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Magnetic Sector Mass Spectrometry

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Last Update: 25.12.2021 10:47

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1 Basic Principles¹

1.1 Introduction

In mass spectrometry, one generates ions from a sample to be analyzed. These ions are then separated and quantitatively detected. Separation is achieved on the basis of different trajectories of moving ions with different mass/charge (m/z) ratios in electrical and/or magnetic fields.

Though the principles of a modern analytical mass-spectrometer are easily understood this is not necessarily true for the apparatus. A mass spectrometer especially a multi-sector instrument is one of the most complex electronic and mechanical devices one encounters as a chemist. Therefore this means high costs at purchase and maintenance besides a specialized training for the operator(s).

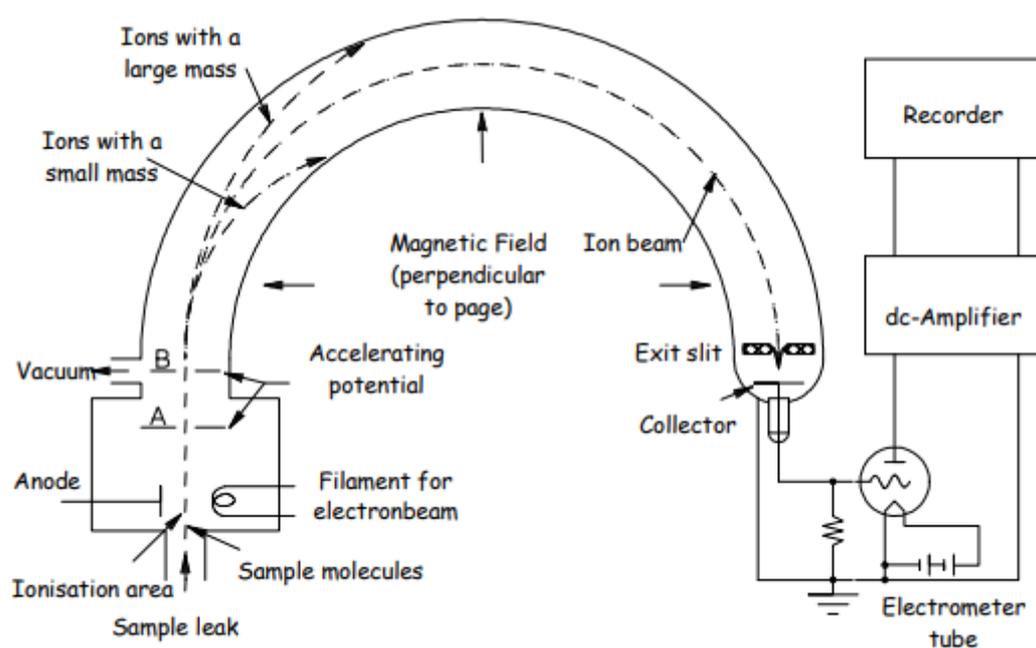


Figure 1.1. Schematic representation of a mass spectrometer

1.2 Measurement principles

In Figure 1.1, the essential parts of an analytical mass spectrometer are depicted. Its procedure is as follows:

1. A small amount of a compound, typically one micromole or less is evaporated. The vapor is leaking into the ionization chamber where a pressure is maintained of about 10^{-7} mbar.

¹ Mass Spectrometry Peter M. van Galen and Martin C. Feiters Department of Organic Chemistry

2. The vapor molecules are now ionized by an electron-beam. A heated cathode, the filament, produces this beam. Ionization is achieved by inductive effects rather than strict collision. By loss of valence electrons, mainly positive ions are produced.

3. The positive ions are forced out of the ionization chamber by a small positive charge (several Volts) applied to the repeller opposing the exit-slit (A). After the ions have left the ionization chamber, they are accelerated by an electrostatic field (A>B) of several hundreds to thousands of volts before they enter the analyzer.

4. The separation of ions takes place in the analyzer, in this example a magnetic sector, at a pressure of about 10^{-8} mbar. A strong magnetic field is applied perpendicular to the motional direction of the ions. The fast moving ions then will follow a circular trajectory, due to the Lorentz acceleration, whose radius is determined by the mass/charge ratio of the ion and the strength of the magnetic field. Ions with different mass/charge ratios are forced through the exit-slit by variation of the accelerating voltage (A>B) or by changing the magnetic-field force.

5. After the ions have passed the exit-slit, they collide on a collector-electrode. The resulting current is amplified and registered as a function of the magnetic-field force or the accelerating voltage.

The applicability of mass-spectrometry to the identification of compounds comes from the fact that after the interaction of electrons with a given molecule an excess of energy results in the formation of a wide range of positive ions. The resulting mass distribution is characteristic (a fingerprint) for that given molecule. Here there are certain parallels with IR and NMR. Mass-spectrograms in some ways are easier to interpret because information is presented in terms of masses of structure-components.

1.3 Sampling

As already indicated a compound normally is supplied to a mass-spectrometer as a vapor from a reservoir. In that reservoir, the prevailing pressure is about 10 to 20 times as high as in the ionization chamber. In this way, a regular flow of vapor-molecules from the reservoir into the mass spectrometer is achieved. For fluids that boil below about 150C the necessary amount evaporates at room temperature. For less volatile compounds, if they are thermally stabile, the reservoir can be heated. If in this way, sampling cannot be achieved one passes onto to direct insertion of the sample.

