

# TOF FUNDAMENTALS TUTORIAL

*Presented By:*

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This is an instructional tutorial dealing with the fundamentals of Time of Flight technology

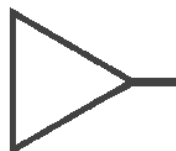
It is divided into three parts dealing with:



The creation of ions in the ION SOURCE...

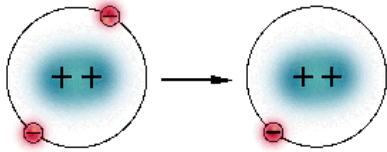


Their separation according to mass in the FLIGHT TUBE...

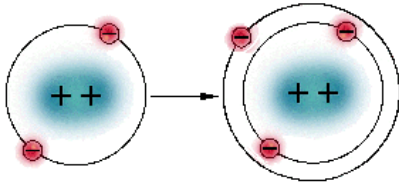


And their detection at the DETECTOR.

The information presented will begin with the very basic and then be repeated in progressively more complex and detailed form. You may also notice that in order to keep things simple, we have taken certain liberties such as using velocity and energy interchangeably. We hope that you don't find this to be distracting.

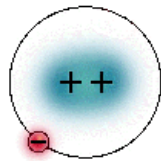


If an atom or molecule loses...

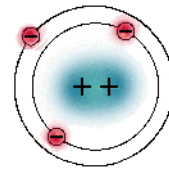


Or gains an electron, it will have an electrical charge:

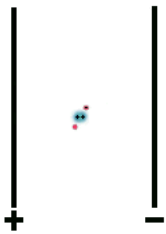
A positive charge if it loses,



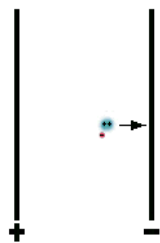
or a negative charge if it gains



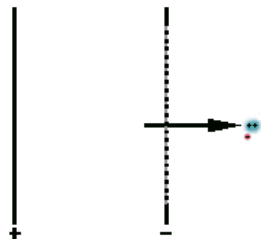
an electron. The resulting charged atom or molecule is called an ion. This process is called ionization. It is because of ionization that mass analysis is made possible.



If an ion is created in an electrical field, it will accelerate in the direction opposite to its polarity.

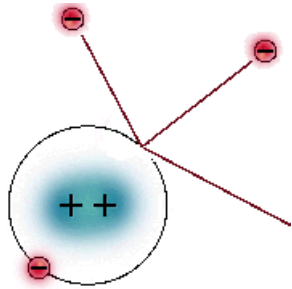


In this case, a positive ion accelerates away from the positive electrode.



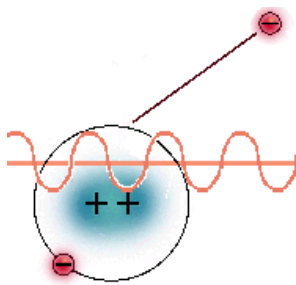
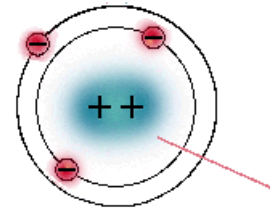
If the negative electrode is replaced with a grid, the ion will pass through it and leave the ion source. In this very simple ion source, ions are created in a field and extracted through a grid which is therefore called the extraction grid. The electrode opposite the extraction grid repels the ions and is therefore called the repeller plate.

Ions can be created in several ways: One way is by electron bombardment in which an electron collides with a molecule,

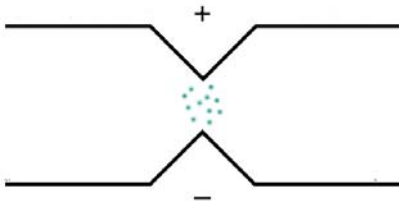


causing it to lose...

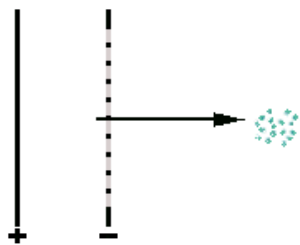
or gain an electron



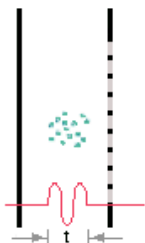
Another way is to expose the molecules to high intensity laser light. The energy of the laser causes it to become excited, and throw off an electron.



Still another way is to charge two surfaces to a very high voltage difference. This causes the gas between them to break down into a plasma; or ion cloud.

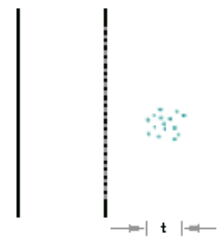


Even though all of these ways can be used to create ions, the ions are not suitable for analysis unless they are all ejected from the ion source with the same starting time.



This is easy to do with a pulsed laser which can be turned on and off very rapidly so that it only creates ions during time "t".

This results in a group of ions being ejected during time "t" only

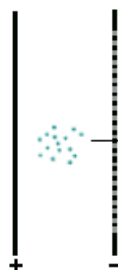


Using electrons or plasma is more complicated. Since the ionizing process cannot be started and stopped quickly, the start time is controlled with an electrical pulse.

To do this, ions are created while the repeller plate and extraction grid are at the same voltage potential.



At the start moving



proper time, the voltages can be switched on rapidly, causing all the ions to at the same time.

The

generator.

Timing circuits are used to coordinate the start time with other events in the experiment.

instrument which does the rapid switching is called a pulser, or pulse



While the ions are being extracted, the ionizing process is stopped so that only the ions which were present at the starting pulse will be extracted.

Notice that this results in a small group of ions which are close together, as if they had been made by a laser.

So far we have discussed ion formation and extraction only. For use in a real instrument, some additional elements, called ion optics are usually added.

