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A Concise Review on Time of Flight (TOF) Mass Spectrum

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Abstract:

Time of Flight Mass Spectrum is a method of mass spectrometer depending on the time which has been taking to reach the detector (usually located between 1 to 2 min from the source to separate ions) where the Sample is taken and mixed with matrix {the matrix is made up by chemical compound (2,4 Benzoic acid and cinamic acid) and they act as chemical cross link to produce matrix}. The energy source of this procedure is laser. Never the less, the ratio between sample and the matrix is 1:10,000 in order to prevent hampering the. However, TOF has some advantages such as unlimited upper (mass /charge) values to be detect, high resolution, good definition of narrow chromatographic peaks , good sensitivity and high quality spectra, High accurate mass measurement to the nearest 0.1 millimass unit for determining the elemental composition for ions less than 500 Da and It can perform tandem MS. Never the less, it has some drawbacks as requiring higher vacuum, Resolution changes with m/z value and high cost equipment. We conclude from this paper that: TOF is considered as one of the best mass filters because of unlimited upper (mass / charge) values to be detected as well as the capability of acquiring rapidly for averaging and good definition of narrow chromatographic peaks.

Keywords: Instrumental analysis, TOF, Detectors and acceleration

1. Introduction

The concept of time of flight analyser was appearing in American physical society program by Stephens in 1946, while the design of a linear TOF was published in 1955 by Wiley and McLaren which later became the first commercial instrument. There has been renewed in these instruments in 1980s. Time of Flight Mass Spectrum is a method of mass spectrometer depending on the time which it took to reach the detector usually located 1 to 2 m from the source to separate ions. Ions are accelerated by using a known strength electric field and due to this acceleration, each ion has the same charge will has the same kinetic energy.

The speed of the ion is depending on the ratio of mass to charge. After pulsing ions from the ion source, they will travel the same distance through the flight tube but with different velocity depending on their (mass / charge) ratio, which mean, the ions with the smaller ratio of (mass / charge) will take the shorter time to reach the detector, while ions with larger ratio of (mass / charge) will take a longer time to reach the detector. Flight tube indicates positive and negative electrodes in order to enforce ions to move in toward direction. The ions are pulsed from the source at the same time and have the same kinetic energy. (Hoffmann and Stroobant, 2003).

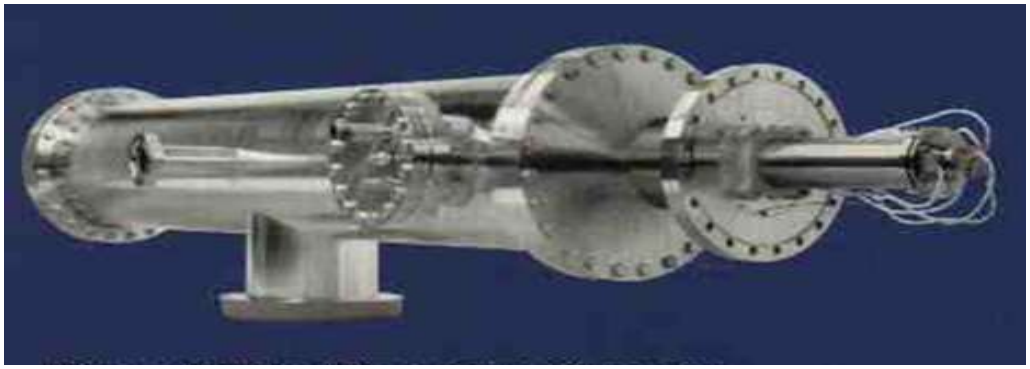

Figure (1): shows TOF mass spectrometer

Theory

The potential energy of ion in an electric field is related to the strength of the field and the charge on the ion $Ep = z\,U$ (1)

Where Ep is the potential energy, z is the charge and U is the voltage.

When ion is accelerated into the flight tube by the electric field (U , the potential energy is converted to kinetic energy ,which mean potential energy (Ep) is equal to kinetic energy (Ek)

Ep = Ek that is lead to Ek = z U (2)

It is known that Ek =1/2 mv2, replacing the value of Ek in equation (2) to be 1/2 mv2 = z U (3)

Where m is the mass, v is velocity (the amount of distance travel over time).

The velocity of the acceleration ion will not change because ion moves in a field-free time of flight tube.

The distance which the ion will cross is known (the length of the tube).

The time of the flight ion can be measured

v = d/t (4)

Where v = velocity, d = distance and t = time

z U = 1/2 m (d/t)2 (5)

by substituting the value of v in equation (3)).

By rearranging equation (5), the flight time will expressed as

t2 = d2 m /2Uz = (d2/2U) x (m/z) (6)

We can consider d2/2U as a constant, the equation (6) will be t2= K (m/z) → t2 α m/z

The ratio of mass to charge varies with the time of flight square which mean the separation of ions depending on time.