1.4 The Ion source

In Figure 1.2, the scheme of an ionization chamber, ion-source, typically electron impact, is presented. In this chamber in several ways, ions of the compound to be investigated can be produced. The most common way is to bombard vapor-molecules of the sample with electrons of about 70 eV. These electrons are generated by heating a metal wire (filament),

commonly used are tungsten or rhenium. A voltage of about 70 Volts (from 5 to 100) accelerates these electrons towards the anode.

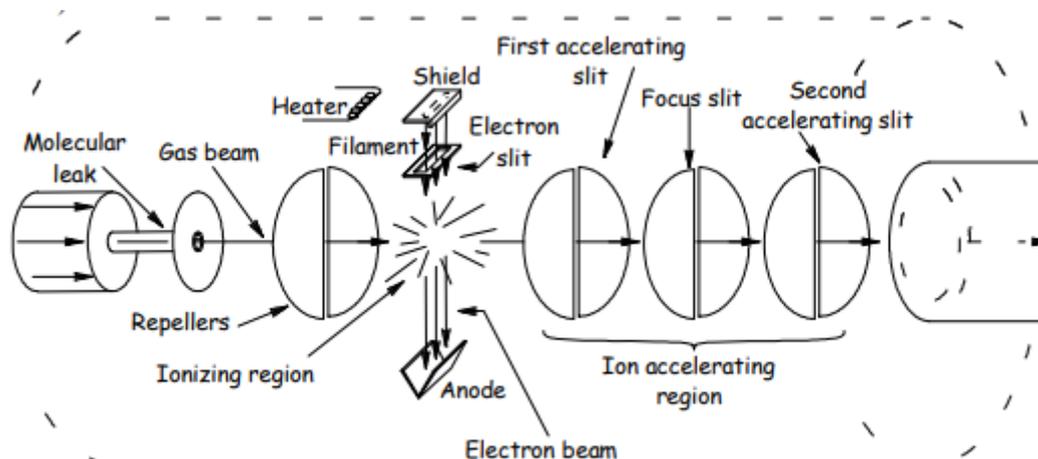


Figure 1.2. Schematic representation of an ion source.

During the bombardment, one or more electron can be removed from the neutral molecule thus producing positively charged molecular radical-ions. Only about one in 10³ of the molecules present in the source are ionized. The ionization probability differs among substances, but it is found that the cross-section for most molecules is a maximum for electron energies from approximately 50 to 100 eV. Most existing compilations of electron impact spectra are based on spectra recorded with approximately 70 eV electrons, since sensitivity is here close to a maximum and fragmentation is unaffected by small changes in electron energy around this value. During this ionization, the radical-ions on average gain an excess energy enough to break one or more bonds hence producing fragment-ions. In Figure 1.3 the possible fragmentation of a molecule ABCD is presented. It should be stated here that this is a simplified presentation and that in real life a multitude of possible ways to form fragments even via re-arrangement reactions exists. Fragmentation of a molecular radical cation to give a neutral molecule and a new fragment radical cation is also possible.

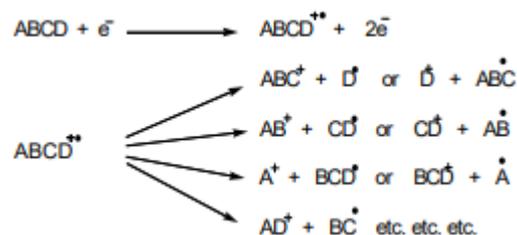


Figure 1.3. Possible fragmentation of a 'molecule' ABCD.

1.5 Magnetic Mass Analyser

Consider an ion of mass m and charge q , accelerated in the source by a potential difference V_s . At the source outlet, its kinetic energy is

$$E_k = \frac{mv^2}{2} = qV_s$$

If the magnetic field has a direction that is perpendicular to the velocity of the ion, the latter is submitted to a force F_M as described in Figure 2.48. Its magnitude is given by

$$F_M = qvB$$

The ion follows a circular trajectory with a radius r so that the centrifugal force equilibrates the magnetic force

$$qvB = \frac{mv^2}{r} \quad \text{or} \quad mv = qBr$$

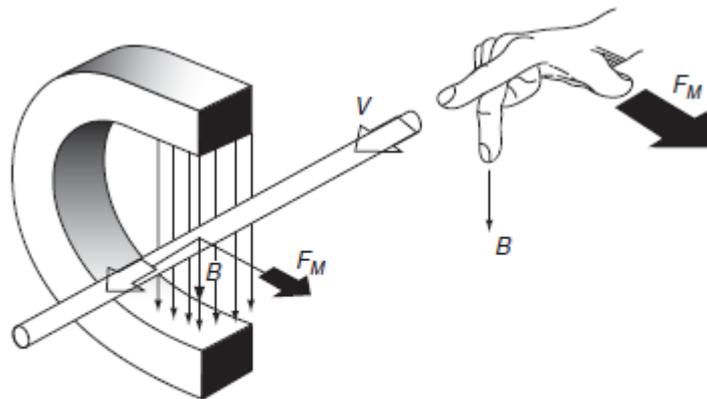


Figure 2.48
Orientation of the magnetic force on a moving ion.