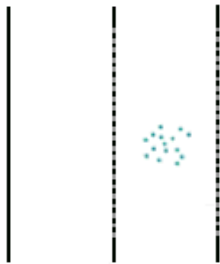
First is an accelerating grid. Its purpose is to accelerate the extracted ions to the correct velocity for entry into the flight tube. The voltage on this grid, A3 is about ten times the difference between that on the repeller plate A1 and extraction grid, A2.

Therefore, if A2 is 100 volts more negative than A1, then A3 will be 1000 volts more negative than A2.

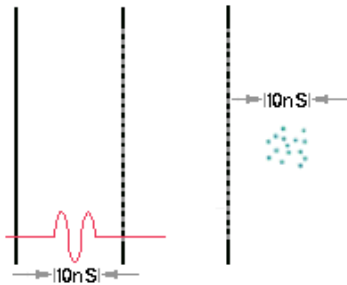
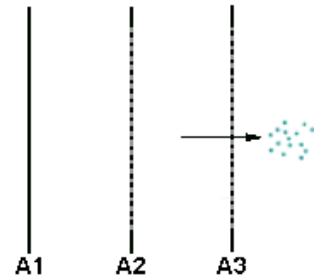


Now lets summarize what we've said so far. When a static molecule is Ionized in the potential field between repeller plate and extraction grid, it...

immediately begins to move toward and through the extraction grid.

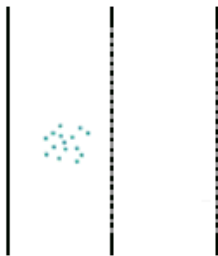


It then enters a much stronger field which causes it to accelerate.....Into the flight tube

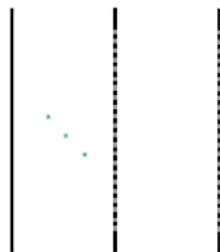


An ionizing pulse of 10 nanoseconds will yield ion packets which are at least 10 nanoseconds wide.

Since this packet width is determined by time, it is known as time or temporal distribution. One way to compensate for temporal distribution is referred to as ion storage, and will be referred to later.



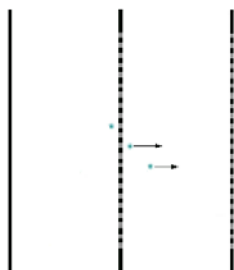
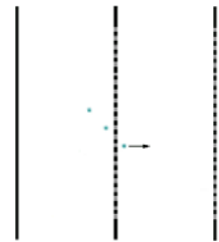
Ion packet width is also determined by the position of the ions when first created or accelerated. This variation in position is known as initial spacial distribution.



Lets look at three ions which are created in an ion source.

One of them is close to the extraction grid,

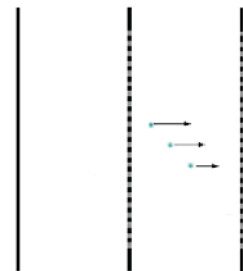
So it will leave first, but it will be moving slower

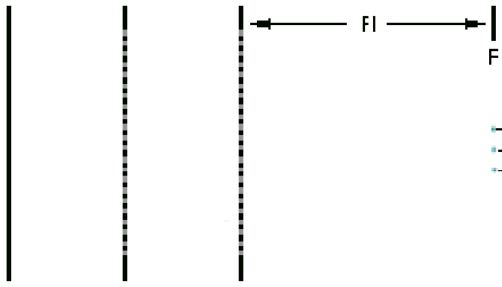


The middle one will leave later, but will be moving faster....

The farthest one will leave last, but will be moving even faster.

This variation in their velocities is called energy distribution.

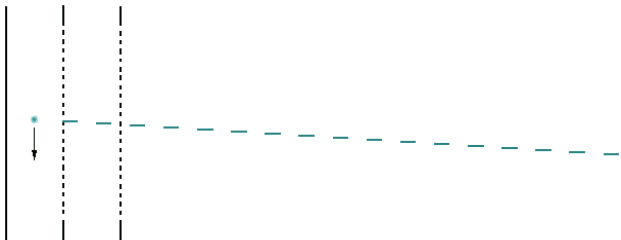




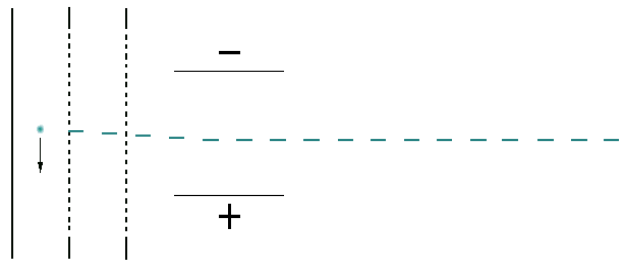
After traveling some distance, F1, the late, faster ions just catch up with the slower ones. This point, F, is known as the primary focal point.

Adjusting the grid voltages and spacing to control the location of this point is called energy focusing. The focusing shown in this diagram is also known as first order focusing. We will return to this later, and discuss ways to take advantage of it. Elements can be added to the ion source for the purpose of extending or otherwise controlling the focal point. This has been referred to as second order focusing. It will be discussed later as it relates to resolution.

Until now we have been considering molecules, which were static when ionized. An ion source must also deal with another kind of energy, called transverse energy.

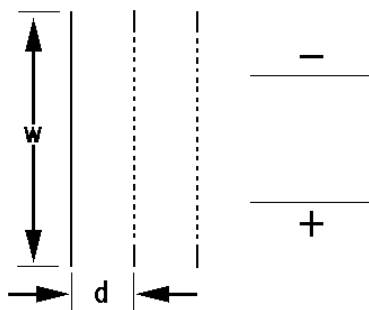


If an ion is moving at the time of its extraction pulse, it's initial velocity can cause it to drift away from the axis of the flight tube.

