

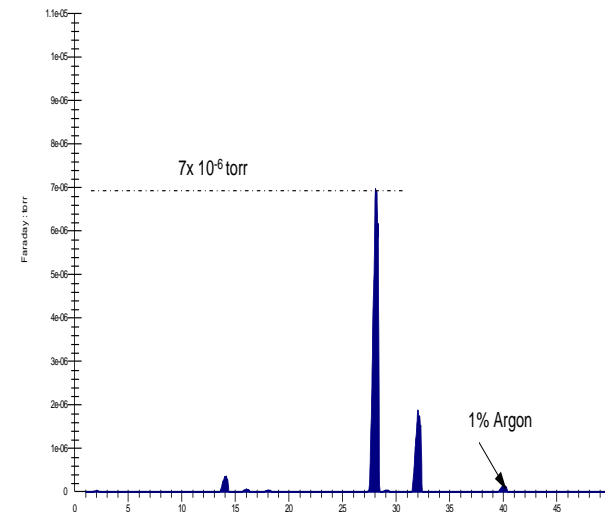
Quadrupole Mass Spectrometry Concepts

Mass Spectrometers for Residual Gas Analysis

Residual Gas Analysis

What does Residual Gas Analysis allow us to do?

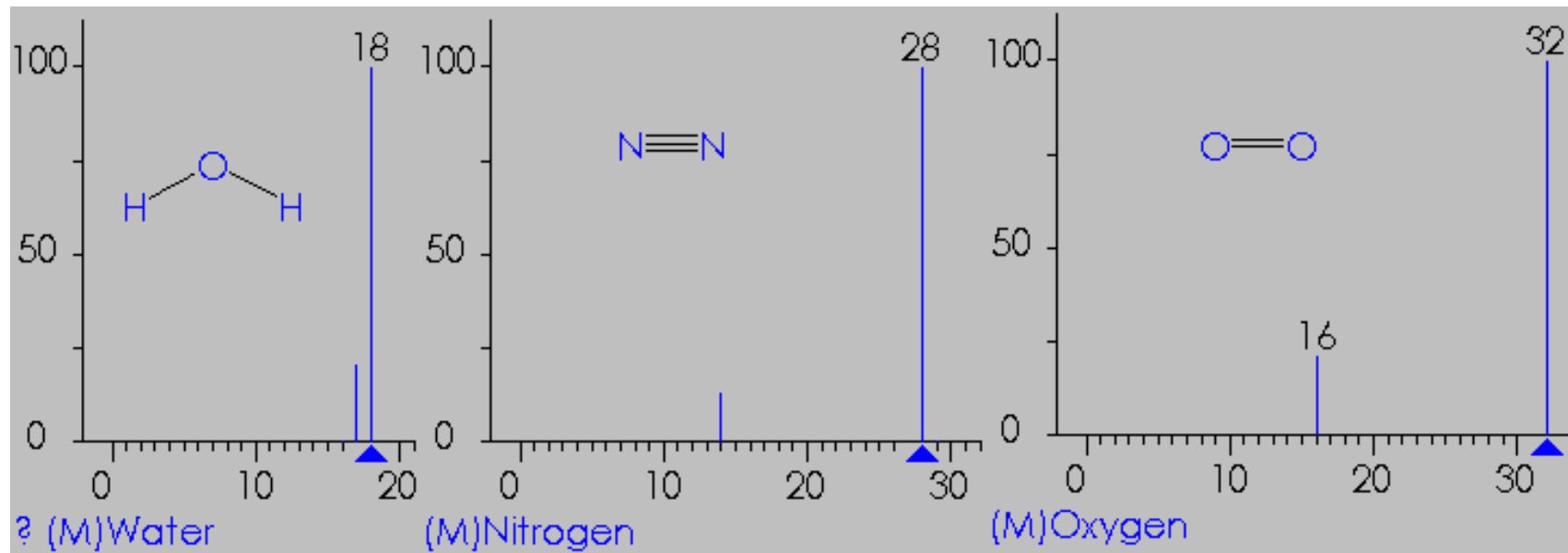
- RGA is the examination of the molecular components present in a vessel or evolved from a system. It allows us to analyse, ON-LINE and in REAL time:
 - Base Pressure Fingerprint
 - Leak Detection
 - Virtual Leaks / desorption
 - Outgassing / Bakeout Cycles
 - Pump Performance
 - Chamber contaminants
- Characterise your system and process for optimum results



Residual Gas Analysis

Typical contaminant species present may be readily identified:

