RGA Theory Notes

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Overview

The term Quadrupole is derived from the principal mass separation unit, which employs a set of four machined, parallel rods to separate mass ions by mass/charge ratio using a complex electrostatic field.

Applications for quadrupole mass spectrometers vary considerably, covering most disciplines and a large range of physical sizes for the quadrupole rod sets. The term RGA is derived from Residual Gas Analyesr, one of the earliest and most common uses of quadrupole mass spectrometers.

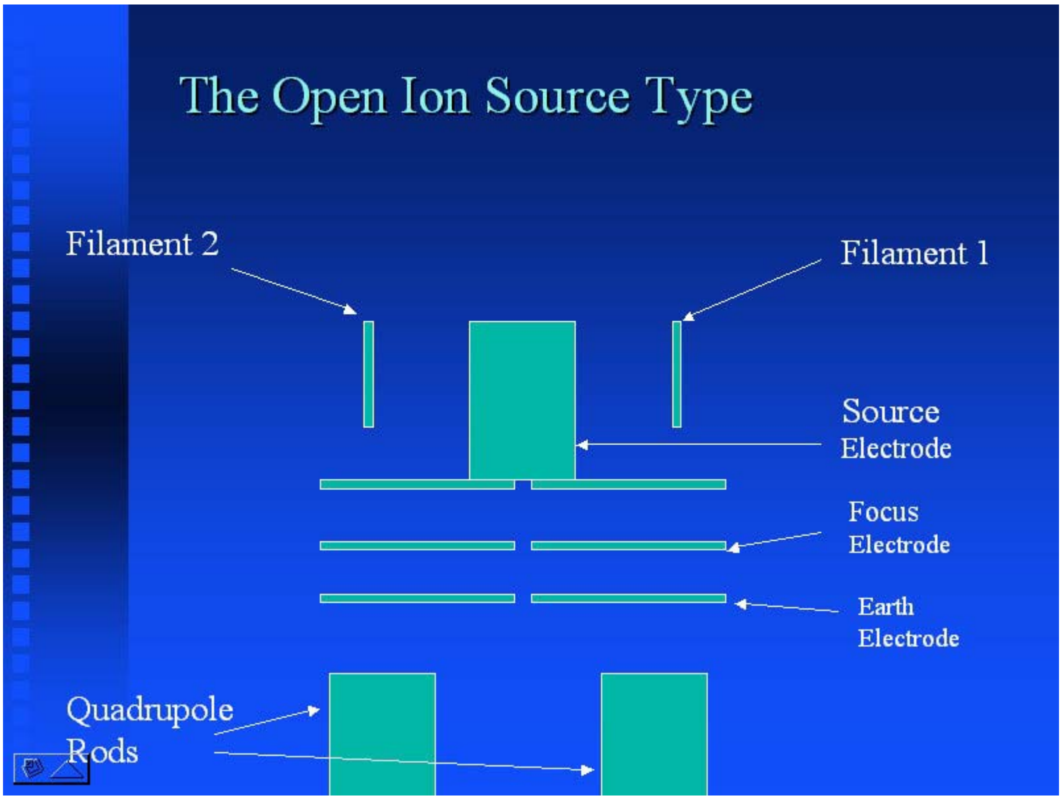
The Quadrupole Residual Gas Analyser is employed to detect and quantify mass ions in a residual gas atmosphere. This will typically be the vacuum system of some other piece of high or ultra-high vacuum equipment in which the composition of the residual gas is significant to quality of operation.

In order to transmit and resolve mass ions, the quadrupole analyser requires a vacuum which is typically better than 5 X10-4 mBA, since many of the types of vacuum apparatus in which quadrupole RGAs are used already have a suitable vacuum range, RGA analysers are typically "bolted-on" to the system, making direct use of the main system vacuum in order to operate.

Design constraints of typical vacuum systems dictate the size of most RGAs and typically, they can be inserted in to a conflat FC-38 port with the associated tube diameter. Since the tube diameter is small, the rod set, Ion Source and Detector elements of the RGA also tend to be small and mounted radially. A perfect design for the quadrupole rod set.

RGA analysers consist of an Ion Source in which mass ions are produced from gas molecules within the source region. A quadrupole mass analyser, often referred to as a "mass filter" which is able to separate ions according to mass/charge ratio and transmit them to the detector. Most RGAs are fitted with a "dual detector" system comprising a Faraday plate and an Electron Multiplier on which the ions emerging from the quadrupole can be measured.