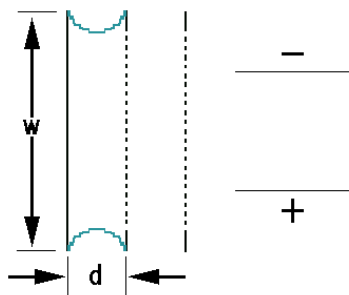


To counteract this, steering plates can be added. A positive voltage on a plate which is opposite the transverse velocity will repel a positive ion back onto a desired course. Likewise, a negative voltage on the other plate will have the same effect. It is sometimes best to apply both of them at the same time to keep the field symmetrical.

Now that we know the basic ion source elements and how they work, lets look at them in more detail.

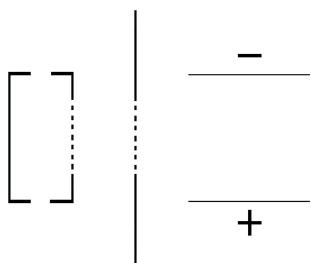
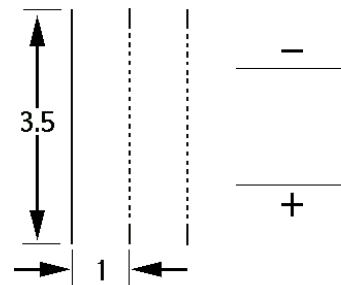


The spacing, (d) of the plates must be kept small compared to the width, (w).

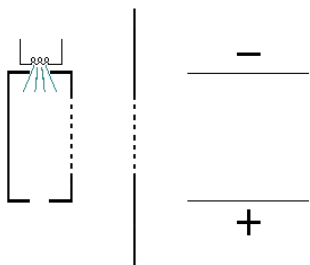


This prevents penetration by outside electric fields which would distort the shape of the ionization and extraction fields.

This ratio is usually 3 or 4 to one

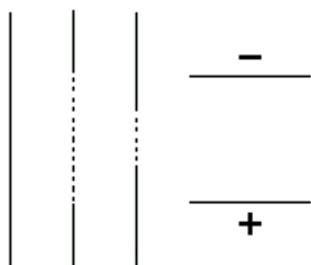
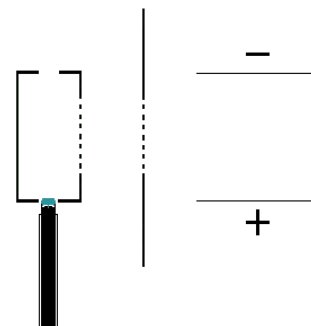


Sometimes it is necessary to make them narrower or farther apart. To allow this, the edges of the plates can be bent inward...



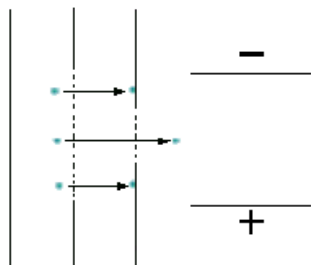
This makes them appear wider electrically. This can also allow close proximity to an EGUN...

Or a sample probe

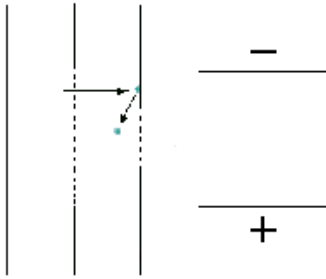


The size of source elements must be controlled to minimize collisions with ions.

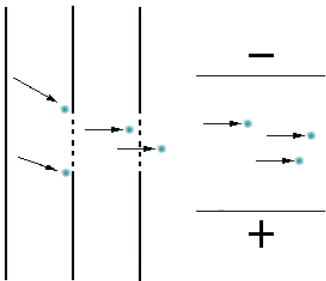
For instance, if the extraction grid is larger than the acceleration grid...



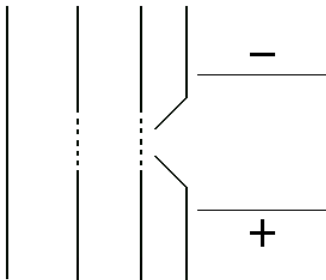
Ions will impact around the edge of the acceleration grid



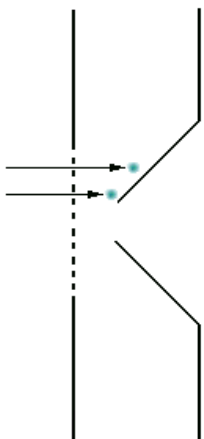
This will form a coating on the face of the grid plate. They can also generate secondary ions, electrons and other collision products which can cause electrical noise and distortion.



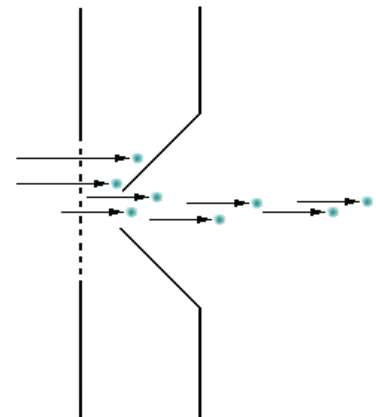
For this reason, grids are made with approximately equal diameters in order to collimate the ion packet.



If it is desirable to reduce the diameter, such as for a pressure differential, a cone shaped orifice can be used. It is sometimes called a skimmer.