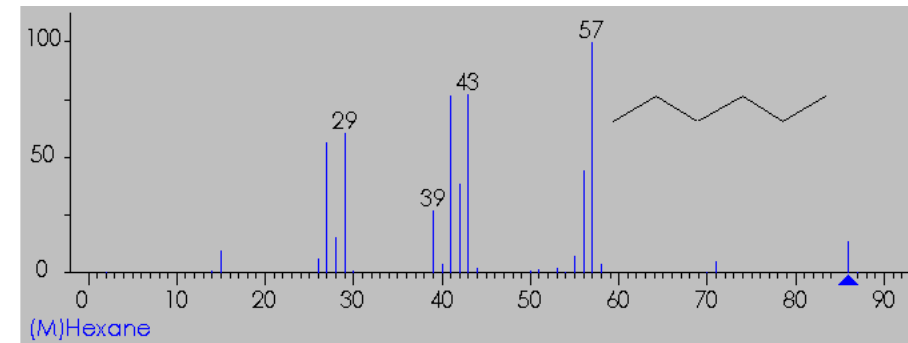
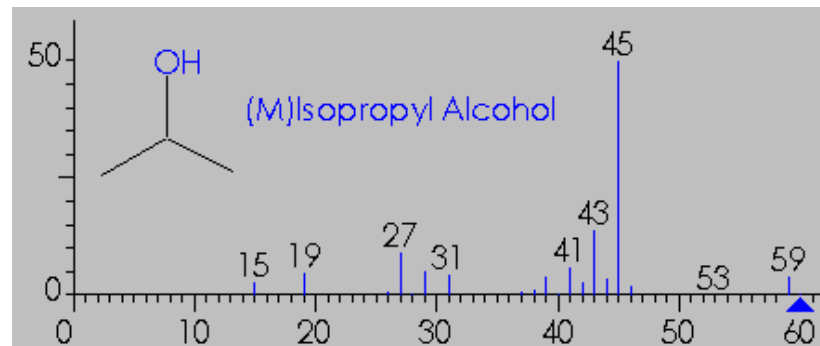
- Air leak: m/e 28 / 32 (ca. 4.5:1 ratio) confirm by the presence of peaks at m/e 14, 16
- Water: m/e 18 confirm by m/e 17



Residual Gas Analysis

Typical contaminant species present may be readily identified:

- Hydrocarbons: characteristic groups of peaks,
typical peaks at m/e 57, 55, 45, 43
- High mass peaks - back-streaming of oil or Vacuum Grease
Low mass peaks - Cleaning fluid / solvent residue



Residual Gas Analysis : How it works

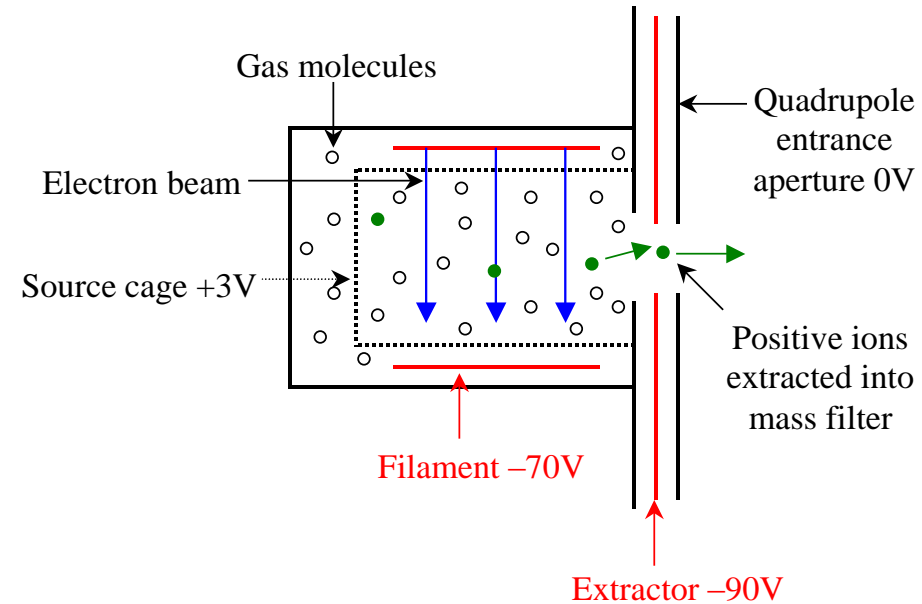
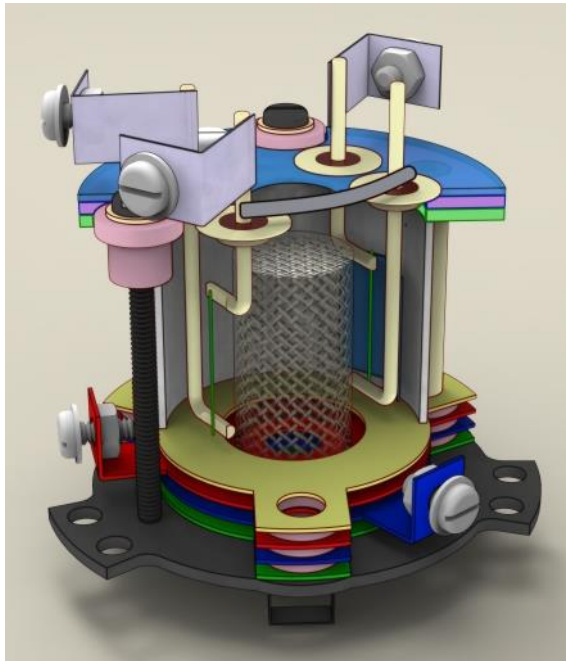
IONISATION – Electron Impact Ionisation (EI)