As can be seen from the above explanation of TOF, there is no theoretical limit to the upper (m/z)

value that can be detect which make MALDI as the most suitable ion source to use with TOF.

Matrix assisted laser desorption ionisation (MALDI)

Principle \ generate molecular ions

Sample is taken and mixed with matrix {the matrix is made up by chemical compound (2,4 Benzoic acid and cinamic acid) they act as chemical cross link to produce matrix}.

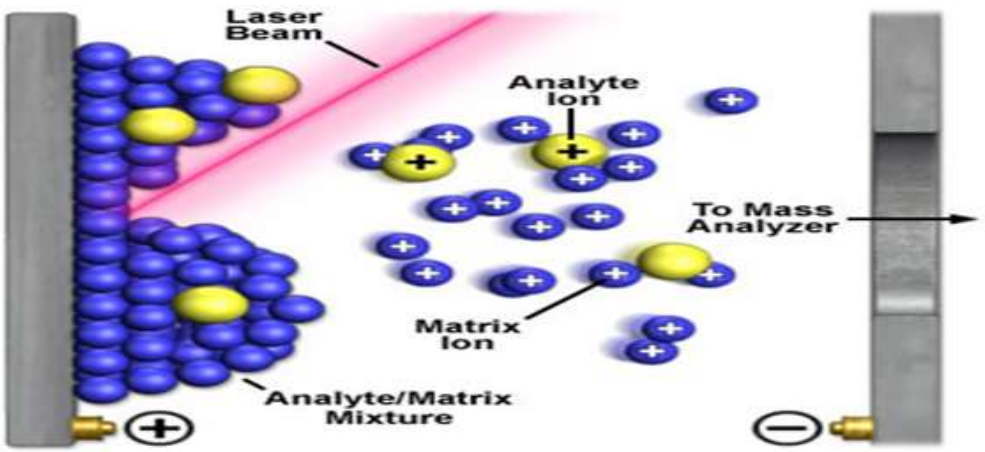

Figure (2): demonstrates MALDI's procedure

The matrix at the beginning is liquid and after adding the sample it should be allowed to be solidify to produce sample with matrix (sample trap in matrix).

Benzoic acid and ceramic acid have aromatic ring which absorb energy (this step is sample preparation step). The energy source of this procedure is laser.

The ratio between sample and the matrix is 1:10,000 which mean that the matrix will take 10,000 times than the sample in order to prevent hampering the sample because of laser.A sample plate is used to hold the matrix and the analyte molecules.The matrix is got the energy from the laser and transmit it to the sample (the sample is not directly hutted by laser in order to protect it from distraction). The sample is kicked out after taking the energy from the matrix because they are charged (they are disrobed from the matrix). (Neville, et al, 2011)

After that, the sample become excited then it generate molecular ions. Next, the sample evaporate from the plate, then the ionised molecules are forced travelling down the flight tube by voltage potential energy. The ionised molecules will being separated according to their molecular mass. Ionised molecules with smaller molecular weight will travel down the tube faster than larger molecules. The mass /charge ratio of each molecule is determined by a detector and used to identify the different components of a sample by measuring the time which ion is taking to reach the detector (the ion is accelerated by an electric field). The result is an output of a spectrum that will give the average molecular weight for the sample analyzed. After pulsing ions into time of flight tube ions with the same energy but having different mass will travel with different velocity.

Delayed extraction

To improve the mass resolution in axial MALDI-TOF, it has to allow the initial burst of ion and the neutrals which have been introduced laser pulse to equilibrate and travel the same distance vertically to the same plate before acceleration ions inside the flight tube. During the ionisation, most of ions start moving from the surface with same velocity. To improve the resolution and to compensate the spread velocity, delay extraction of ions from ion source toward the tube by a few nano second was introduced. Delayed extraction is based on compensation for the initial momentum of the ions. (Rousu, Herttuainen, Tolonen, 2010)

By other words, it provide the same arrival time to the detector for ions which have the same ratio (m/z) but with different initial velocity. The lower momentum ions in the direction of extraction are accelerated at higher potential energy because they are further from the extraction plate when the extraction field turned on.

On the other hand, the ions that have greater momentum start accelerating at lower potential energy due to being closer to the extraction plate. At the exit of acceleration region, the faster ions at the front of the plume will be accelerated to lower velocity than the slower ions at the back of the plume. (Pozo, et al., 2011)

After delaying extraction, group of ions that leaves the ion source later have greater velocity in the direction of acceleration than the other group of ions which have left the ion source earlier have lower velocity. At some distance from the ion source, the faster group catches up the slower group.

