



A REVIEW ON MASS SPECTROMETRY DETECTORS

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ABSTRACT

Mass spectrometry is an analytical technique for "weighing" molecules. Obviously, this is not done with a conventional scale or balance. Instead, mass spectrometry is based upon the principle of the motion of a charged particle that is called an ion, in an electric or magnetic field. The mass to charge ratio (m/z) of the ion affects particles motion. Since the charge of an electron is known, the mass to charge ratio (m/z) is a measurement of mass of an ion. Mass spectrometry research focuses on the formation of gas phase ions, and detection of ions. Detectors in mass spectrometer detect the separated ions according to m/z ratio. The main disadvantages of conventional detectors are very low sensitivity and poor detection efficiency. Detectors are of a great interest to a wide range of industrial, military, environmental and even biological applications. In recent developments, molecules of higher mass can also be detected and enhanced lifetime under the less than ideal environments typically encountered in mass spectrometers. This review deals in detail about the design, working and principle of mass spectrometric detectors and their recent developments.

Key words: Mass Spectrometry, Detectors, Mass to Charge Ratio

INTRODUCTION

Mass Spectrometry is also known as mass spectroscopy. It is an analytical technique used to measure the mass-to-charge ratio of ions and also provide quantitative and qualitative information about the atomic and molecular composition of organic and inorganic materials.

Definition

"Mass spectrometry is the analytical technique in which a mixture of ions is separated according to mass to charge ratios".

A mass spectra is a plot of relative abundance or concentration of gaseous ion against the mass to charge ratio (m/z value)

Advantage

- In mass spectrometry spectrum can be recorded on very small sample size from nano gm to micro gm up to 10-12 gm
- High sensitivity
- High specificity due to specific fragmentation pattern of ions
- High Resolution of time

Disadvantage

- Destructive nature of the process so sample recovery is not possible.
- There is difficulty in introduction of the small size sample into the high vacuum system.
- Very costly

Applications

- Identifying unknown compounds by the mass and fragments of the compound molecules.
- Determine the isotopic composition of elements in a compound.
- Determine the structure of a compound by observing its fragmentation pattern.

Compare the spectra of the elements with the standard record.

- By using carefully designed methods the amount of a compound in a sample quantify. (Mass spectrometry is not inherently quantitative).

Compare the intensity of peak with the standard.

- Studying the fundamentals of gas phase ion chemistry (the chemistry of neutrals and ions in vacuum).

- Determining other chemical, physical, or even biological properties of compounds with a variety of other approaches.

It is used in understanding of kinetics and mechanism of uni-molecular decomposition of molecules¹.

Principle

Steps of operation:-

- 1) Ionization
- 2) Acceleration
- 3) Separation
- 4) Detection
- 5) Vacuum system
- 6) Recorder

In mass spectrometry, organic molecules are bombarded with highly energetic beam of electrons and converted in to positively charged ions. The collision between energetic electron and analyte molecule occurs at right angle so high energy that imparts enough energy to the molecule with removal of the electron by electrostatic repulsion to leave the molecular ion in an excited state. When relaxation occurs, its result is the molecular ions undergo fragmentation to produce number of small ions of lower mass². These ions have a different charge and mass, which means that their speed and direction will be changed in an electric or magnetic field (in analyzer) . In analyzer the magnetic field applies a force to each ion which is perpendicular to the plane, making them curve instead of traveling in a straight line to differing degrees depending on their m/z ratio. Thus the magnetic field deflects the lighter ions more than the heavier ions. This deflection of each resulting ion beam is measured by detector. From this measurement, the mass-to-charge ratios of all the ions which are produced in the source can be determined.

Instrumentation

The operation in mass spectrometer requires a collision free path for the ions, for this, the pressure in the spectrometer should be less than 10^{-6} torr. Figure 1 is a block diagram that shows the basic parts of a mass spectrometer.

Various parts of mass spectrometer which involves specific steps within the mass spectrometer are:

- 1) **Sample inlet system:** This allows introduction of the sample

- 2) **Ionic source:** Producing ions from the gaseous sample.
- 3) **Mass analyzer:** Separating ions of differing masses based on m/z ratio.
- 4) **Detector:** Detecting the number of ions of each mass produced.
- 5) **Vacuum system:** Create vacuum in the mass spectrometer
- 6) **Recorder:** Collating the data and generating the mass spectrum¹.

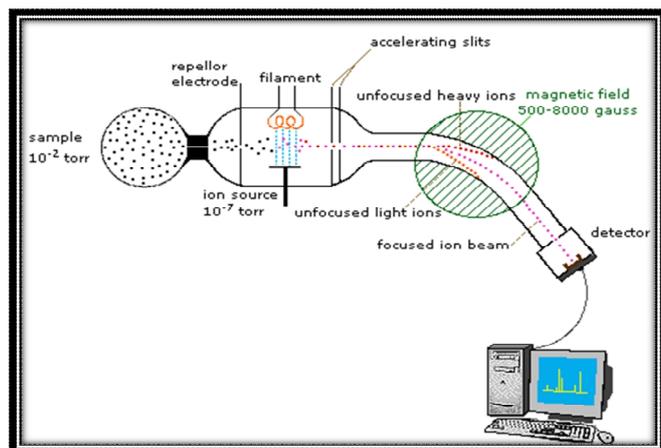


Figure 1: Mass Spectrometer³

1) Sample inlet system:- In sample inlet gaseous and volatile samples are introduced through a leak (pinhole restriction in a gold foil) of about 0.013 to 0.050mm in diameter into the ionization chamber from the inlet system.