Typical RGA Ion Source

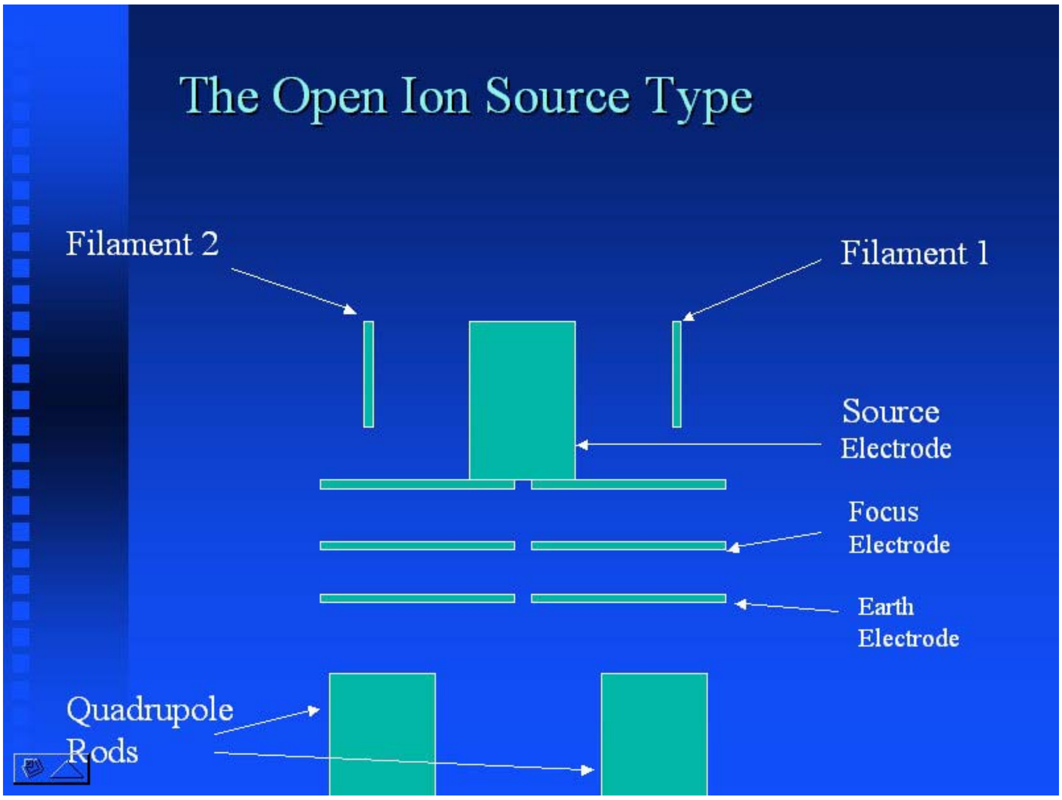


Electron Impact (EI) source overview

Almost without exception, quadrupole RGAs are fitted with an Electron Impact (EI) ion source system. Due to the design constraints, this is generally of a basic radial design and mounted in the first 25mm or so of the analyser assembly.

The figure above, shows a typical cross-section through an Electron Impact open ion source. In this design the ion source is "open" to the residual gas of the vacuum system which surrounds it, hence the term open source.

The source typically consists of a dual filament assembly, with one filament either side of a central mesh electrode. This central electrode is the "source" electrode. Below the source electrode is a focus electrode(s) and generally an earth electrode just above the quadrupole rod set.

1 

Electron Impact (EI) source operation

The drawing above shows a typical EI ion source of the open radial type, which is often fitted to a quadrupole RGA.

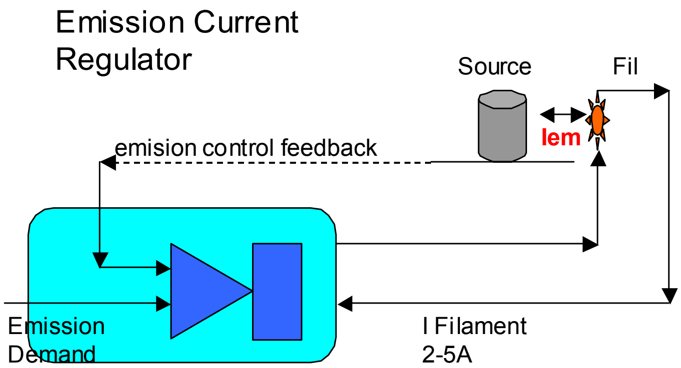
Molecules from the surrounding vacuum chamber are free to pass through the ion source region where they may be ionised by an electron beam.