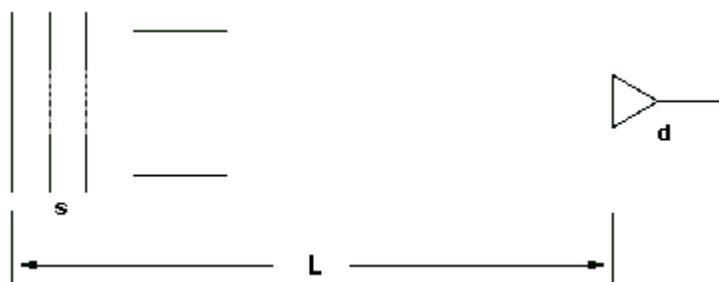
Shown in close up we can see that when ions do hit the skimmer, they will be “around the corner” where contamination and noise are away from the ion beam





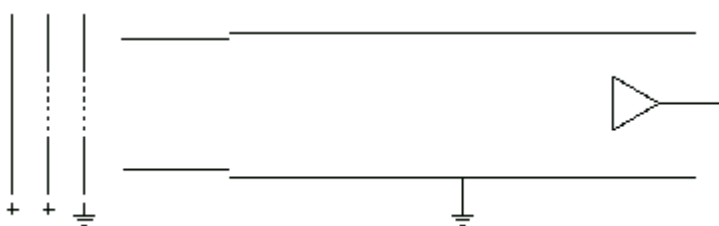
## THE FLIGHT TUBE (Ion Separation)

The flight tube is usually a vacuum enclosure, free of electrical fields, between the ion source and the detector. It is sometimes referred to as a “field free drift region”.

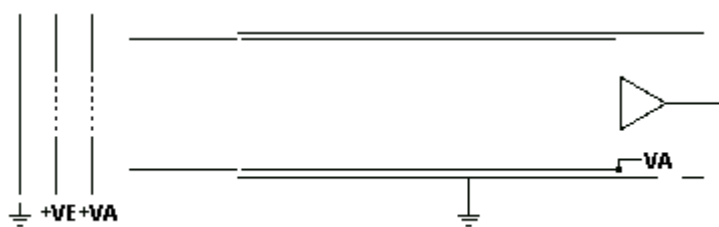


The ions which are under study exit the ion source (s) and enter the flight tube with the proper velocity and direction to arrive at the detector (d)

The flight tube does not usually interact with the ion packets along their flight path (L)



If the ions are created at a positive voltage and accelerated to ground potential, the flight tube can be a simple pipe.



Sometimes the ion source must be at ground, or a different potential from the flight tube. So a shield tube is used to protect the ion packets from the electrical field of the flight tube. This tube is often called a liner. It is usually made from sheet metal and perforated to improve pumping.

## FLIGHT TUBE PUMPING

Adequate pumping is required to prevent the ions from colliding with molecules on the way to the detector. Pumping requirements can be determined by considering several factors.

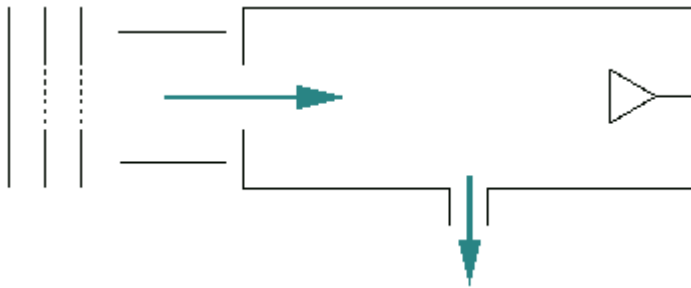


The detector which is usually a microchannel plate, must be operated below  $1 \times 10^{-5}$  torr. This usually determines the maximum allowable pressure in the flight tube.

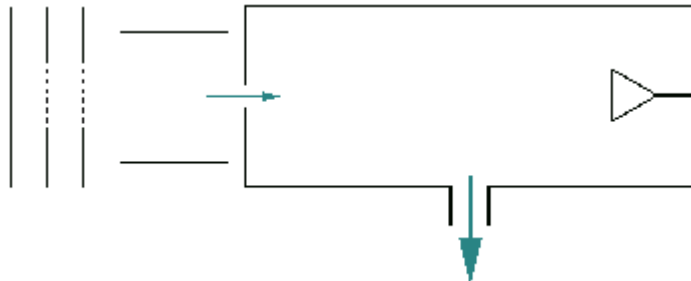


Often the source region is at a suitably low pressure. In this case the flight tube is pumped by the opening into the source region.

If the source pressure is higher than required by the flight tube, supplemental pumping is used to remove in-flow of gas from the source chamber.



This is suitable for moderate increases in source pressure...

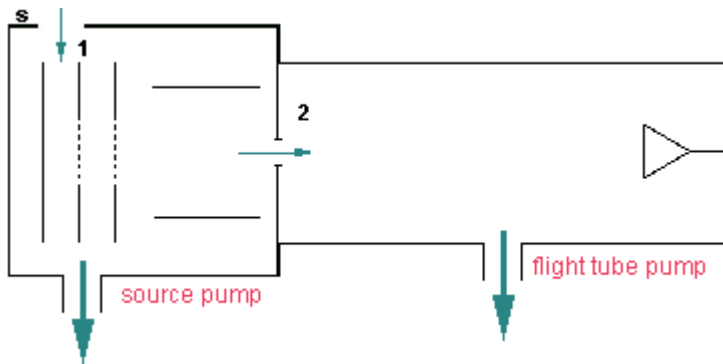


But for higher pressure it is necessary to put a restriction, or pumping impedance between source and flight tube to reduce this flow.

Now let us look at the relationship between the size of the restriction, the speed of the pump and the resulting pressure.

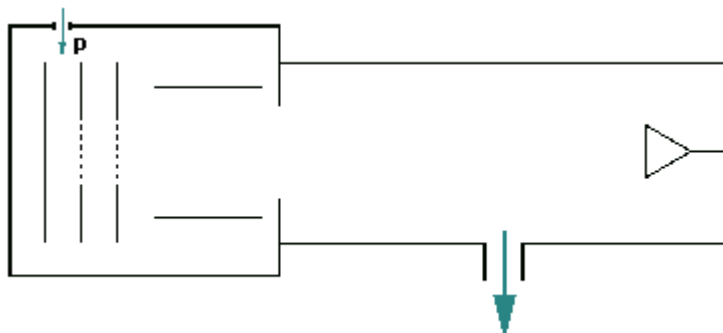
A restriction which is 3mm in diameter will allow about 1 liter/sec to pass into the flight tube. Thus, if the exhaust pump has a net speed of 10 liters/sec., the pressure in the flight tube will be about  $1/10^{\text{th}}$  that in the source. More practical values are a 10mm diameter orifice and 80 liters/sec pump to yield a similar pressure differential.