In this liquids are introduced in various ways like by touching a micropipette to a sintered glass disk under a layer of molten gallium, break-off device by hypodermic needle injection. Solids are directly incorporate in ion chamber with very low vapor pressure.

2) Ionic source:- From inlet system, the sample is introduced into ionization chamber where a beam of electrons is strike on the molecule of sample. These molecules become positively charged then they are accelerated by high voltage so that the energy of the electrons will be increased. Then the collisions occur between molecules and electrons which result in the production of fragments. Ionization methods in mass spectrometry are divided into two categories first, in gas phase ionization, the analyst is deal with volatile substance and sample is vaporized outside the ionization chamber. Second, in desorption technique, ions are formed from samples in the condensed phase inside the ionization chamber.

Gas Phase

- 1) Electron impact
- 2) Chemical ionization
- 3) Field ionization

Desorption

- 1) Field desorption.
- 2) Electron sprays ionization.
- 3) Matrix assisted laser desorption.
- 4) Plasma desorption.
- 5) Fast atom bombardment.
- 6) Secondary ion mass spectrometry.
- 7) Thermal ionization.
- 8) Ionization by ionic bombardment¹.

Acceleration: The positive ions which are formed in the ionization chamber are withdrawn by the electric field. These ions exist between the first accelerator plate and second

repeller plate. A strong electrostatics field accelerates the ions of masses to their velocities⁴.

3) Mass analyzers: In mass analyzers the ions are separated according to their mass/charge ratio. All mass spectrometers are based on principle of dynamics of charged particles in electric and magnetic fields in vacuum. In magnetic field the ion is go in to circular motion, and at the equilibrium⁵

$$BZV = mv^2/r^5$$

Various mass analyzers are

- Magnetic analyzer
- double focusing analyzer
- Time of flight analyzer
- Quadrupole analyzer
- Ion cyclotron analyzer
- Ion trapped analyzer

4) Detectors: Ion beams after passing through mass analyzer, strikes on the detector. The ions, which have been separated according to their m/z ratio in the mass analyzer, can be electrically detected by detector.

5) Vacuum system: For the working of mass spectrometer, the ion source, the mass analyzer, and the mass detector must be kept under high vacuum condition of 10^{-6} - 10^{-7} torr (1.3×10^{-4} to 1.3×10^{-5})¹. This high vacuum in spectrometer requires two pumping stages. The first stage is a mechanical pump which provides rough vacuum down to 0.1 Pa (10-3 torr) and the second stage uses turbo molecular pumps or diffusion pumps to provide high vacuum⁶.

6) Recorder: First of all, the sample is introduced into ionization chamber to produce positive ions. Then, the accelerating voltage (V) is adjusted to a high voltage to accelerate the mass particles to high velocity. Under these conditions particles of the lowest mass numbers will be deflected by the magnet. Particles with the lowest mass numbers reach the collector and are count. The accelerating voltage is then decreased so that mass numbers reaching the collector. When accelerating voltage becomes zero, the record of the distribution of the masses in the sample is complete and is present as a mass spectrogram.

Two essential features of recorder are that

- Recorders must have a very fast response, and able to scan several hundred peaks per second
- They must be able to record peak intensities varying by a factor of more than 10^3 .²

Detectors

Ion beams after passing through mass analyzer, strikes on detector. The ions can be electrically detected by detectors which have been separated according to their mass / charge ratio in the system¹. The choice of detector is based on the required detection sensitivity and the speed and it is also determined by other application-specific requirements, such as the thermal and chemical stability, required stability, and the amount of space available

Desirable Detector Properties

High amplification, Fast time response, Low noise, High collection efficiency, Low cost, Narrow distribution of responses, Same response for all masses, Large dynamic range, Long term stability, Long life, Mounted outside of the vacuum if possible, etc⁷.

Type of detectors

There are various types of detectors which are used in mass spectrometry.

- Electron Multipliers
- Faraday Cups
- Photographic Plate

- Scintillation Counter
- Channel Electron Multipliers
- Resistive Anode Encoder Image Detectors
- High mass detection Detector

Conversion dynodes

- Helium Leak Detector
- Advanced Detectors

Cryogenic Detectors

- Multi-Pixel Photon Counter
- Other Detectors

Electron Multiplier Detector

For ion current less than 10^{-15} Amp An electron multiplier detector (EMT) is used. An electron multiplier detector is used to detect the ion signals emerging from the mass analyzer of a mass spectrometer¹.

Principle: The basic principle that allows an electron multiplier detector to operate is called secondary electron emission. When a charged ion (particle or electron) strikes on detector surface it causes secondary electrons which are released from atoms in the surface layer. The number of secondary electrons produced depends on the type of incident primary particle, its energy and characteristic of the incident surface⁸.