In order to produce an electron beam capable of ionising the molecules found in the ion source region, one of the filaments is heated. Filaments materials are designed to emit electrons when heated sufficiently. This is done by driving a large heating current (around 2-5A) through the filament. At the same time, a negative potential known as the ***"Electron Energy"*** is applied to the filament. This encourages electrons produced on the surface of the wires to migrate across the space within the ion source.

Some Electrons from the filament will encounter molecules, which may ionise in a number of ways:

- ***Lose a single electron from the outer shell and become a single positive charged Ion***
- ***Lose a second electron and become a double positive charged ion.***
- ***Gain an electron and become a single negative charged ion.***
- ***Fragment to form a number of ions.***

The remaining electrons will encounter the source electrode mesh. Electrons hitting the mesh are monitored by the source control electronics in order to maintain a fixed ***"emission current"*** between filament and source electrode. This current is much lower than the filament current and is typically around 1.5mA.



The emission current regulator operates by sensing the electron emission current between filament and ion source compared to a fixed demand input. The large ***heating current*** in the filament is regulated in order to maintain the desired ***emission current***.

It is essential to maintain the emission current at a constant level since the EI ionisation process is essentially statistical.

The chance of an electron producing an ion in the source is directly related to the number of emitted electrons and the number of available molecules

Thus it should follow that if the number of electrons (the emission current) is maintained at a constant level,

the number of ions produced will be directly related to the number of available molecules in the source region

With the emission current constant therefore, ***the number of ions produced by the source is directly related to the concentration*** of a particular species within the source region. This is a desirable feature in any system, which may subsequently be used to provide quantitative or semi-quantitative analyses.

The ions produced by this process are focused in to the top of the quadrupole fringe-field by a simple lens system, generally consisting of a focus electrode and earth plate.

All of the molecules produced in the ion source by EI ionisation will be focused in to the fringe-field at the top of the quadrupole rod assembly or ***"mass filter"***

If the overall sensitivity of the process is known, the number of ions produced within the ion source for a given emission current can be related to the number of molecules present. Since the number of molecules present within the ion source in typical RGA applications is directly related to the ***"partial pressures"*** exerted by residual molecules within the vacuum system, the number of ions produced may be directly related to the partial pressures exerted.

Raw data from the mass spectrometer is typically collected in Amps, since each individual charged ion reaching the collector will have a charge equal to 1x10-16 coulombs.

It is typical to express the sensitivity of a Residual gas Analyser in terms of Amps per mBA, i.e. the detector current in Amps which will be exerted for a given source pressure in millibar.

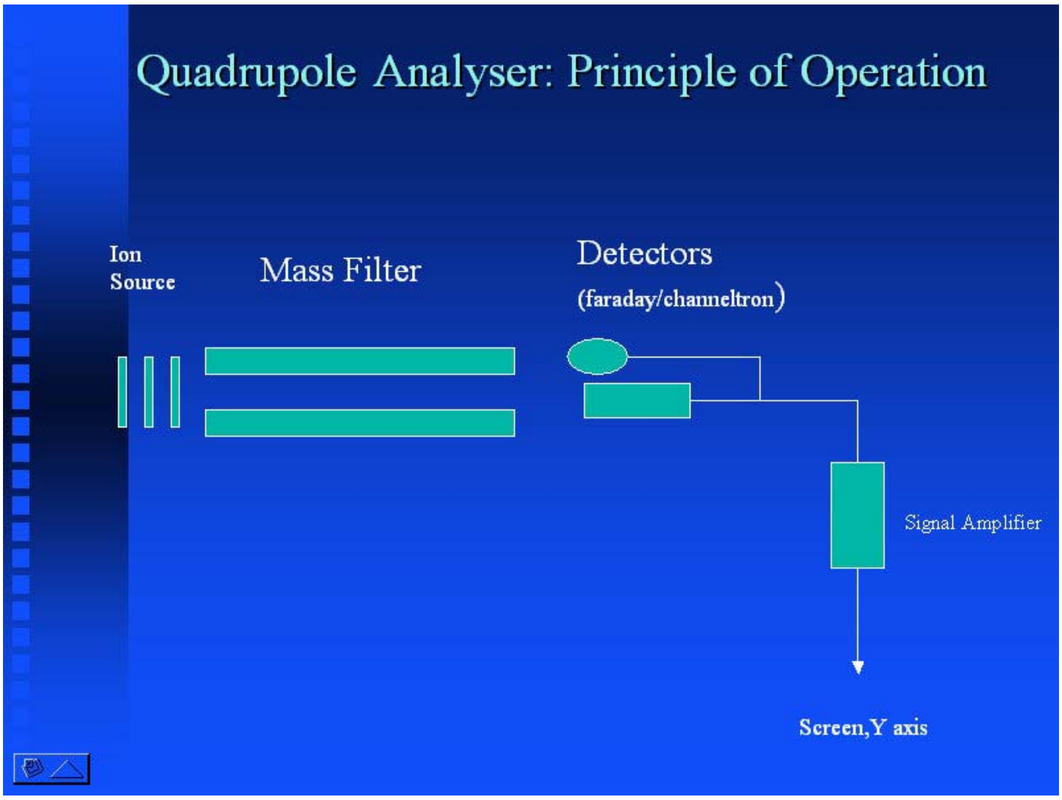
For a typical RGA, this figure will be around