So, detector plate which has placed at this distance detects in the same time the arrival groups of these ions. (Kind and Fiehn, 2007)

Reflectron time of flight

Reflectron is used to correct the distribution of kinetic energy in the direction of the ion flight

The principle \ reflecting the ion beam toward the detector by using a constant electric field.

Ions with higher kinetic energy penetrate deeper into the reflectron and take a slightly longer path to the detector, while ions of the same ratio (m/z) but with lower kinetic energy penetrate a shorter distance into the reflectron, as a result, they will take a shorter path to the detector.

Micro channel plate MCP (the flat surface of the ion detector) is placed at the point where ions of the same mass and charge but with different energies reflected by the reflectron hitting the surface of the detector at the same time.

It is providing the high mass accuracy with wide dynamic range.

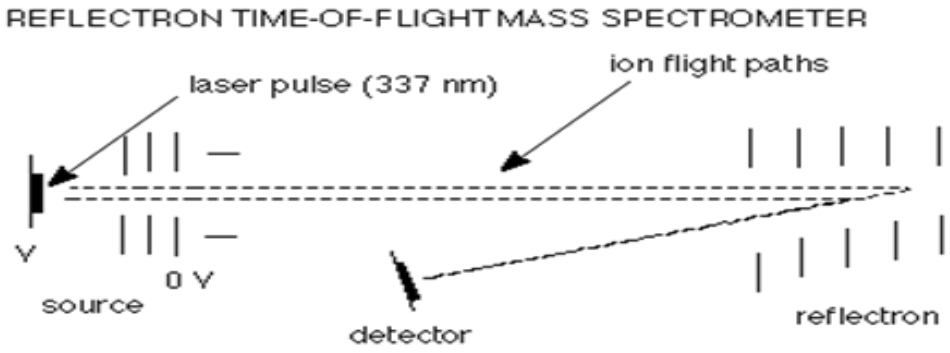

Figure (3) illustrates the aim of reflectron TOF

Detectors

In modern time of flight instrument, the detector is micro channel plate (MCP) which used to detect charge particles and radiation.It is made from high sensitive material of array of thousands of micro diameter channel each one of the latter is effectively a continuous dynode take a place under a strong electric field. Conversion dynode is used to convert ions to electrons and the latter colliding with phosphorescent material in order to convert electrons into photons.

Since these photons enter one of the micro channels throughout a small orifice, they start hitting the wall of the micro channel because the channel is at a special angel to the plate this angel known as (the angel of impact). Consequently, electrons are produced because of this impact and spreading through the micro channel, which amplifies the original signal. The electrons which went out from the opposite side of the channel were detected by a photomultiplier detector. (Watson and Sparkman, 2007)

1-Time-Slice Detection

TSD which typically acquire spectra by sampling only a single time -slice in each transient corresponding to only one value of m/z position in spectrum. A complete mass spectrum can be reconstructed by collecting other time-slice at different time delays after source pulses.

2-Time-Array Detection

With TAD all ions at all value of m/z ratio are detected during each TOF cycle, 10,000 times more data are available with TAD than TSD.

3-TAD with Transient Recorders

Recording all available information in transient signal at the detector facing a problem because of the amount of data and the rate at which they are produced.

Nevertheless, using high speed transient records have allowed many arrival -time window to be sampled for each individual ion source pulse. (Watson and Sparkman, 2007)

4-Hadamard Transform TOF-MS

It is a developed instrument of MS that can analyse many ion packets travelling in the flight tube at the same time, while the traditional TOF was waiting one packet of ions to reach the detector before introducing another one.

5-Tandom TOF-TOF

The aim of this instrument is recording a full spectrum of parent ions by using two time-of-flight spectrometers consecutively. The precursor ions of choice are isolated by a velocity filter in the first TOF mass spectrum, while the second TOF analyses the fragment ions. In order to reduce the instant current load on the ion detector, the second TOF provide with precursor signal quenchers.

TOF is a high resolution mass analyser and the increasing in flight distance and using new type of ion gun are useful to improve resolution. As it known, each mass analyser has a negative and positive aspects depending on the ion source, the procedure, sensitivity, resolution, mass accuracy or the cost of the instrument. (Herttuainen and Tolonen, 2010)

Conclusion

TOF consider as one of the best mass filters because of unlimited upper (mass /charge) values to be detect as well as the capability of acquiring rapidly for averaging and good definition of narrow chromatographic peaks. In addition to that, a good sensitivity and high quality spectra because of capability of detecting all ions of all mass / charge values without the needing for SIM. Although, Resolution changes with m/z value and higher vacuum is required. One the other hand, Pulsed mode of operation make MALDI suitable as ion source to use with TOF and can perform tandem MS.

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