Features of ETP Electron Multipliers

- It has specialized surface material resulting in very high secondary electron emission.
- Air stable.
- Discrete dynode design results in extended operating life⁹.

Detector design: There are two basic designs of electron multipliers that are commonly used in mass spectrometry are: the discrete-dynode electron multiplier and the continuous-dynode electron multiplier⁸.

Discrete-dynode electron multiplier: A typical discrete-dynode electron multiplier (as shown in figure 2) has between 15-18 dynodes with a metal oxide that has the property of high secondary electron emission. The dynodes are arranged in either box-and-grid fashion or venetian blind. Secondary electrons are constrained by a magnetic field to follow in circular path, causing them to strike on the dynodes¹.

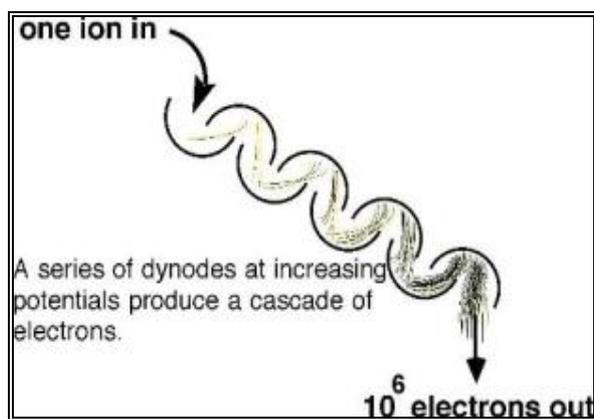


Figure 2: Principle of the Discrete-dynode electron multiplier⁷

Continuous - dynode electron multiplier

The tube is made of glass which is impregnated with lead (as shown in figure 3) to produce a desired resistance between the anode and cathode. Thus there is a continuous voltage drop along the tube to accelerate the electrons; the curvature ensures that the accelerated electrons will undergo secondary electron emission¹⁰.

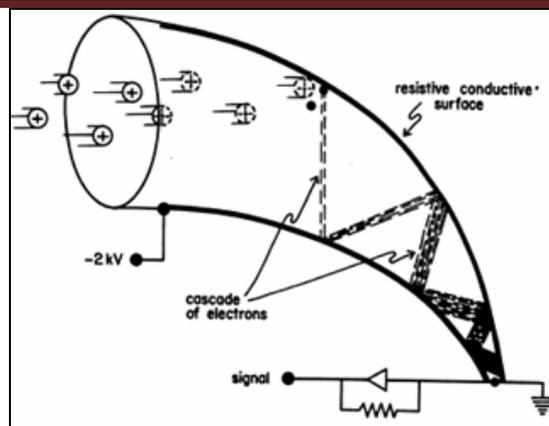


Figure 3: Continuous - Dynode Electron Multiplier⁷

Working

Each dynode is connected to a resistor chain and the first dynode is at ground potential, so that both positive and negative ions may be detected. The last dynode can be between +1500 to +3500 V depending on the type and age of electron multiplier. When an ion (electron, neutral, etc.) strikes the first dynode it may produce a few (1, 2 or 3) secondary electrons which are accelerated to the second dynode that is held at higher positive potential to generate more secondary electrons and a cascade of secondary electrons ensues. Figure 4 shows a basic EMT.

For optimum performance, the electron multiplier should operate at sufficiently high voltage So that every ion arrival produces a pulse and then this pulse is amplified and as long as it is above a set threshold, it will be passed to the counting circuit. The time taken for the multiplier, discriminator, and amplifier to produce a pulse is known as the dead time (t). With fast pulse-processing circuitry, this is in the order of 15 to 20 ns and the maximum count rate of electron multipliers is about 5×10^6 c/s if the dead time correction is to be kept low. The percentage correction is about 1.3% when a dead time of 25 ns and count rate of 5×10^5 c/s. The true count rate (n) may be calculated from the observed count rate (n_0) by the equation:

$$n = \frac{n_0}{1 - n_0 \tau}$$

n= true count rate

n_0 = observed count rate

t= dead time

Pulse counting detectors based on the principle Poisson statistics which require that each ion arrives independently of all other ions. If, in a fixed interval of time, n counts are detected, the standard deviation of the measurement is given by:

$$SD = \sqrt{n}$$

And the relative standard deviation is given by¹¹:

$$RSD = \frac{\sqrt{n}}{n} = \frac{1}{\sqrt{n}}$$

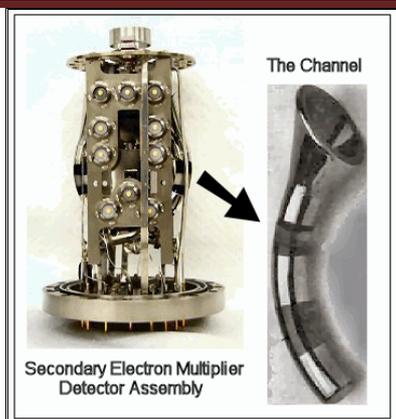


Figure 4: Electron Multiplier Detector assembly¹²

Recent developments

In recent developments, molecules of higher mass can also be detected and enhanced lifetime under the less than ideal environments typically encountered in mass spectrometers.