5x10-4 A/mBA

If this value is known and constant, it is possible to express the detected ions in terms of ***pressure units.*** This is often the unit of choice for RGA systems since it can be readily related to a gauge pressure measured in the vacuum system to which the unit is attached.

Since the vacuum comprises the sum of the individual partial pressures exerted by residual molecules, the ability to display these partial pressures on the RGA is fundamental to vacuum system diagnosis.

Quadrupole Analyser (Mass Filter) Overview



Ions emerging from the source region will encounter the quadrupole rod set or ***"Mass Filter"*** system.

This consists of a set of four rods arranged at 90 degree intervals around a circular ceramic spacer. The rods are precision ground and are kept parallel to a very high tolerance, along the length of the ***mass filter.***

A complex RF and DC field is applied to the rod set, with Sine and Cosine of the RF component and positive or negative polarity DC applied to opposing pairs of rods.

For any given physical design of the rod assembly, a stable region for mass transmission can be achieved with a certain combination of RF Frequency, RF Voltage amplitude and DC voltage amplitude.

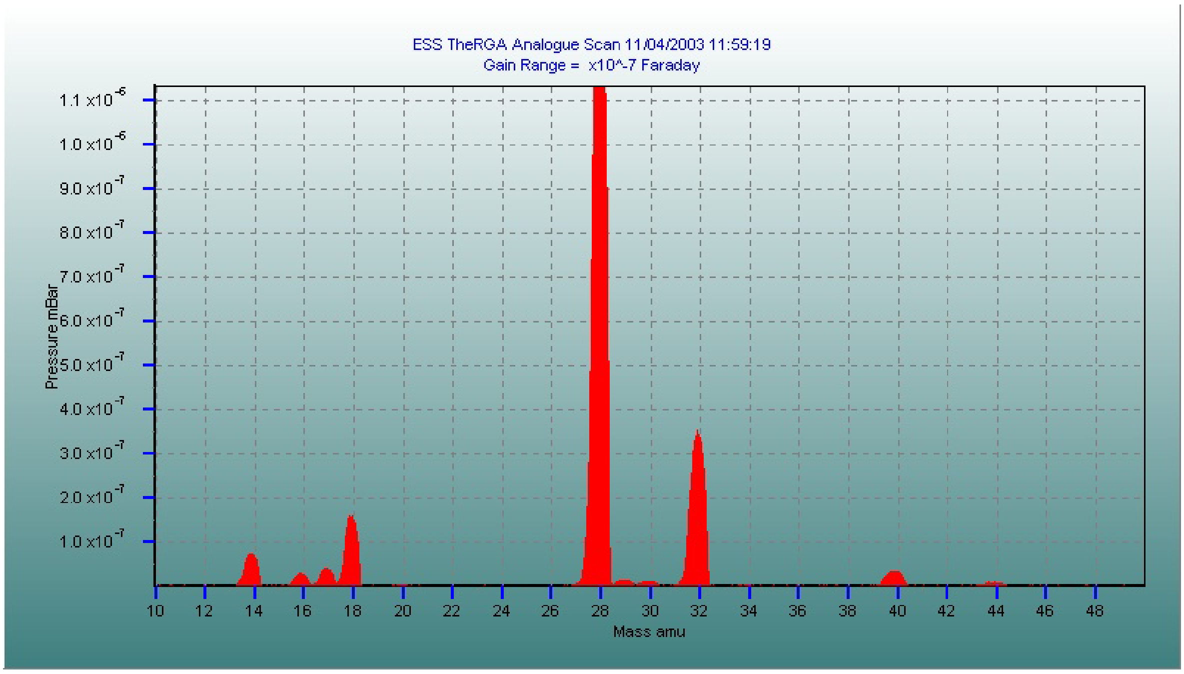
The field along the mass filter can be set by varying the RF and DC amplitudes, whilst maintaining a fixed ratio between RF and DC components.
The ratio of RF and DC is set at a level, which allows a 1AMU wide transmission window. As the combined amplitudes are varied, a stable field for a given mass/charge ratio may be achieved.
Thus, the rod assembly may be considered as a variable 1AMU ***mass filter.***