2

Ions at the source outlet leads to

$$mv^2 = 2qV_s$$

Hence

$$\frac{m}{q} = \frac{r^2 B^2}{2V_s}$$

(bending magnet)

² Mass Spectrometry Principles and Applications Edmond de Hoffmann

Universite Catholique de Louvain, Belgium & Ludwig Institute for Cancer Research, Brussels, Belgium

1.6 Detectors²

The ions pass through the mass analyzer and are then detected and transformed into a usable signal by a detector. Detectors are able to generate from the incident ions an electric current that is proportional to their abundance.

Several types of detectors presently exist. The choice of detector depends on the design of the instrument and the analytical applications that will be performed. Varieties of approaches are used to detect ions. However, detection of ions is always based on their charge, their mass or their velocity. Some detectors (Faraday cup) are based on the measurement of direct charge current that is produced when an ion hits a surface and is neutralized. Others (electron multipliers or electro-optical ion detectors) are based on the kinetic energy transfer of incident ions by collision with a surface that in turn generates secondary electrons, which are further amplified to give an electronic current. Because the number of ions leaving the mass analyzer at a particular instant is generally quite small, significant amplification is often necessary to obtain a usable signal. Indeed, 10 incident ions per second at the detector corresponds to an electric current of 1.6×10^{-18} A. In consequence, subsequent amplification by a conventional electronic amplifier is required. Furthermore, with the exception of Faraday cup and image current detection, the other detectors multiply the intensity of the signal by a cascade effect.

Ion detectors can be divided into two classes. Some detectors are made to count ions of a single mass at a time and therefore they detect the arrival of all ions sequentially at one point (point ion collectors). Others detectors, such as photographic plates, image current detectors or array detectors, have the ability to count multiple masses and detect the arrival of all ions simultaneously along a plane (array collectors). These detectors are effective for most of the applications in mass spectrometry. Nevertheless,

if a detector must ideally be free of any discrimination effect, its efficiency generally decreases when the mass of the ion increases. This induces limitations for the detection of high-mass ions and can compromise a quantitative analysis from these data because the signal decreases exponentially with increasing mass. On the other hand, progress in mass spectrometry has led to the advent of entirely new ionization sources and analyzers that allow the study of analytes with very high molecular mass. For these reasons, the development of new detectors, which eliminate these limitations, is required. These new classes of detectors such as the charge or inductive detector [2] or cryogenic detector [3] are under development. They are based on physical principles that differ from those used for the current detectors and their efficiencies are the same for all the detected ions and are unrelated to their masses. They have near 100% efficiency for very large slow ions.

Indeed, the inductive detector simply produces a signal by inducing a current on a plate generated by a moving charged ion. Its efficiency is related to the charge of the ion but is

independent of its mass and its kinetic energy. In the same way, the cryogenic detector is a kinetic energy sensitive calorimetric detector operating at low temperatures.

1.6.1 Faraday Cup

A Faraday cup is made of a metal cup or cylinder with a small orifice. It is connected to the ground through a resistor, as illustrated in Figure 3.1. Ions reach the inside of the cylinder and are neutralized by either accepting or donating electrons as they strike the walls. This leads to a current through the resistor. The discharge current is then amplified and detected. It provides a measure of ion abundance.

Because the charge associated with an electron leaving the wall of the detector is identical to the arrival of a positive ion at this detector, secondary electrons that are emitted when an ion strikes the wall of the detector are an important source of errors if they are not suppressed. In consequence, the accuracy of this detector can be improved by preventing the escape of reflected ions and ejected secondary electrons. Various devices have been used to capture ions efficiently and to minimize secondary electron losses. For instance, the cup is coated with carbon because it produces few secondary ions. The shape of the cup and the use of a weak magnetic field prevent also any secondary electrons produced inside to exit.

The disadvantages of this simple and robust detector are its low sensitivity and its slow response time. Indeed, the sensitivity of such detectors is limited by the noise of the amplifiers. Furthermore, this detector is not well adapted to ion currents that are not stable in the same time as during the scanning of the analyzer because of its slow response time. These detectors are nevertheless very precise because the charge on the cylinder is independent of the mass, the speed and the energy of the detected ions. The Faraday cup was widely used in the beginning of mass spectrometry but all the characteristics of this detector mean that it is now generally used in the measurement of highly precise ratios of specific ion species as in isotopic ratio mass spectrometry (IRMS) or in accelerator mass spectrometry (AMS). To obtain a highly accurate ratio in such relative abundance measurements, the intensities of the two stable beams of specific ions are measured simultaneously with two Faraday cups.

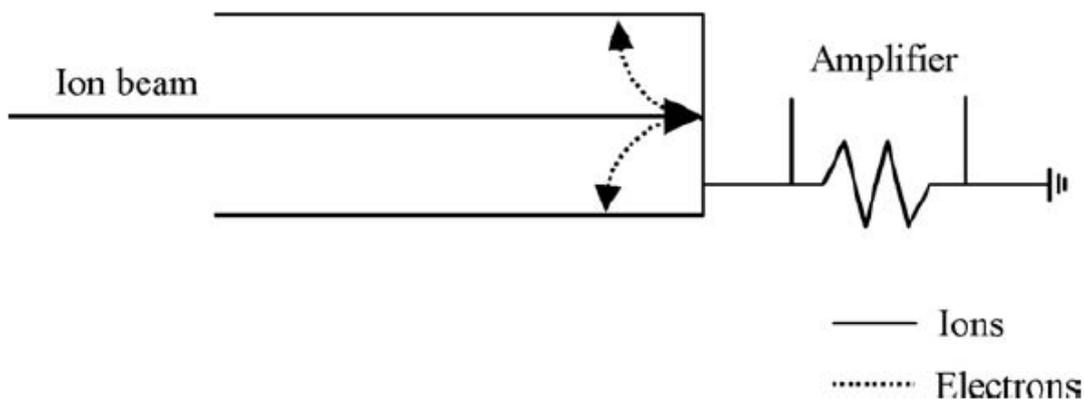


Figure 3.1
Schematic diagram of a Faraday cup.