- Operation depends on the conversion of gas molecules into charged particles, typically positive ions / fragments.
- Achieved by electron impact ionisation via thermionic emission from a hot filament.
- A typical current is 1×10^{-4} Amps.
- Ions extracted into the mass filter.

- *Note:* Ionisation depends on the nature of the species involved.
- If a species is readily ionised it produces a higher MS signal than one which is poorly ionised.
- Use N_2 as a standard, RELATIVE SENSIVITY = 1
- *c.f.* Benzene = 5.9 and Helium = 0.14.

Residual Gas Analysis: How it works

IONISATION – Electron Impact Ionisation (EI)



Residual Gas Analysis

How it works : IONISATION

The choice of filament material is important:

| Material | Operating Temperature | Comments |
|-----------------------------------|-----------------------|---|
| Tungsten | 2400 K | Too hot for RGA use Reacts with oxygen to give CO, CO ₂ |
| Rhenium | 2300 K | Too hot for RGA use Forms compounds which are insulators |
| Thoria (Thoria coated Iridium) | 1900 K | Good general purpose Robust |
| LaB ₆ | 1300 K | Not robust enough for RGA use Very brittle |

Lower operating temperature = lower outgassing

Residual Gas Analysis

How it works : IONISATION

It is also important to note that EI yields several types of ions:

| Ion | Description |
|----------------|---|
| Molecular | The molecule with a positive charge by loss of an electron |
| Base | The most abundant ion in the spectrum |
| Fragment | Formed by cleavage of one or more bonds in the molecule |
| Rearrangement | Formed by bond cleavage and atomic migration |
| Doubly Charged | 2+ Ions from 2 electron loss steps appearing at 1/2 mass i.e. $m/2$ |
| Metastable | Fragmentation of ion into an ion of lower mass + a neutral particle |

See cracking pattern section for further details.

Note: Fragment ions are also known as Product or Daughter Ions

Residual Gas Analysis

How it works : THE MASS FILTER

- The mass filter differentiates the ions produced and selects species for detection.
- The most common form of mass filter is the Quadrupole.
- A Quadrupole is 2 pairs of parallel, equidistant metal rods (poles) biased at equal, but opposite potentials
- These twin potentials contain fixed DC and alternating RF components. By varying the RF component the resultant field produced by the rods may be varied.