Magnum ETP

Magnum ETP (see figure 5) offers exceptional performance for optimum mass resolution, detection sensitivity and dynamic range¹². Finally, the use of the Spiraltron[®] technology in (as in the Magnum [®] Electron Multiplier) mass spectrometer which is coupled with improved materials and processing has the potential to significantly enhance the lifetime of current detectors over those detectors which are manufactured in the early days of the industry¹³.



Figure 5: Magnum Electron Multiplier¹²

The exceptional performance of the detector results in reduced system linearity due to the limitation of the electron multiplier supplied as original equipment. The ETP detectors overcome this limitation that showed in identical performance Comparison undertaken at independent laboratories⁸. (Figure 6)

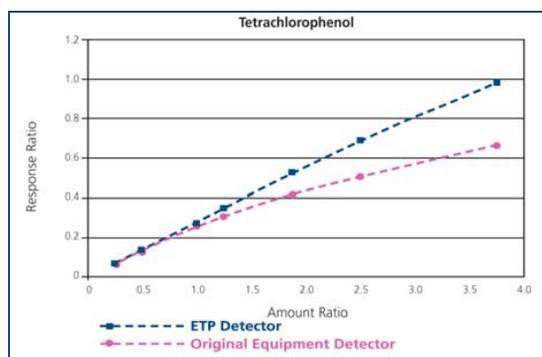


Figure 6: Detector response comparisons for tetrachlorophenol⁸

Advantage

- The multi-dynode approach of all electron multiplier detectors which results in longer lifetimes and better sensitivity compared with channel electron multipliers (CEM) or continuous-dynode multipliers.
- Optimized ion and electronic optics for maximum performance.
- Increased surface area for enhanced sensitivity and extended operational life.
- Low noise⁷

Disadvantage

The main disadvantage of electron multiplier detector is that the bias voltages for each element have to generate in a chain of resistors, and this chain draws a fair amount of current from the negative voltage supply.

FARADAY CUP COLLECTOR

The count rates of Faraday cup detector is about 5×10^4 c/s upwards.

Design: - A faraday cup is a metal conductive cup designed to catch charged particles in vacuum with suppressor electrode and then producing current which can be measured and used to determine the number of ions striking the cup.

Working: - The Faraday cup detector consists of a hollow conducting electrode connected to ground through a high resistance. The ions strike on the collector cause electrons flow from ground via the resistor. The resulting drop of potential is amplified across the resistor. A plate is held at about -80 V in front of the collector as in figure 7 that prevents ejected secondary electrons from escaping and causing an anomalous reading. A single charge on a single ion is 1.6×10^{-19} C. Therefore a count rate of detector is 1×10^6 c/s that would produce a current of 1.6×10^{-13} Amps. With a resistor of 10 MW connected to ground and the amplifier must be able to detect a potential drop of 1.6×10^{-6} (0.0016 mV). The detection limit of the Faraday cup collector is limited by the quality of the amplifier and the thermal noise in the resistor. Often these components will be enclosed within thermally controlled evacuated chamber. Faraday cup collectors are not as sensitive as electron multiplier detectors, but they have high accuracy because of the direct relation between the numbers of ions and measured current¹¹.

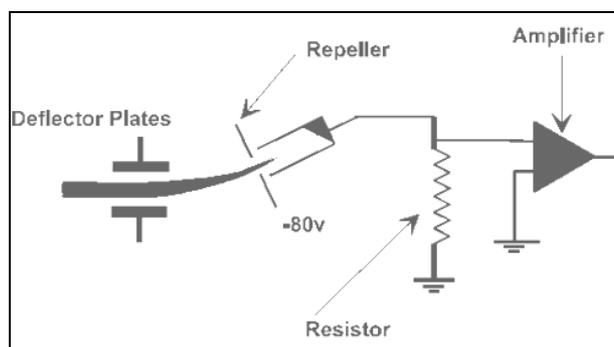


Figure 7: Faraday cup collector¹¹

Advantage

- More sensitive and produce current up to 10^{-15} Amp. and larger
- Signals from this collectors are stable and reproducible
- Simple Construction¹¹.

Disadvantages

- They have low sensitivity due to the current induced in the circuit by ion beam are very small.
- It does not identify between the type of ions or its energy¹⁴.

PHOTO GRAFIC PLATE DETECTOR

Photographic plate detector can give great resolution and high speed than other electronic devices. It can detect ions of all masses simultaneously and provides reverse- geometry. It is a time integrating device. These detectors generally used with radio frequency spark instruments. This is the simplest and oldest form of detector and they can be used in plane-focusing instruments and detects all ions and the intensity of the mark on the film is proportional to the abundance of the ion. The main advantage of the photographic plate detector is when it is used in a double-focusing mass spectroscope in which the whole or a major part of the mass spectrum is focused in a plane. In this case, one can make use of the integrating action of the photographic plate. When the ions strike the plate they leave dark tracks on plate (shows in figure 8) when the plate is developed. The intensity of these dark tracks is related to the number of ions of mass to charge ratio striking the plate at each point¹⁵.