1.6.2 Electron Multipliers

At present (2006), the most widely used ion detector in mass spectrometry is the electron multiplier (EM). In this detector, ions from the analyzer are accelerated to a high velocity in order to enhance detection efficiency. This is achieved by holding an electrode called a conversion dynode at a high potential from ± 3 to ± 30 kV, opposite to the charge on the detected ions. A positive or negative ion striking the conversion dynode causes the emission of several secondary particles. These secondary particles can include positive ions, negative ions, electrons and neutrals. When positive ions strike the negative high-voltage conversion dynode, the secondary particles of interest are negative ions and electrons. When negative ions strike the positive high-voltage conversion dynode, the secondary particles of interest are positive ions. These secondary particles are converted to electrons at the first dynode.

These are then amplified by a cascade effect in the electron multiplier to produce a current. The electron multipliers may be of either the discrete dynode or the continuous dynode type (channeltron, microchannel plate or microsphere plate). The discrete dynode electron multiplier is made up of a series of 12 to 20 dynodes that have good secondary emission properties. As shown in Figure 3.2, these dynodes are held at decreasing negative potentials by a chain of resistors. The first dynode is held at a high negative potential from -1 to -5 kV, whereas the output of the multiplier remains at ground potential. Secondary particles generated from the conversion dynode strike the first dynode surface causing an emission of secondary electrons. These electrons are then accelerated to the next dynode because it is held at a lower potential. They strike the second dynode causing the emission of more electrons. This process continues as the secondary electrons travel towards the ground potential. Thus, a cascade of electrons is created and the final flow of electrons provides an electric current at the end of the electron multiplier that is then increased by conventional electronic amplification.

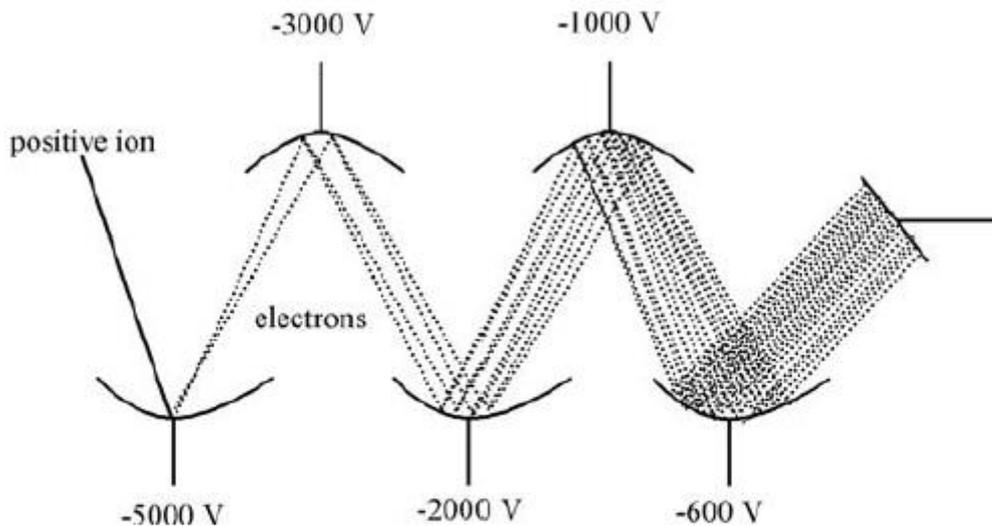


Figure 3.2
Schematic diagram of electron multiplier. The first dynode is a conversion dynode to convert ions into electrons.

There is another design of electron multiplier for which the discrete dynodes are replaced by one continuous dynode. A type of continuous-dynode electron multipliers (CDEM), which is called a channeltron, is made from a lead-doped glass with a curved tube shape that has good secondary emission properties (Figure 3.3). As the walls of the tube have a uniform electric resistance, a voltage applied between the two extremities of the tube will therefore produce a continuous accelerating field along its length. Secondary particles from the conversion dynode collide with the curved inner wall at the detector entrance and produce secondary electrons, which are then accelerated by the field towards the exit of the tube. These electrons pass further into the electron multiplier, again striking the wall, causing the emission of more and more electrons. Thus a cascade of electrons is created and finally a metal anode collects the stream of secondary electrons at the detector exit and the current is measured.