It can be seen that the upper allowable limit to the source pressure is determined by the maximum size of the vacuum pump on the flight tube.



To control this limit it is sometimes possible to differentially pump the source region by using a shroud (s).

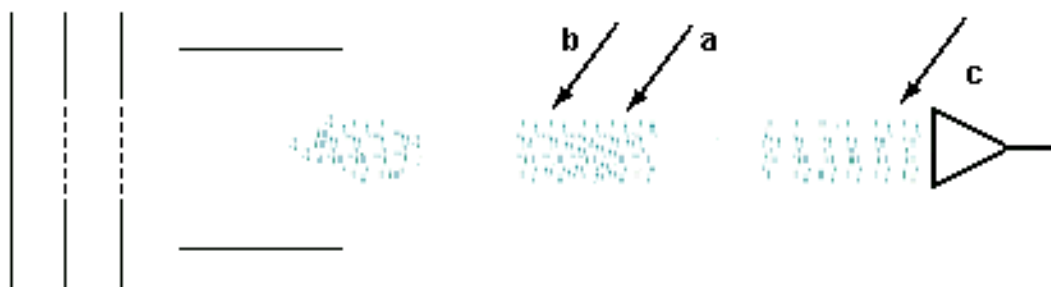
Now the molecular inlet expands into the source region across a primary impedance (1) with a secondary impedance (2) into the flight tube.



If the primary impedance (p) can be made small enough, the source pump and secondary impedance can be deleted.

Now all the pressure differential is at the primary impedance, and the flight tube pump becomes the main pump for the mass spectrometer portion of the experiment.

We will look at this in more detail later when we discuss molecular beams. We have wandered a little bit, so let's get back to what happens in the flight tube.



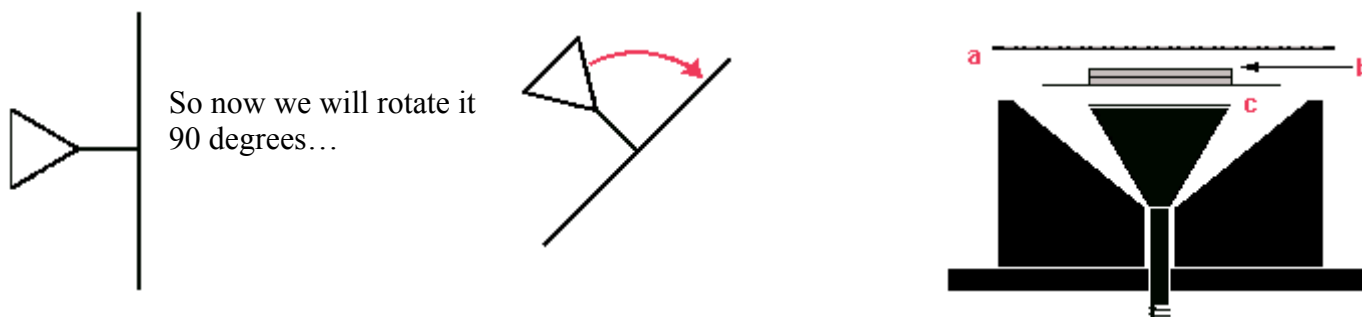
### MASS SEPARATION

Ions are pulsed into the flight tube in short, well defined packets. All the ions are given the same energy in the source. Since the light ones were kicked just as hard as the heavy ones, they will travel faster. The term “kick” may not sound very scientific, but it helps us to understand why their velocities are different.

Since they are traveling at different velocities, the ion packets become strung out as they travel down the flight tube. The light ions (a) in front, and the heavier ones (b) in back. Given sufficient flight time, the ions become separated into individual packets (c) by mass number. The detector amplifies them sequentially, and each packet becomes a mass peak.

### THE DETECTOR (The conversion of ion packets into peaks)

This is a brief, functional description of the detector. Until now we have shown the detector horizontally as a symbol at the end of the flight tube.



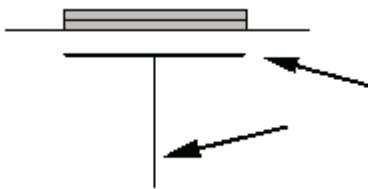
and show it in cross section so that we can see what's inside.

The top element (a) is the entry grid. It is normally at the same voltage as the flight tube liner. It serves two functions. The first is to act as an exact end in space for the drift region. This is the finish line for the ions in their trip down the flight tube. The second function of the entry grid is to shield the flight tube from the high voltages that are used in the detector. This insures a field free drift region all the way to the end of the flight tube.

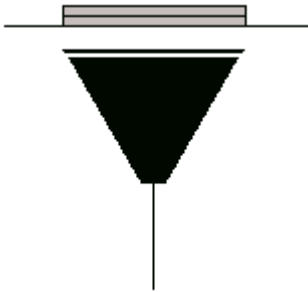
Immediately after passing through the grid, the ions are accelerated to a collision with the top of the first microchannel plate (b), which is at minus 2.2KV. This collision jars loose one or more electrons from the surface of the plate. They, in turn go bouncing down a channel in the plate. At each bounce (collision), additional electrons are liberated. These secondary electrons in turn bounce down the channel, creating still more electrons.

This avalanche continues all the way through the plates so that over a million electrons come out of the bottom of the plates for each ion that hits the front.