Figure 8: Band patterns in mass spectrum captured with photographic plate



Figure 9: Photographic plate¹⁵

SCINTILLATION DETECTOR

Scintillation counter detectors are very similar to the detector used in radiochemical application.

Design: - A modern scintillation detector consists of three parts: a scintillator, a photomultiplier and signal processing electronics (figure 10). These detectors consist of conventional end window photomultiplier on this a thin disk of crystalline phosphor is mounted that maintained at a potential of +10KV. Photomultiplier absorb the light emitted by the scintillator and reemit this light in the form of electrons via the photoelectric effect.

Principle: - In the scintillation detector the energy of the incident particle is converted into light pulses. This scintillation light travels through the scintillator volume and hits the photocathode of the photo multiplier, where it releases photo electrons.

Working:- When a charged particle strikes on the scintillator, the atoms of the phosphor are excited and emit photons, which are directed at the photocathode of the photomultiplier tube. The tube is connected to the negative of a high voltage source. Each incident photon releases an electron. A number of accelerating electrodes are arranged in the tube at increasing positive potentials called dynodes and the electrons are accelerated by this electric field towards the

first dynode. The incident electron causes multiple numbers of secondary electrons to be emitted, which accelerate towards and strike on the second dynode. More secondary electrons are emitted and the electron multiplication chain continues through the increasing the dynodes potentials, with increasing numbers of secondary electrons generated each time. By this time the electrons reach the anode, enough have been released to generate a measurable voltage pulse across resistors. This voltage pulse is amplified and recorded by the processing electronic.

Advantages

- This detector has an extended life and more stable than the conventional electron multiplier.
- It opens the possibility of using photon counting techniques.
- High sensitivity

Uses

Scintillation counters are used to measure radiation in various applications.

- Hand held radiation survey meters
- Environmental and personnel monitoring for Radioactive contamination
- In medical imaging
- Homeland and national security
- Safety of nuclear plant
- Radon levels in water¹⁶

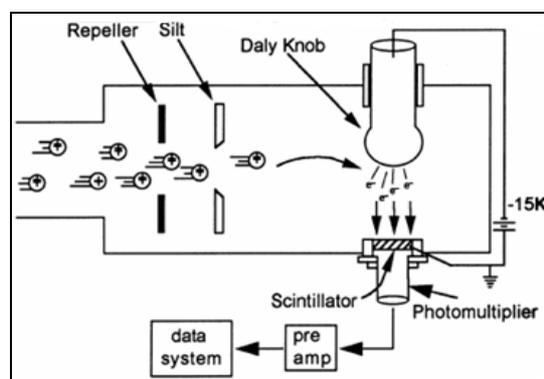


Figure 10: Scintillation Detector⁷

CHANNEL ELECTRON MULTIPLIER

Channel Electron Multipliers (CEMs) are efficient and durable detectors that directly detect and amplify charged particles and energetic photons such as positive and negative ions, electrons and assorted molecular and subatomic particles¹³.

Design

In CEMs each channel is made from semiconducting lead glass with a high voltage applied between the ends like before. A large number of glass optical fibers are combined together, which are drawn out to decrease their cross section (in figure 11). The core of the fiber is dissolved away leaving hollow tubes and the cut into slices. The faces of the plate are coated with Specific metal which provide a conducting path for the bias voltage. Each slice is about 2 mm thick and 25 or 50 mm in diameter. Each fiber ends up about 12 μm in diameter with a channel about 10 μm across and these channels are tilted with respect to the plate so that incident charged particles do not pass straight path. The plate emits 10³ to 10⁴ electrons and often two of them are stacked together. These detectors can be used in image intensifies (e.g. in night vision goggles), of in situations where large dynamic range in ion flux is needed. Since each channel

works as a separate multiplier, and there are a large number of channels, the device is linear up to fairly large incident flux¹⁷.

Working

An ion strikes on the input surface of the device that produces 2-3 secondary electrons. These secondary electrons are accelerated down the channel by a positive bias voltage and strike the channel walls (shows in figure 12), producing additional secondary electrons (and so on) until, at the output end a pulse of 10^7 to 10^8 electrons emerges. For detection of positive ions, the input is generally at a negative potential of about 1200 to 3000 volts and the output is at ground potential. For detection of negative ions, the input is at ground or some positive potential and the output is at a high positive voltage. This requires some form of decoupling in order to handle the high voltage signal¹⁸.