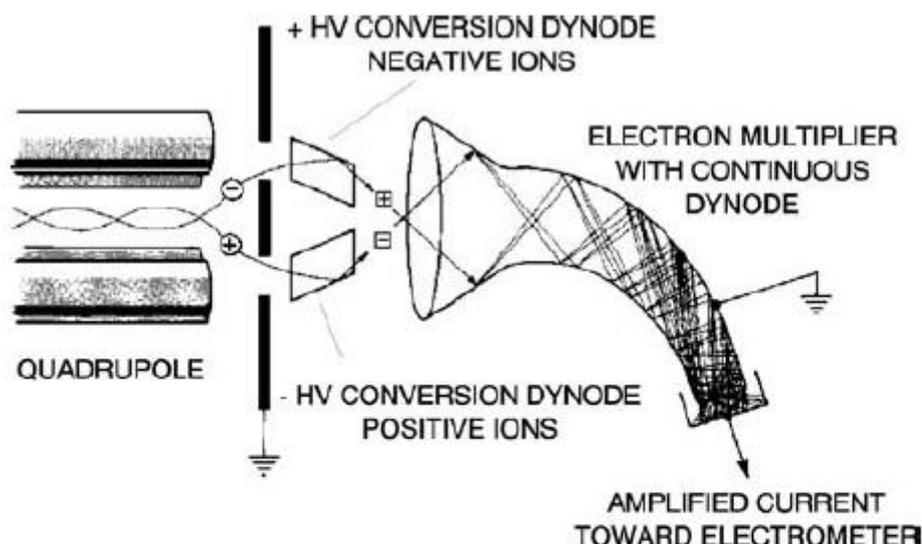


Figure 3.3
 Continuous dynode electron multiplier, also known as the channeltron. ○, incident ions; □, secondary particles. Reproduced (modified) from Finnigan MAT documentation, with permission.

The amplifying power is the product of the conversion factor (number of secondary particles emitted by the conversion dynode for one incoming ion) and the multiplying factor of the continuous dynode electron multiplier. It can reach 10^7 with a wide linear dynamic range (10⁴–10⁶). Their lifetime is limited to 1 or 2 years because of surface contamination from the ions or from a relatively poor vacuum. Their high amplification and their fast response time allow their use with rapid scanning of the analyzer. The conversion factor is highly dependent on the impact velocity of the detected ions and on their nature (mass, charge and structure), so these detectors are not as precise as Faraday cups. Since the detection efficiency on all electron multipliers is highly dependent on ion velocity, they are characterized by the mass discrimination effect for ions with constant energy. Because of their slower velocity, large ions produce fewer secondary electrons and thus the efficiency decreases when the mass of the ion increases. However, as already mentioned, the conversion dynodes at high voltages reduce the mass discrimination effect and serve to increase signal intensity and therefore sensitivity because they accelerate ions to a high velocity in order to enhance detection efficiency. Conversion dynodes are thus very useful for detecting high-mass ions, especially with analyzers delivering ions at low kinetic energy, such as quadrupoles or ion traps.

1.7 Mass Spectrometry / Gas Chromatography

In order to analyse a complex mixture, for example natural products, a separation technique – gas chromatography (GC), liquid chromatography (LC) or capillary electrophoresis (CE) – is coupled with the mass spectrometer. The separated products must be introduced one after

the other into the spectrometer, either in the gaseous state for GC/MS or in solution for LC/MS and CE/MS. This can occur in two ways: the eluting compound is collected and analysed off-line; or the chromatograph is connected directly to the mass spectrometer and the mass spectra are acquired while the compounds of the mixture are eluted. The latter method operates on-line.

1.8 VG-70S Magnetic Sector Mass Spectrometer

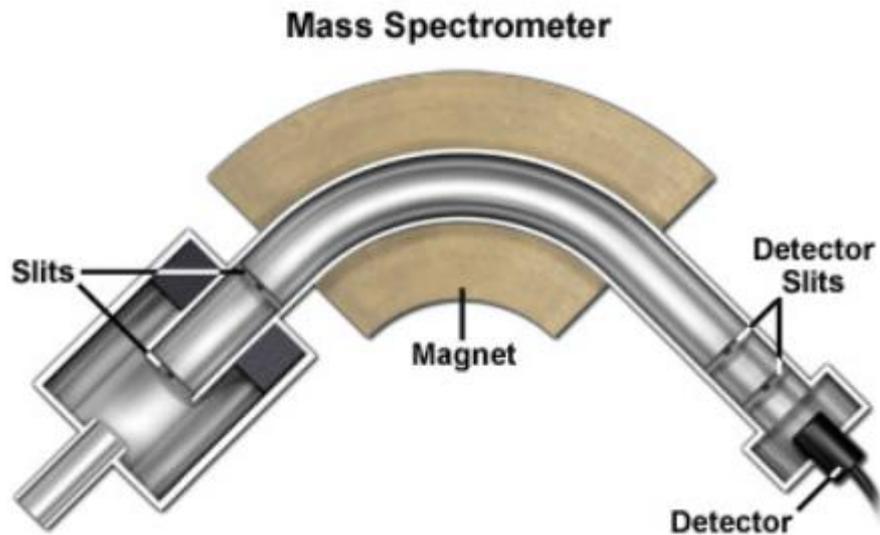
Check this magnetic mass spectrometer at JHONS HOPKINS Krieger school of arts and sciences

<https://sites.krieger.jhu.edu/mass-spec/facility-instrumentation/vg-70s-magnetic-sector-mass-spectrometer/>