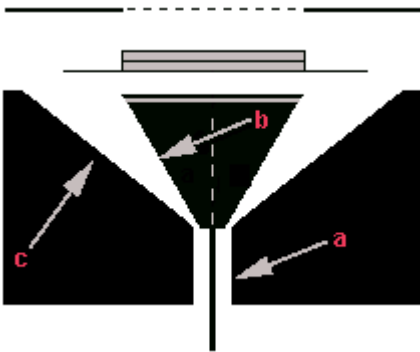
These electrons are collected by a clean, flat plate (c). It is at a voltage that is more positive than the electrons so it is usually called the anode. The signal is now an electrical current passing through a solid metal conductor.



There is one more mechanical design detail, which we should explain. Since the anode is a flat plate, if it were simply connected to the center conductor of the signal cable which is a wire, the sudden change in capacitance from plate to ground and wire to ground would cause ringing.



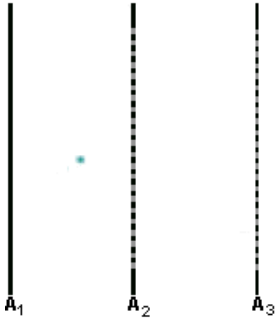
To avoid this, the anode is machined in a funnel shape to make a gradual change from plate to wire



Likewise, the shield of the signal cable (a) must be extended to a gradual taper to enclose the anode (b). There is a precise value for the convergence of the angles (c) to match the impedance of the cable and data system. This impedance is usually 50 ohms.

At this point we have concluded the preliminary tutorial for the Time of Flight aspects of ion creation, separation and their detection. The following is a continuation beyond this basic explanation into a more advanced discussion of ion separation, the use of a reflector and second order focusing.

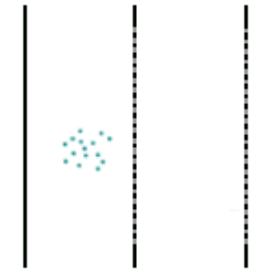
## THE REFLECTOR (Energy compensation and second order focusing)



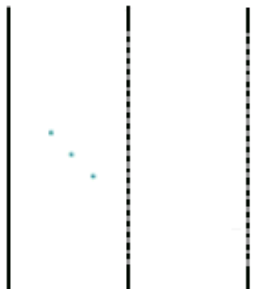
A discussion of the reflector should begin here in the ion source.

You may remember that in our discussion of the ion source, we explained how a normal source can eject ions with different energies.

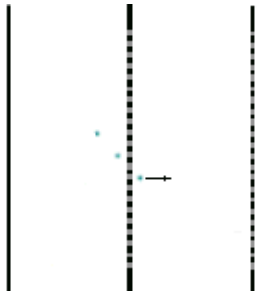
Ions are not usually made at a point, like this...



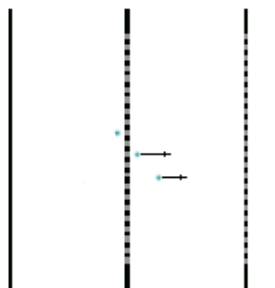
...but in a space, like this.



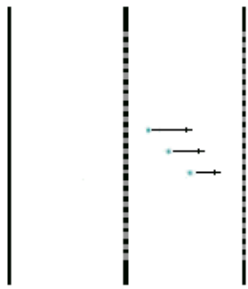
Lets look again at three ions to represent this group.



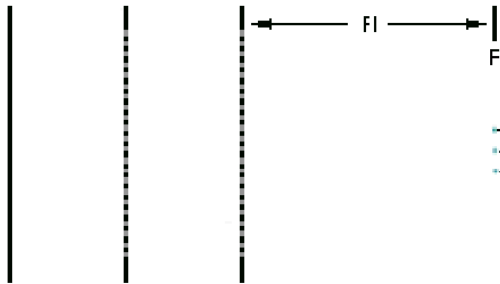
The one that is created nearest the extraction grid will leave first, but will be moving slower.



The middle one will leave later, but will be moving slightly faster.



The farthest one will leave last, but will be moving even faster. The difference in their velocities is sometimes called velocity distribution.



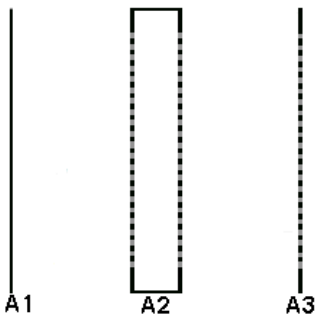
At some point, the faster ions which started late will just catch up with the slower ones.

This point (F), is known as the primary focal point

It can be seen that if the detector could be located at point F, the resolution would be higher. In fact, the width of the ion packet would be at its narrowest point. Unfortunately, the distance F1 in most instruments is only 100mm or so. This is not enough flight time for peak separation to occur. Therefore, the peaks although narrow, would overlap each other in time.

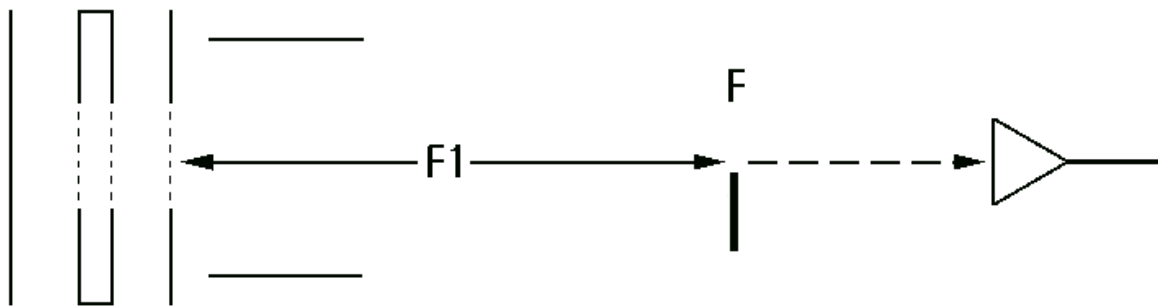
So now for the remaining 90% or so of their flight time, the faster ions will continue to run away from the slower ones. This will cause the width of the ion packets to grow larger. This characteristic of short focal length is the principal limitation to the maximum resolution that can be obtained in a simple linear time of flight instrument.