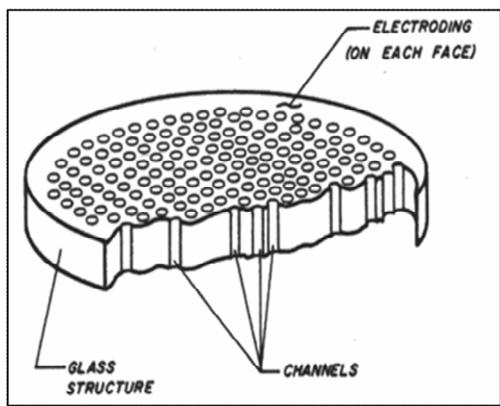


Figure 11: Cross section of channel plate¹⁷

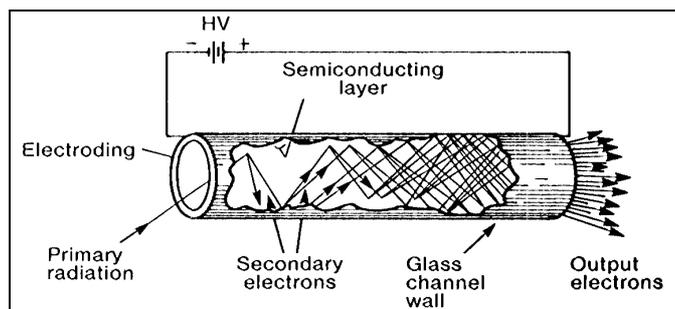


Figure 12: Electron Multiplications in the Channel Plate¹⁸

Advantages

- High gain
- High temporal and spatial resolution.

Applications

They can be used in various applications including

- In imaging spectroscopy
- In electron spectroscopy and microscopy
- In astronomy
- Molecular and atomic collision studies¹⁹

Recent development of Channel Electron Multiplier

Miniature Channeltron® Electron Multipliers: - These detectors are the ideal choice for low-cost instruments or pulse counting applications due to a combination of gain (greater than 10 million) and low noise (as shown in figure 13).

Applications

In leak detectors, portable mass spectrometers, and environmental sensors.



Figure 13: Miniature Channeltron® Electron Multiplier

Spiraltron™ High Pressure Electron Multipliers

These are specifically designed for high pressure applications, such as portable mass spectrometers. It consists of a six channel structure (as in figure 14) which has been spiraled for optimally reduce ion feedback. The number of spirals per inch can be changed that resulting in a longer or shorter travel path. Spiraltron™ Electron Multipliers can operate at pressures 10^{-3} Torr range.

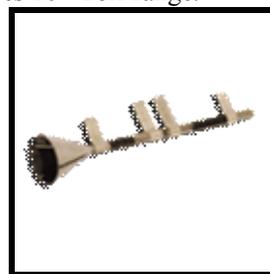


Figure 14: Spiraltron™ High Pressure Electron Multiplier

Mega Spiraltron™ High Pressure Electron Multipliers

The Mega Spiraltron™ uses the same technology as a Spiraltron™, but in a small housing which results high gain and low noise. These detectors can be manufactured with customized options to enhance detection capability. The Mega Spiraltron™ operates at pressures as high as 10^{-2} Torr²⁰ (in figure 15).



Figure 15: Mega Spiraltron™ High Pressure Electron Multipliers²⁰

RAE (RESISTIVE ANODE ENCODER) IMAGE DETECTORS

The resistive anode encoder (RAE) is a position-sensitive detector. It is used to digitally record images of ions. The background count rate is high, but it is constant over a period of time, and the maximum count rates must be less than 4×10^4 c/s. Because this detector uses a micro-channel plate for the ion to electron conversion so the detector discriminates between species.

An ion strikes on a channel in the first of two micro-channel plates. The ion to electron conversion results formation of pulse of electrons that emerge from the back of the first plate to initiate a second electron cascade in the channels of a second plate. The resulting electron pulse strikes a resistive anode plate (shows in figure 16) comprising a thick resistive film which is deposited on a ceramic plate. The geometry of

this detector is designed to avoid image distortion. The charged pulse is partitioned off to four electrodes at the corners of the resistive plate.

The pulses are amplified and then passed to the position computer where the X and Y position is calculated by the equations:

$$X = IB+IC / IA+IB+IC+ID$$

$$Y = IA+IB / IA+IB+IC+ID$$

The calculation of the electron impact position can take a long time (2-3 μs), resulting in an overall dead time of 4.3 μs¹¹.

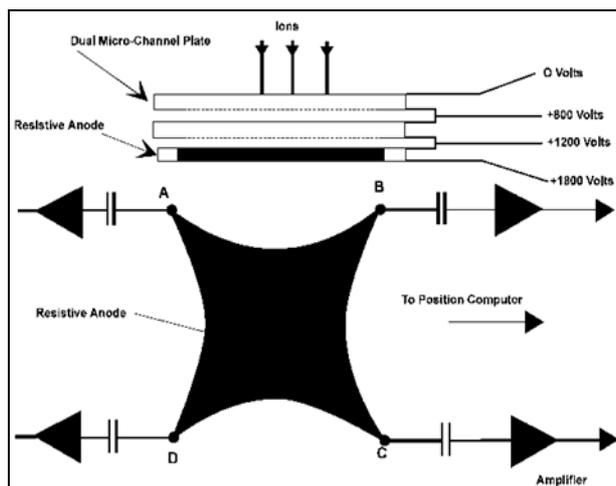


Figure 16: Resistive Anode Encoder¹¹

HIGH MASS DETECTION DETECTOR

There has been a significant increase in interest in detection of ions that have high mass. The definition of high mass depends on one's perspective that those engaged in residual gas analysis, high mass of ions might be anything in excess of 200 Daltons, while a LC/MS and biomedical applications require detection of ions from tens and even hundreds of thousands of Daltons and GC/MS application may require detection of ions from 700-2000 Daltons. The detection efficiency decreases nearly exponentially with increasing mass of ions and becomes negligible to solve this problem several approaches have been developed, including the use of higher impact energies and high energy conversion dynodes

CONVERSION DYNODES

A conversion dynode is used to increase the secondary electron emission characteristics for high mass ions and reduce the mass discrimination of the detector.