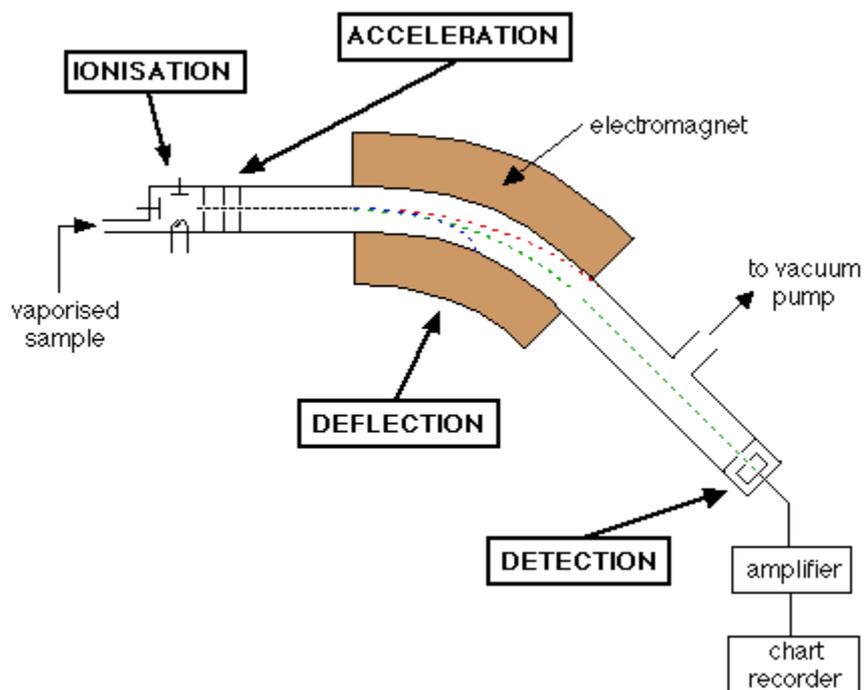


2 Our Device

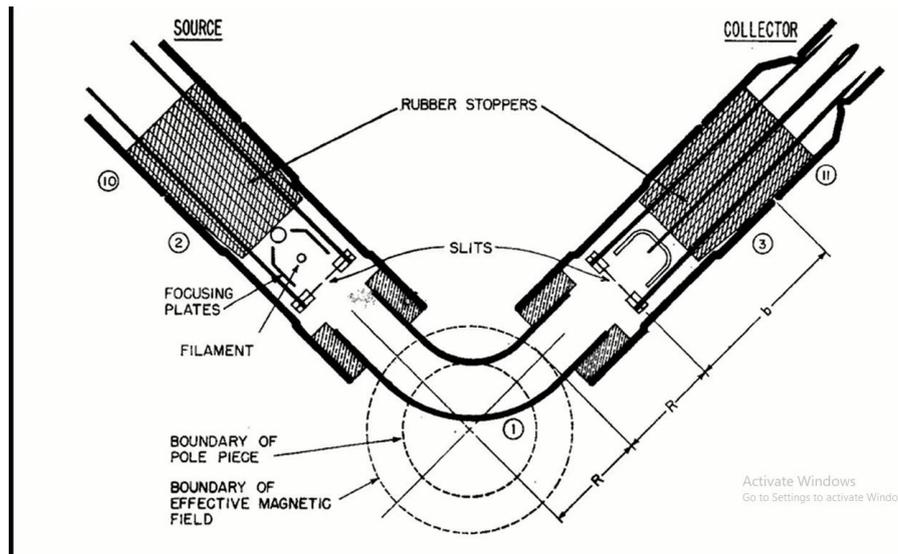
2.1 Overview



<https://nationalmaglab.org/education/magnet-academy/learn-the-basics/stories/mass-spectrometry>



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https://www.youtube.com/watch?v=nIKhUizkXxA&ab_channel=AppliedScience

1 Ionization

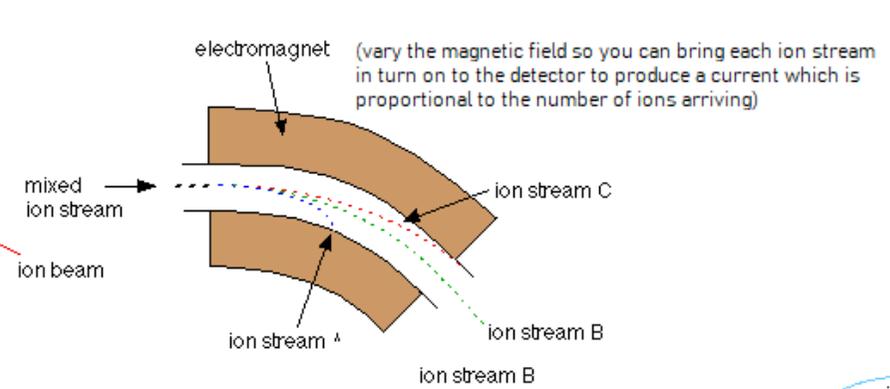
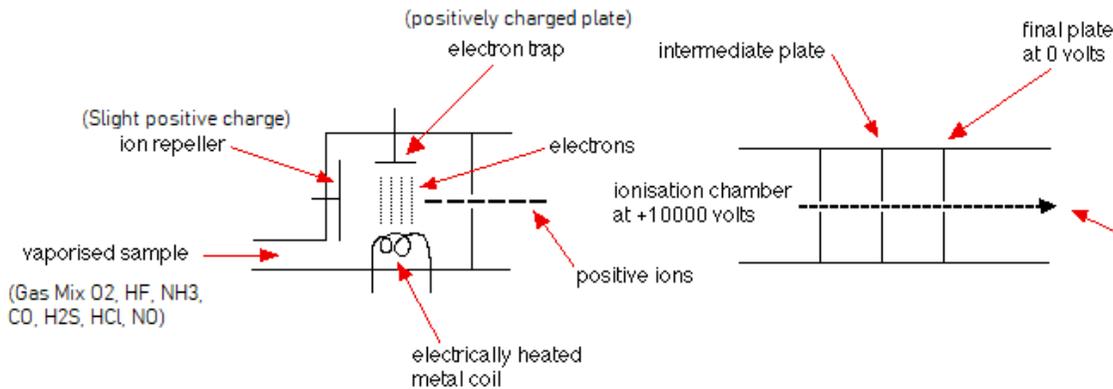
The atom is ionised by knocking one or more electrons off to give a positive ion. This is true even for things which you would normally expect to form negative ions (chlorine, for example) or never form ions at all (argon, for example). Mass spectrometers always work with positive ions.

