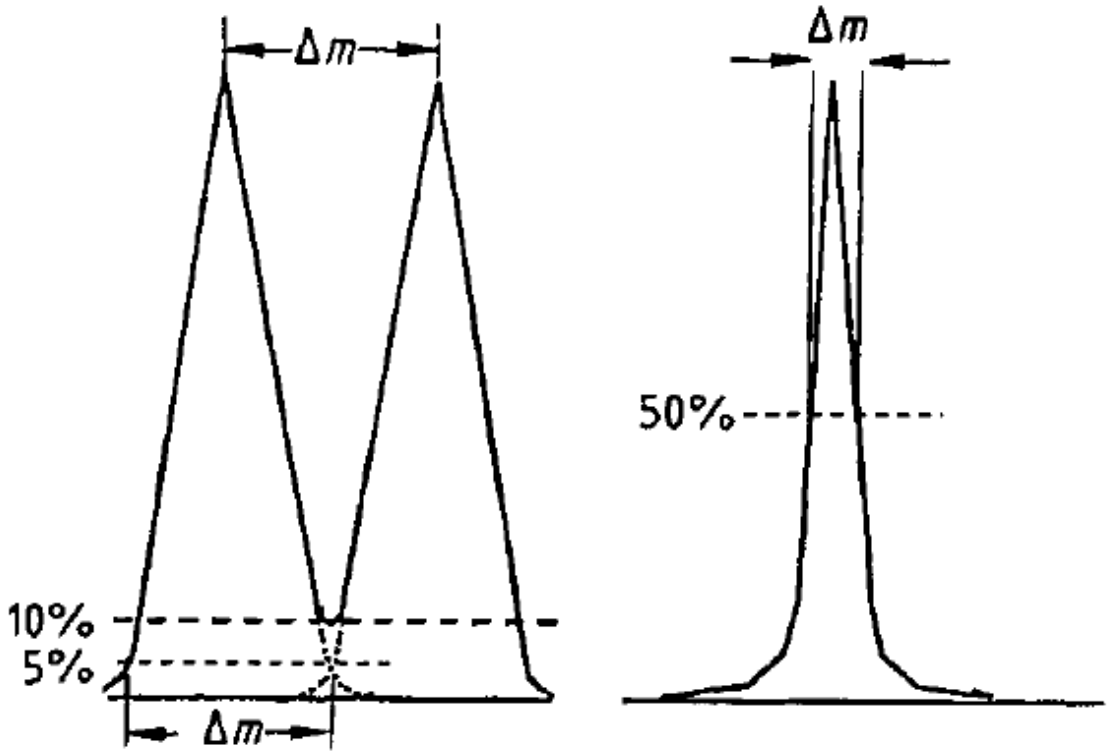

Figure . Resolution of two peaks, defined for the 10 % height of the valley, for one signal at the *5* % (sector field MS), or the 50% (all others) height

of two signals in a spec trum or to calculate the resolution necessary to separate two species of different elemental composition.For example, consider **C7HI6** and C6H120. The mass difference at *dz*= 100 is 0.0364 amu. Thus, a resolution of ca. 3000 is required to resolve the two signals. The same result **is** obtained when the peak width at 5 % overlap is used for the calculation. **A** different definition uses the peak width at half height as ***Am*** (50% definition) for the calculation (see Fig.). This approach is used often for Fourier transform mass spectroscopy (FTMS) and time-of-flight (TOF) instruments. In modern mass spectrometers, the resolution is calculated directly by the computer from the

peak width. More information can be extracted if the elemental composition of fragments or molecular ions can be determined. For this purpose two different requirements have to be fulfilled. First, the signal must be homogeneous, i.e., even isobaric ionic species have to be separated (resolved) and, secondly, the accuracy of the mass measurement has to be sufficient to allow a calculation with small errors.

High Resolution.

The separation of isobaric ionic species (i.e., high resolution, with *R*> lOOOO), is a relative requirement. It depends on various factors, such as the type of heteroatoms, but with *R* = 10 000 most common species can be resolved. Exceptions can be ions containing, e.g., sulfur. Increasing the resolution requires reducing the width of the ion beam in the mass spectrometer. Thus, in theory, the height of the signal is inversely proportional to the resolution. In reality, this relation is not linear over the full range of possible resolutions, and generally the loss of peak height becomes much greater when the resolution is increased above 10000. Merely instruments like the ion trap (with very large molecules) or especially the FT mass spectrometers are capable of achieving resolution exceeding I *05*, even up to lo6 under optimal circumstances without deterioration in detection power. The scan speed and the scan width may be affected. Thus, for applications in analytical problem solving, the resolution should be set as high as necessary yet as low as possible.

Accurate Mass Measurements.

For accurate mass measurements a signal containing sufficient ions must be recorded on a precisely calibrated mass scale. In the past this was a cumbersome undertaking because each peak had to be determined separately by comparison to a known reference signal. The accelerating voltage *U,*, was changed by the amount necessary to shift the signal of the mass ***m,*** to the position of the reference ***mo*** on the monitor. This can be performed very accurately by switching between the two voltages *Uo* and *U,* (for the unknown). Since *U, mo* = ***Uxmx, m,*** can be calculated from ***m,*** = ***mo*** . *(UdUJ.* This technique, known as peak matching, is still the most precise method, and today computerized versions are available. Techniques were then developed that allow accurate mass measurement of many signals in a spectrum simultaneously. **A** reference compound such as perfluorokerosene (PFK) is introduced into the ion source together with the analyte in such a concentration that signals of both can be acquired simultaneously. The reference compound is chosen so that its signals are easilyresolved from those of the analyte. The computer then searches for the reference signals in the spectrum, interpolates between them, and calculates the