Design: - A conversion dynode is simply a metal separate surface which can be held at a high voltage at 3 to 20kV or more. The potential of dynode serves to accelerate the ions to a point where good conversion efficiency for either electrons or secondary ions occurs. The CEM is then used to detect the secondary electron emission from the dynode surface.

Working:-

Conversion dynodes are used in the detection of positive ions and the conversion products are thought to be lower mass ions and electrons. The high negative potential on the dynode surface serves to direct electrons toward the channel electron multiplier input which is held at a low negative potential. A high positive potential on the Conversion dynode will not produce many secondary electrons being collected by the CEM (as given in figure 17) since the dynode will tend to recapture electrons²¹.

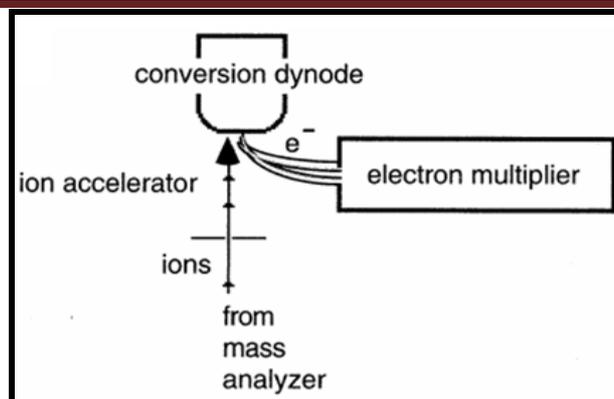


Figure 17: High Energy Dynode Detector⁷

Table 1: Comparison of Detectors⁷

Detector	Advantages	Disadvantages
Faraday cup	Good for checking ion transmission and detector sensitivity	Low amplification (≈10)
Scintillation counter	Extremely robust, Long life time (>5 years) Good sensitivity (≈106)	Cannot be exposed to light
Electron multiplier	Fast response Sensitivity (≈106)	Short lifetime (1-2 years)
High energy dynodes with electron multiplier	Increase high mass sensitivity	May shorten lifetime of electron multiplier

HELIUM LEAK DETECTOR

A helium leak detector is an instrument commonly used to locate and detect small leaks.

Principle

A helium leak detector (in figure 18) allows the localization of leaks and the quantitative determination of the leak rate such as the gas flow through the leak. Such a leak detector is a helium flow meter and performs this task by firstly evacuating the part to be tested, so that gas may enter through a leak from the outside due to the pressure difference present. If only helium is in front of the leak (e.g., by using a spray gun) this helium flows through the leak and is pumped out by the leak detector. The partial pressure of helium present in the leak detector is measured by a sector mass spectrometer and is displayed as a leak rate. This is usually given in terms of volume flow of the helium (pV-flow)²².

Advantages: - It is very Fast, More sensitive, more reliable, improved product quality, Easy operation, and Cost saving²³.

Uses:- Helium mass spectrometer leak detectors are used in production industries such as refrigeration and air conditioning, food packages, automotive parts, carbonated beverage containers and aerosol packaging, as well as used in the manufacture of steam products, gas bottles, tire valves, fire extinguishers and various other products including all vacuum systems²².



Figure 18: Helium Leak Detector²²



Figure 19: Cryogenic Detector²⁵

ADVANCED DETECTORS

At present, routine DNA analysis is done by mass spectrometry is seriously constrained to small DNA fragments and the application of mass spectrometry on those procedures that identify short DNA sequences. This approach helps the molecular biologists which are associated with LBL's Human Genome Center to identify redundant DNA sequences and vector contamination in clones, thereby improving sequencing efficiency. With the use of conventional electron multipliers one of the limitation of mass spectrometry in DNA analysis is its poor efficiency. To solve this problem, alternative detection schemes which works on heat pulse detection is developed. When ions strike a detector, the kinetic energy of striking ions is converted into heat and then measures indirectly such heat pulses. Developing a type of cryogenic detector (as given in figure 19) called a superconducting tunnel junction device which produced photons when ions strike the detector. This detector does not base on the principle of the production of secondary electrons. This type of detector to be at least two order of magnitude which is more sensitive, on an area-normalized basis, than micro channel plate ion detectors. These detectors could extend the upper mass limit large ions. In this electro spray ion sources generate ions of mega-Dalton DNA with minimum fragmentation, but the mass spectrometric analysis of these large ions usually leads only to a mass/charge distribution. If charge of ion was known, actual mass data could be determined. To solve this problem, develop a detector that will measure the velocity and charge of individual ions. Mass analyze DNA molecules in the 1 to 10 Mega Dalton range using charge-detection mass spectrometry. In this technique, individual electro spray ions are strike through a metal tube which detects their image charge. When ions of known energy are sampled than simultaneous measurement of their velocity provides a way to measure their mass. By this method several thousand of ions can be analyzed in a few minutes, thus generating statistically significant mass values regarding the ions in a sample population²⁵.