## SECOND ORDER FOCUSING

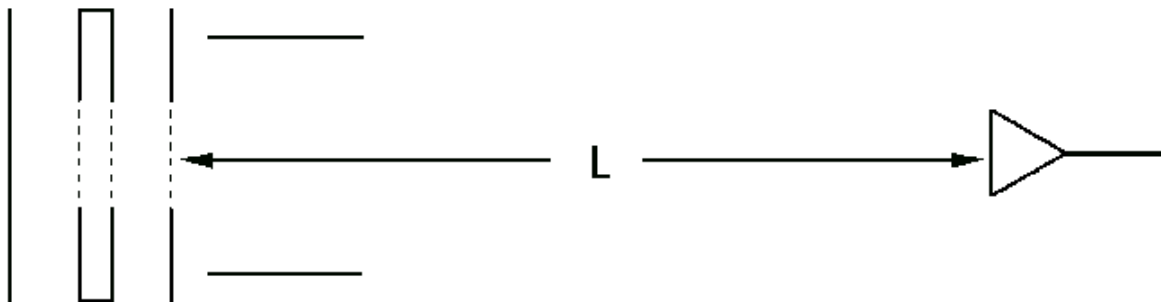


Sometimes the focal length can be increased by adding other lens elements, such as the drift region between the double grid A2 shown here.

Simply put, these elements have the same effect as increasing the head start of the slower ions.

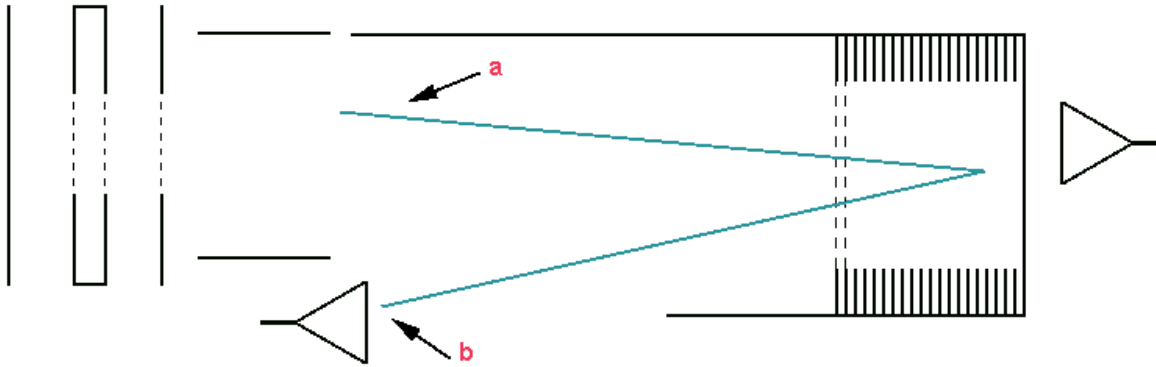


This technique of extending the focal length is useful for increasing resolution, even if the focal point cannot be moved far enough for adequate peak separation. The reason for this is that since the distance between fast and slow ions is now converging at a slower rate between the source and point F, it will also diverge at a slower rate between F and the detector. Also notice that the detector is now closer to F, which also helps. Thus, the resolution can be made higher, even if it is not ideal.



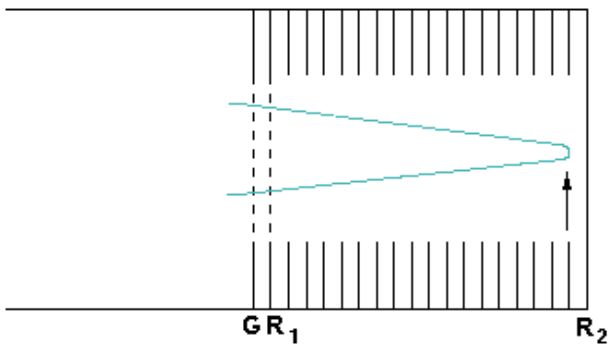
This second order focusing at the source is limited by the fact that such an instrument must be designed for specific, controlled ionizing conditions. In an instrument such as this, source optics, both mechanical and electrical are matched so that the length of the flight path L is exactly equal to the focal length of the source for specific ionizing conditions.

Designing such an instrument for a special purpose can be desirable for commercial applications where ionization conditions are always the same. Doing this can result in a relatively high resolution instrument with a flight path of less than 1/2 meter. As useful as this technique can be, it is not usually adaptable to a general purpose laboratory instrument in which many different ionizing conditions are used in the same instrument.



There is another way to extend the focal length of the instrument. This is with the use of a reflector. When a reflector is used, ions from the source converge until they reach the primary space focus, (a). They then diverge until they penetrate into, and are stopped in the reflector.

They are reflected, and then converge on the way to the secondary, or reflected focal point, (b). Placing the detector at this point has the same benefit to resolution as it did at the primary focal point. The flight times are longer in this case, which allows for adequate peak separation.



Lets take a look inside the reflector to see how it does this

Ions from the flight tube enter the reflector. As they pass through grid (G), which is at flight tube or liner potential, they enter the first stage of the reflector.