Ions emerging from the source region are orbiting around the central axis of the analyser assembly. Varying the field on the mass filter will allow a suitable path through the field region for a single mass. Heavier or lighter ions will have trajectories, which cause them to spin out of the central axis path before reaching the detector.

Each mass/charge ratio has a fixed set of RF/DC amplitudes, which will provide a stable path through the mass filter to the detector. As mass/charge increases, the RF/DC amplitude required to provide a stable path through the mass filter increases.

Thus if we slowly increase the RF/DC amplitudes, we will successively focus increasing mass/charge ratios through the stable field. By scanning the RF/DC amplitudes from low to high, it is possible to sequentially focus each mass/charge ratio within the physical design capability of the quadrupole rod set at the detector.

The result is the typical analogue scan data-set in which the RF/DC amplitude at which a peak appears is directly related to mass/charge on the ion and amplitude is directly related to the number of ions produced within the ion source. Since a smooth scan is employed, successive 1AMU wide stable regions are scanned producing a series of Gaussian peaks as individual mass/charges are provided with a stable path through the mass filter field.



A typical RGA mass-scan result.

Summary of key parameters in quadrupole design:

Physical design of the rod assembly

In general terms, the physical size of the assembly in terms of rod diameter and rod length determines transmission and consequently mass range. In general terms, the larger the rod set, the greater the likely mass range.

Frequency of the RF component.

Frequency of the RF component influences mass transmission properties of the mass filter. In general terms, it is typical to lower RF frequency in order to increase the mass range of a given physical design.

RF and DC Amplitude

In general terms the RF and DC voltage component amplitudes increase as mass increases, the actual values required to focus a given mass will be determined by physical design of the rod set.

The ratio of RF and DC voltage components determines the mass transmission window of the mass filter. In general terms, decreasing the DC component relative to the RF component will increase the mass transmission window (decrease resolution) and increasing the DC component relative to RF will reduce the mass transmission window (increase resolution).

The ratio is normally set to give a 1AMU wide transmission window across the mass range. This results in the typical 10% valley resolution between adjacent peaks of equal height.

Two further important conditions can be set by adjusting RF and DC amplitude ratios.