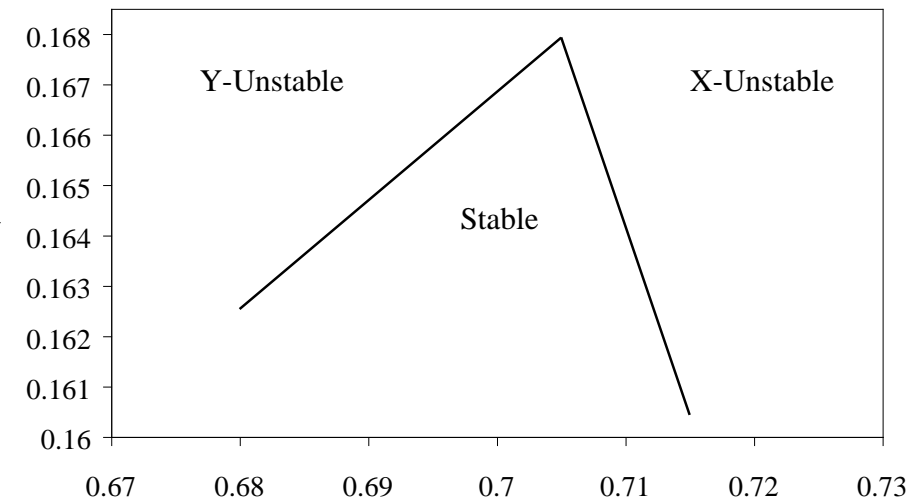
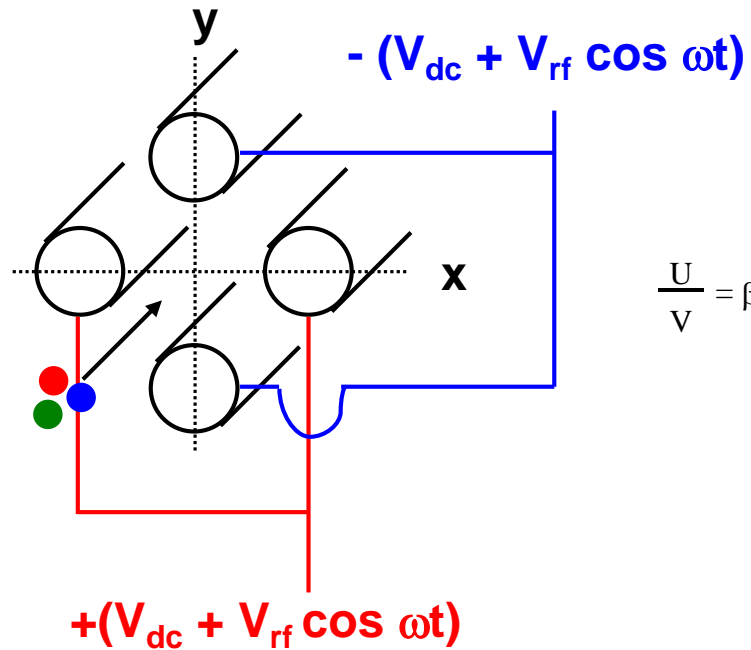
Residual Gas Analysis

How it works: THE MASS FILTER

- Any ions entering the quadrupole field experience potential differences deflecting them from their original trajectory.
- The extent of deflection of any ion entering the field is related to its mass : charge (m/e or m/z) ratio.
- At each interval on the RF scan only one m/e ratio resonates with the field allowing the ion to pass along the z-axis.
- All other species are deflected and neutralised by impact upon the rods of the quadrupole

Residual Gas Analysis

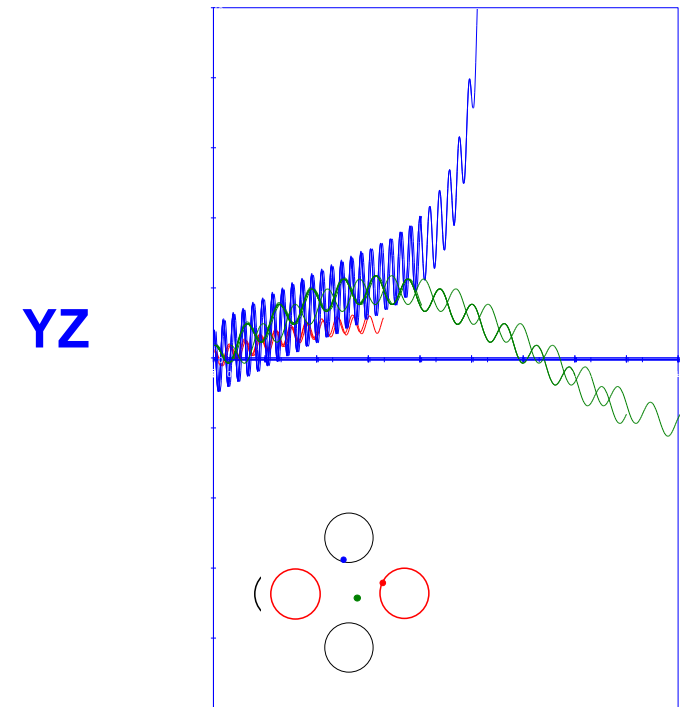
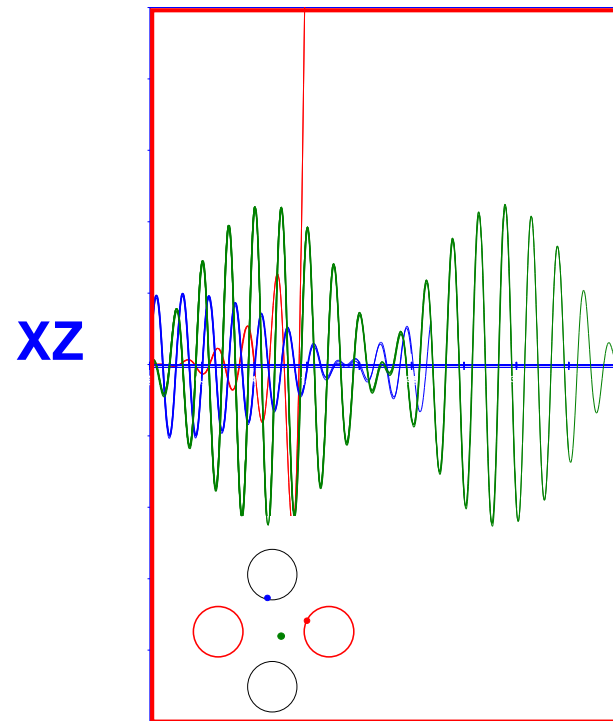
How it works : THE MASS FILTER