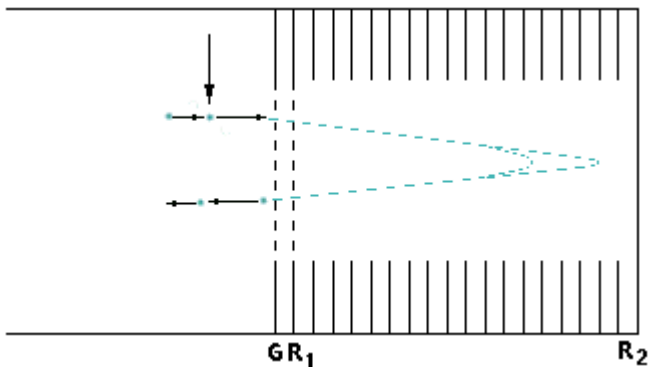
The second grid (R1) is at a voltage that is about 75% of the ion source voltage. It is therefore a decelerating, or retarding field that slows the ions to about 75% of their flight tube velocity.

After they pass through grid R1 into the second stage of the reflector, they are in another decelerating field which is determined by the voltages on R1 & R2. The voltage on R2 is chosen to be a few volts above, or in opposition to the source voltage. This causes them to penetrate almost to R2 and stop.

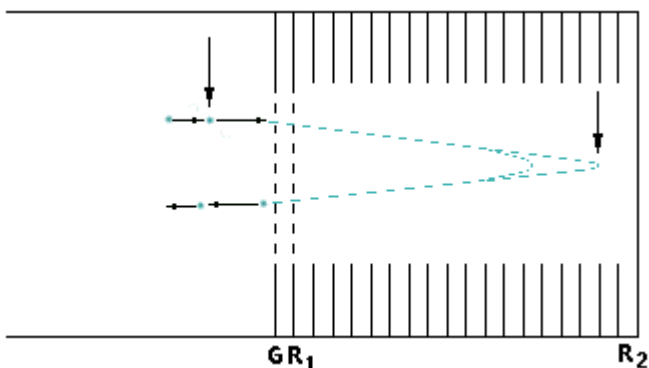
The same electrical fields that slowed the ions down as they entered the reflector will now accelerate them back out of the reflector so that they leave with the same velocity that they entered it.



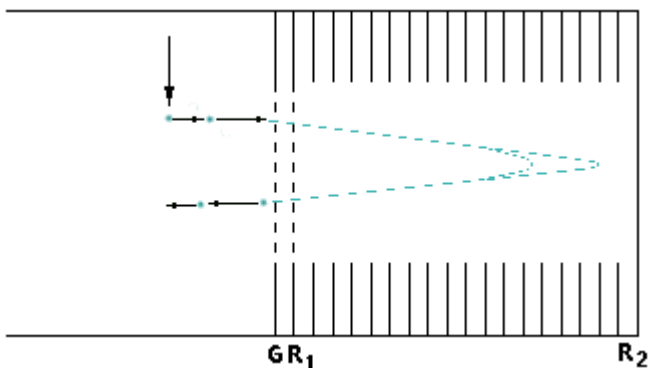
Remember that we said before, that the space between ions of the same mass would decrease, or converge on their way to the reflected, or secondary focal point? This is what makes it happen.



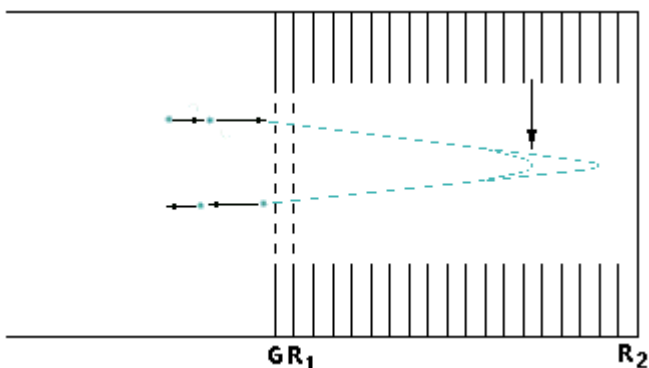
When the ions with the same mass enter the reflector, the ones that are traveling faster will enter sooner,



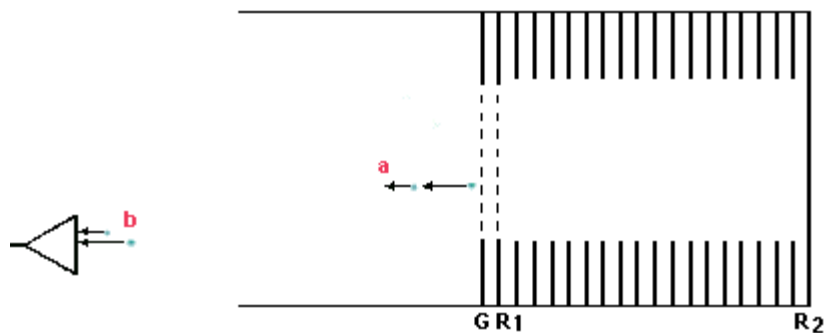
And because of their higher speed, or kinetic energy, will go deeper into the reflector before they stop and turn around.



The less energetic ions enter later,



But do not go as deep before they turn around.



So now we have a situation similar to the ion source, where the slow ions (a) have a head start on their way to the detector, due to their shorter time in the reflector. Because of their longer path length in the reflector, the more energetic ions will leave later, moving faster, and will just catch up at the detector (b).

### ENERGY COMPENSATION

You will notice that in this discussion of the reflector we have been talking about two things, velocity, and energy. The reflector has the ability to both increase the focal length, and to compensate for energy distribution.

If two molecules of the same mass have different axial velocities when they are ionized, the reflector will compensate for an energy difference of up to 20 electron volts. This, at the same time that it is compensating for the difference in that energy which is due to spacial distribution.

It can also be used for energy separation by allowing the more energetic ions to crash, or pass through. This makes it a very powerful tool.

This ends our Time of Flight Tutorial.