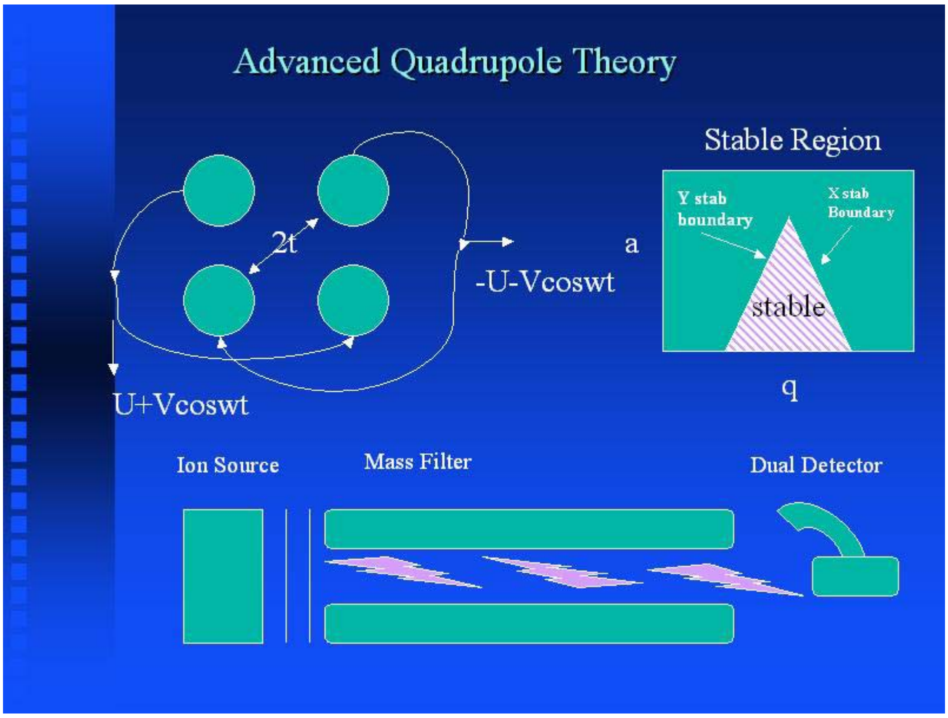
Beam Off

Beam off is a condition which blocks transmission of all ions formed in the source and allows a dark current (zero reading) to be made at the detector. This is achieved by increasing the DC amplitude well above the value required for 1 AMU transmission.

Total Current

If the DC component is removed, theory dictates that all ions formed in the source should be transmitted to the detector. In reality, a broad peak is produced which has a maxima around the mass 28 equivalent RF position. This is often used to take a measure of total ion current or ***"total pressure"*** which can be compared to a system pressure gauge in RGA applications.

Quadrupole Theory in Detail



Let us consider quadrupole mass filter design parameters in a little more detail.

Ions produced in the source tend to form an orbit around the central axis of the analyser in an oscillating fashion. When physical design and electrostatic field parameters are correctly set, it is possible to tune the mass filter to select a single stable path for one mass/charged ion to the detector.

The potential (Φ) required at any point can be written as:

$$\Phi = (U + Vcoswt) (X2\text{-}Y2)\text{-}r\text{-}2$$

Where w = angular frequency and M= the mass of the ion.

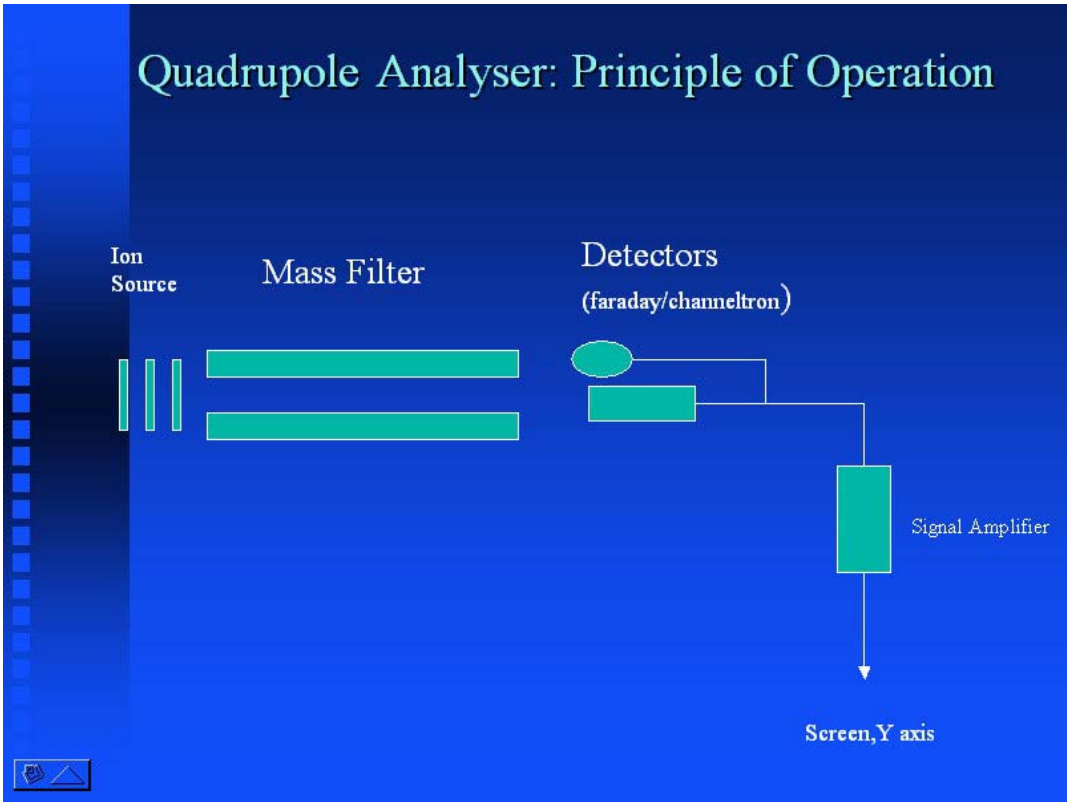
We can map the stable transmission region of the quadrupole by defining two dimensionless parameters "a" and "q" where