2 Acceleration

The ions are accelerated so that they all have the same kinetic energy.

3 Deflection

The ions are then deflected by a magnetic field according to their masses. The lighter they are, the more they are deflected. The amount of deflection also depends on the number of positive charges on the ion - in other words, on how many electrons were knocked off in the first stage. The more the ion is charged, the more it gets deflected.

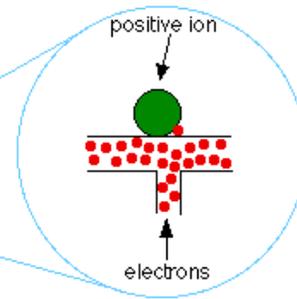


4 Detection

The beam of ions passing through the machine is detected electrically.

(When an ion hits the metal box, its charge is neutralized by an electron jumping from the metal on to the ion. That leaves a space amongst the electrons in the metal, and the electrons in the wire shuffle along to fill it)

(flow of electrons in the wire is detected as an electric current which can be amplified and recorded)



2.2 Parts

Parts	Qty	Description
Metal Plate	2	slight positive charge
Slits	4	2 acceleration slits (slight negative potential) 1 Focusing Slit (extremely high voltage) 1 Detecting Slit
* metal coil	1	Tungsten filament
electromagnet	1	strong magnetic field is applied perpendicular to the motional direction of the ions
Vacuum pump	1	10^{-7} mbar
Faraday cup	1	
Amplifier	1	
Metal Tube	3	2 horizontale tubes 1 curved tube 60°



2.3 Acceleration Slits

The simplest way to accelerate ions is to place them between a set of charged parallel plates. The ions are repelled by one plate, attracted to the other, and if we cut a hole in the second plate, the ions emerge with a kinetic energy determined by the potential difference between the plates.

$$K = q | \Delta V |$$

Definition of acceleration slits

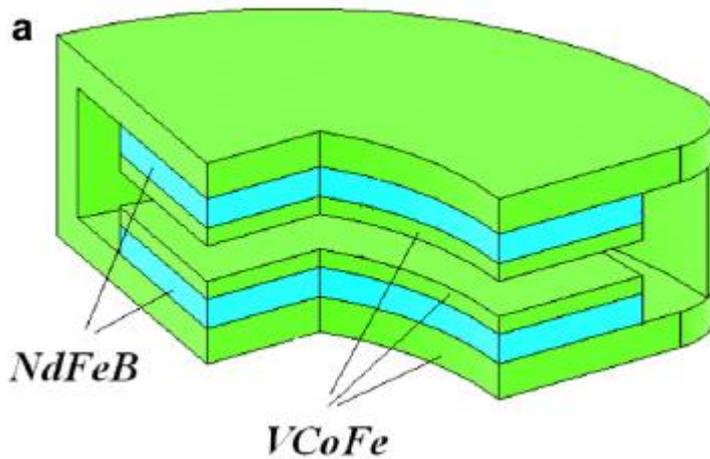
Positively charged ions produced in an ionization chamber of a mass spectrometer are passed into the analyzer by the acceleration slits. Generally, two acceleration slits are used; one has a slight negative potential with respect to the ionization chamber in order to attract the positive ions, and the other slit has an extremely high voltage, which accelerates that ions to up to half the speed of light.

How can I give a metal surface a static negative or positive charge?

By adding or subtracting electrons.

Here is one approach. Rest the object on foam polystyrene sheet (very high resistivity). Charge a capacitor with several hundred volts DC. Ground the cap's negative lead. Touch the positive lead to the metal plate. This extracts electrons. Recharge the capacitor. Ground the cap's positive lead. Touch the negative cap lead to the plate. This adds electrons.