correct position of the unknowns on the mass scale. Sufficient precision can be achieved to allow the calculation of possible elemental compositions for the signal, provided the number of ions is sufficient. It has been shown that the number of ions ***N*** required to define the peak position is a function of resolution *R*, where ***0*** is the standard deviation of the mass measurement in parts per million

$$N = \frac{1}{24}\left(\frac{10^6}{R\sigma}\right)^2$$

Thus, to obtain an accuracy of 2 ppm, the number of ions required for *R*= 10000 is ***N*** **=** 105, but for *R=5000,* ***N=420.*** **As** long as the reduction of signal intensity with increasing resolution is linear, higher resolution can be beneficial, because fewer ions are required for a given accuracy. However, if the intensity of the signal is also of relevance (e.g., for quantitative determinations) more ions must be detected. Thus, in this case the optimal resolution may be lower to allow better detection power.

3. Sample Inlets and Interfaces

3.1 Direct Probe

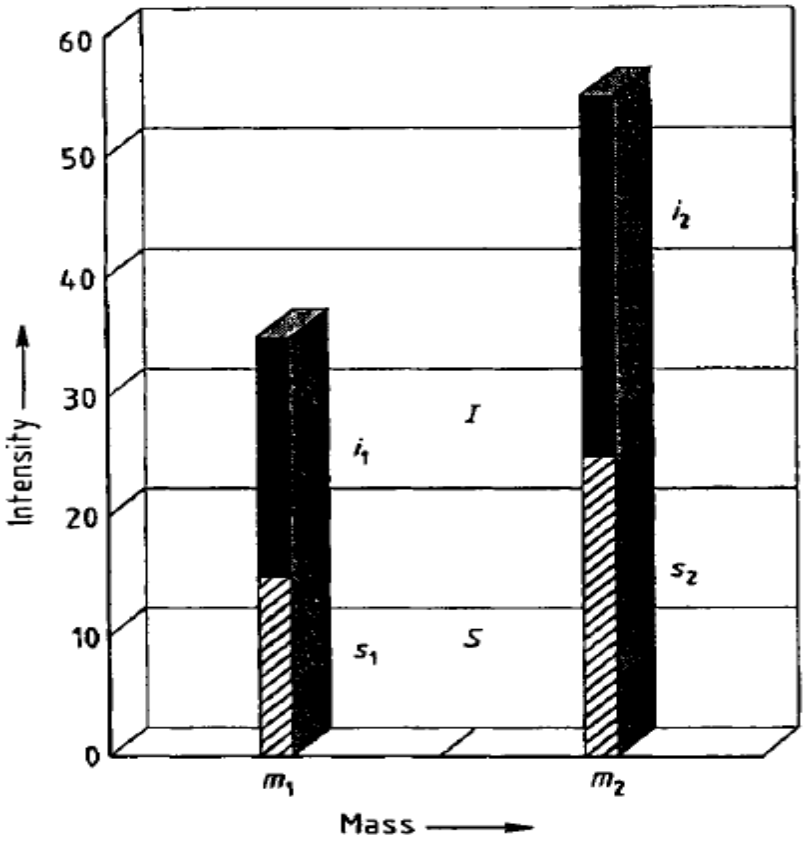

Figure . Isotope dilution

For many years the direct probe for introducing samples into the spectrometer has dominated all the others. The sample **is** transferred into a small cup with a volume of a few microliters, made of gold, silica, or aluminum. Some of them have a cap with a small hole to exploit the Knudsen effect for controlled evaporation. The cup is placed in the tip of the removable probe. The probe is introduced into the ion source housing with the sample cup inside the ion volume without interfering with the electron beam. It can be heated and cooled directly under computer control, when necessary as a function of the total ion current or of a single ion current.

3.2 Batch Inlets

Batch inlets used to be important for the analysis of gases, volatile liquids, and mixtures such as hydrocarbons in oil samples. The inlet consists of a capillary, which connects a heated reservoir with a volume of several hundred milliliters, normally glass-lined to prevent cracking and pyrolysis, to the ion source. The capillary acts as a throttle, controlling the flow into the ion source; alternatively, a diaphragm can be used. The sample is introduced in the reservoir through a septum by means of a syringe or via a small sample inlet connected to the reservoir. This type of inlet has been largely replaced by GClMS interfaces.

3.3. Pyrolysis

Pyrolysis is a powerful tool for the analysis of very high molecular mass samples, where there is no possibility for separating mixtures and determining the components or where the compounds are too complex to give mass spectra . Examples are the attempts to characterize different fractions of humic acids, strains of bacteria, and unusual components in intact DNA of a variety of animals. In all such cases, mixtures of smaller molecules are prepared by carefully controlled pyrolysis (e.g., Curie point pyrolysis). The distribution of the resulting mixture of thermally stable compounds is characteristic of the starting material. Since the identity of the pyrolytic decomposition products is not known in most instances and the chemistry involved is complex, only the appearance of the particular distribution is significant, and techniques for cluster analysis based on pattern recognition must be used. Field desorption, field ionization, direct chemical ionization, and low-energy EI are mainly used with pyrolysis, because molecular ions are mostly formed and the pattern is not further complicated by fragmentation in the ion source. The desorption process in FDMS can be considered a pyrolysis technique. Often, the pyrolysis products are injected into a GC, separated, and soft ionization techniques such as FIMS, low energy EI, or photoionization are used to detect the components of the mixture.