$$Q= 2eVo/Mw2r2 \text{ and } a = 4eU/Mw2r2$$

Mapping a / q space reveals stability regions which allow us to optimise the parameters a,q,U,V,w and r. The highest resolution being at the top of the stable region. If the ratio U/V is constant then e/m is proportional to V and the mass scan is linear. Alternate masses are focussed at the detector by varying both U and V but maintaining the ratio U/V

Signal Detection and Amplification

Most RGA analysers are fitted with a ***"dual detector"*** assembly, comprising a Fraday Plate and Secondary Electron Multiplier (SEM or EM) which is used to collect the ions emerging from the mass filter.



Refer to the detector section of the drawing above.

Ions emerging from the mass filter will remain on axis and encounter the Faraday Plate detector.
This is a simple plate on to which the charge from the ions is transferred. The plate is connected to an electronic amplifier which typically takes the form of a straight electrometer amplifier or a charge integration system.

The detected charge from ions at the detector plate is amplified and scaled, typically to be displayed as a "***partial pressure***" signal by the instrument software.

Since the sensitivity is typically around 5x10-4A /mBA, it follows that the signal at the Faraday Plate will be relatively small, especially at low pressures.
This means that at pressures below the 10-10mBA range, the signal to noise ratio for Faraday plate detection exceeds acceptable levels and precludes reasonable acquisition times due to the excessive filtering required to differentiate it.

To get around this problem and increase the useful pressure range of the RGA, a secondary detector is usually fitted. This typically takes the form of an off-axis "***secondary electron multiplier*** " mounted close to the Faraday plate.

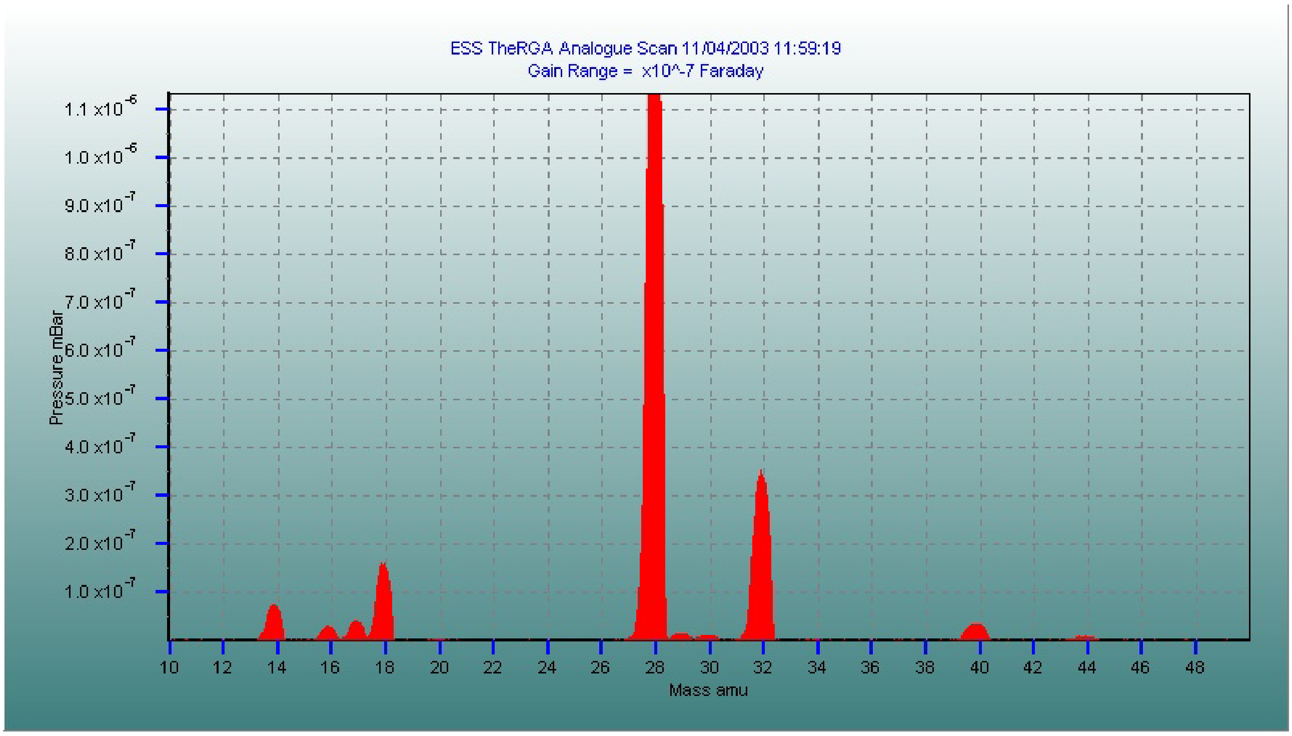
The multiplier has a coating which readily emits secondary electrons. In order to use the multiplier, a large negative potential is applied to the top of the device. This potential attracts the positive ions as they emerge from the mass filter causing them to impact the coating at the top of the device.