2.4 Magnet



Iron Cobalt Vanadium Alloy (VCoFe)

A neodymium magnet (also known as NdFeB, NIB or Neo magnet) is the most widely used type of rare-earth magnet.³

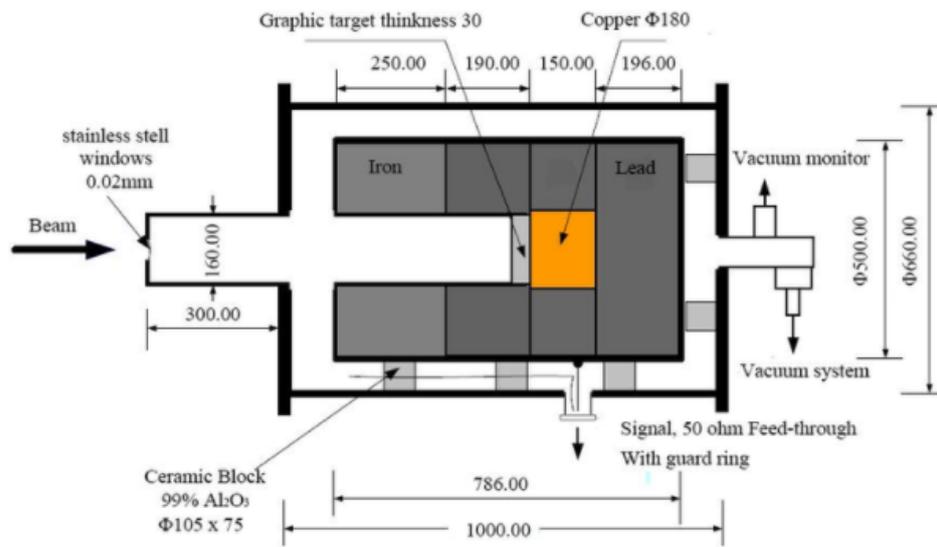
2.5 Detector

Dyanode detector



<https://www.photonis.com/products/discrete-dynode-detector>

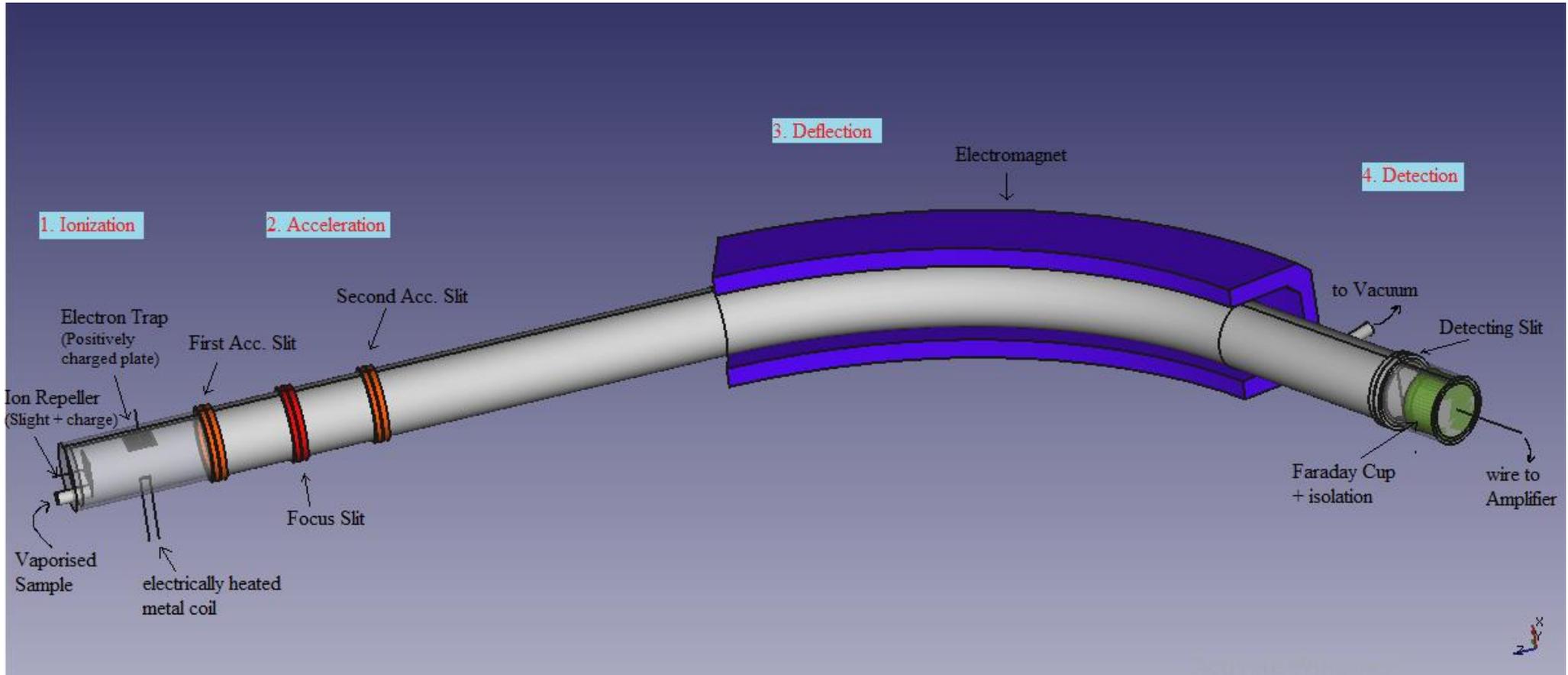
³ Development of a miniature magnetic sector mass spectrometer Detian Li, Meiru Guo, Yuhua Xiao*, Yide Zhao, Liang Wang



design structure of Faraday Cup at E2 line

https://www.researchgate.net/figure/The-design-structure-of-Faraday-Cup-at-E2-line_fig1_283762179

2.6 FreeCad



MassSpectro.FCStd