Applications of cryogenic detectors:

- For the study of low energy beta decays to investigate the existence of massive neutrinos.
- For the identification of biological macro-molecules e.g. DNA-sequences, proteins, and polymers is essential for research in modern bio-chemistry and for the fabrication of new materials, and medication²⁵.

MULTI-PIXEL PHOTON COUNTER (MPPC)

Multi Pixel Photon Counter is a novel type semiconducting photon sensor or counter. It has great photon detection ability, good cost performance and very compact size. It will displace the expensive and big Phototubes in near future²⁶.

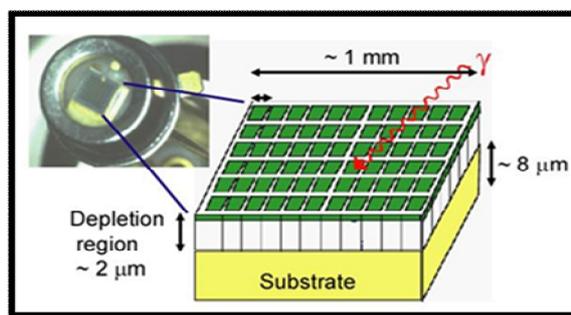


Figure 20: Multi-Pixel Photon Counter²⁶

Design: It consists of an array of Avalanche Photo-Diode pixels on area of $1 \times 1 \text{ mm}^2$. Each pixel consists of p and n-type semiconductor above p- layer (as figure 20) called depletion region that is surrounded by guard ring placed for isolation from other pixels. Apply about 70 V of reverse bias voltage to the p-n junction plane that creates strong electric field in the depletion region. If a photon strike on a pixel, the photon blow up an electron and the electron induces inundation in the depletion region. Thus the pixel "fires" signal.

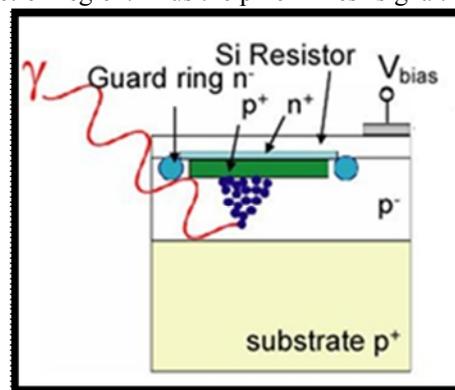


Figure 21: Multi-Pixel Photon Counter²⁷

Since each pixel exist in two states, "fired" or "not fired", the MPPC have multi-pixel structure. By counting number of "fired" pixels, one can know number of photons injected into the detector²⁶.

Working: - Each Avalanche Photo-Diode micropixel independently works in Geiger mode with an applied voltage a few volts above the breakdown voltage. When a photoelectron is produced and induces a Geiger avalanche. This avalanche is passively quenched by a resistor integral to each pixel. (In figure 21) The output charge Q from a single pixel is independent of produced photoelectrons within the pixel, and can be written as

$$Q = C (V - V_{bd}),$$

Where V is the applied voltage and C is the capacity of the pixel. Combine the output from all the pixels, the total charge from counter that is quantized to multiples of Q and proportional to the number of pixels that underwent Geiger discharge. The number of fired pixels is proportional to the number of injected photons if the number of photons is small and compared to the total number of pixels. This detector has an excellent photon counting and detection capability²⁷.

OTHER DETECTOR

KEVO® TQD TANDEM QUADRUPOLE MS DETECTOR

This detector collect high specific quantitative data for target compounds, while provide the ability to visualize all other components.

Features: This detector has wide range of ionization capabilities today, future-proofing for the innovations. These are designed to reduction of complexity; ensure correct result and increase ease of use is delivered every time. (Figure 22)



Figure 22: Kevo® TqD Tandem Quadrupole Ms Detector

PHOTONIS BI POLAR MALDI TOF DETECTOR

Theses detectors improve the detection efficiency of very high mass of ions.

Features: - It has large 250 mm² collection area which allows higher sensitivity without the need for higher post acceleration voltage. It consists of a high-sensitivity microchannel plate, a photomultiplier and a high-speed scintillator (shows in figure 23) which can detect both positive and negative ions with 30 kV isolation.



Figure 23: Photonis Bi Polar Maldi Tof Detector

FLEXAR SQ 300 MS DETECTOR

Features: - This detector has advanced design in ion source and mass spectrometry technology that Provides soft ionization in rugged design. This detector attains a new level

of sample insight through speed, confirmatory analysis and high sensitivity²⁸. (Figure 24)



Figure 24: Flexar Sq 300 Ms Detector²⁸

CONCLUSION

Currently, the old detection techniques used in Mass spectrometry are replaced by recent detection techniques for their higher sensitivity, more quantitatively accurate information, or more immediate data availability are required. Mass spectrometry detectors are capable of determining the spatial distribution of particles, whether photons, neutrons, atoms, or others, have long existed. More recently, detectors has been applied to mass spectrometry for the simultaneous detection of multiple ions of differing mass-to-charge (m/z) values. When simultaneous detection is utilized in mass spectrometry, benefits such as improved detection limits and precision can be obtained.

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