The amplitude of this negative potential determines the kinetic energy of the ions as they impact the top of the device. As ions impact the coating, secondary electrons are emitted and an "avalanche effect" takes place along the length of the device. The greatly increased electron signal is then detected by a secondary Faraday Plate at the base of the multiplier and fed to the signal amplifier.

Varying the attraction potential at the top of the multiplier varies the kinetic energy of the ions hitting the top of the device. This in turn determines the intensity of the avalanche effect and consequently the ***"gain"*** along the device.

The attraction potential is typically set to give a gain of between 10+3 and 10+4 times. This allows the amplifier to detect a greater signal from the secondary Faraday plate for a very low ion current at the top of the device. Signal to noise ratio is improved and the detection limit of the anlyser is increased.

Understanding Spectra



The spectra shown above represents a typical result from a Residual Gas Analyser, a number of Gaussian peaks centred on a mass position, with good separation (resolution) and differing intensities. The spectrum represents components within a vacuum system which are often referred to as "Partial Pressures".

Since this spectrum has been produced by Electron Impact Ionisation, some "fragmentation" will be evident along with some "double charging". In understanding the spectrum, it is important to separate these effects.

The spectrum shows peaks for Nitrogen at mass 28, Oxygen at mass 32 Argon at Mass 40 and CO2 at mass 44. The 5:1 ratio of Nitrogen / Oxygen is indicative of an air leak.

The water peaks can be seen at mass 17 & 18 this is a result of electron impact fragmentation of the H2O molecule. A peak from the OH ion is present at mass 17 and H20 at mass 18. Fragmentation is an inevitable result of EI ionisation at electron energies above around 8eV. Fragmentation patterns are fixed and often help to identify components based on the peak ratios within the fragmentation pattern.

The peaks visible at mass 14 and 16 are not fragment ions. These represent double charged Nitrogen and Oxygen molecules. The mass filter transmits ions based on mass / charge ratio. Consequently, double charged ions are transmitted at half the mass.

Glossary of Terms

Double Charged Ion A mass ion produced when a molecule loses two electrons, transmitted at half or the molecular mass.

Dual Detector A detector assembly comprising a combined Faraday Plate and SEM.

Electron Energy The energy applied between the source and filament in an electron impact ion source, the voltage at which electrons are produced for electron impact ionisation.

Electron Impact (EI) ionisation A method of ionisation utilising an electron beam / molecule collision.

Emission Current The current of the electron beam emitted between filament and source in an electron impact ion source. Critical to stable operation and sensitivity.

Faraday Plate An electrode used to capture charge from ions.

Filament (heater) Current A current passed through the filament of an EI Ion Source in order to produce electrons.

Fragmentation (patterns) Fragmentation occurs when molecules are "split" by the high energy (70eV) of the electron beam. This causes a single molecule such as H2O to produce a group of characteristic peaks with known ratios. Often these "Fragmentation patters" are used as a "fingerprint" to positively identify the molecule.

Ion Current The current presented at the detector by ions transmitted through the mass filter, the raw data signal from a mass spectrometer.

Ion Energy The energy of an ion formed within the ion source relative to the ground or float potential of the mass filter

Mass Filter A term often applied to the Quadrupole Analyser because of the way in which it is able to separate mass.

Partial Pressure The pressure contribution from a single component within a vacuum system . E.G Water Vapour.

SEM or EM Secondary Electron Multiplier, a variable gain electron multiplier detection device.

Total Pressure The total pressure within a vacuum system, considered to be the sum of the individual partial pressures exerted.