$$\frac{4qV}{\omega^2 m r_0^2} = 2\alpha$$

Residual Gas Analysis

How it works : THE MASS FILTER -Mathieu Stability Diagrams



Residual Gas Analysis

How it works : THE DETECTOR

- Filtered ions strike the detector to result in an ion current which is measured by a sensitive amplifier.

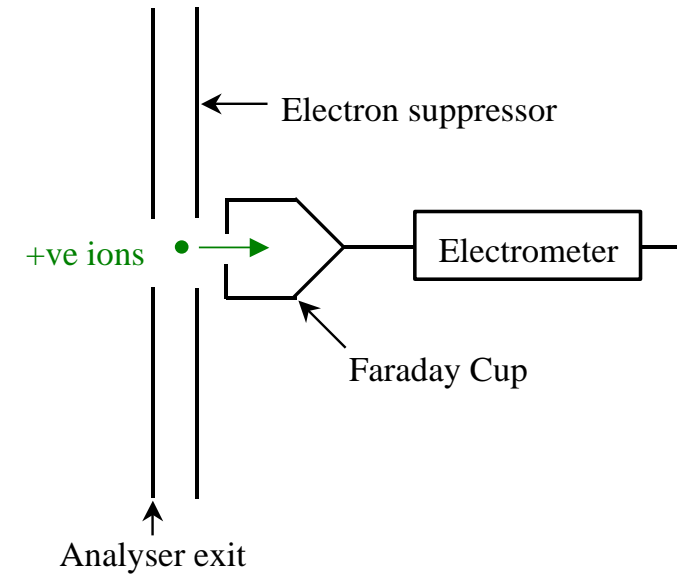
Two main types of Detector:

- **a) The Faraday Cup** – an earthed passive conducting surface with a suppressor electrode to avoid false measurement.
- Fast moving ions strike the cup cause a 'shower' of 'secondary' electrons. The use of the 'cup' rather than a plate, allows all electrons to be collected.
- Hence, one ion arriving at the Faraday needs one electron for neutralisation but causes several electrons to be emitted; this provides amplification – several electrons for each ion.

Residual Gas Analysis

How it works : THE DETECTOR

- The Faraday Cup: Detection limits
- Ion current for N_2 is 10^{-4} amps / Torr
- At 10^{-8} Torr of N_2 ,
 $10^{-8} * 10^{-4} = 10^{-12}$ amps
- At 10^{-11} Torr of $N_2 = 10^{-15}$ amps



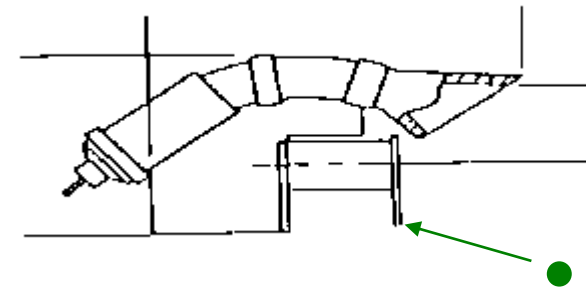
⇒ Detection limit for conventional analogue amplifier

Residual Gas Analysis

How it works : THE DETECTOR

- **b) Secondary Electron Multiplier / Single Channel Electron Multiplier (SEM / SCEM):**
A surface designed to generate secondary electrons.
 - The ion impacts the surface generating 2 or 3 electrons each of which undergo further surface collisions generating more electrons, and so on in a cascade effect.
 - Power for this cascade provided by an applied voltage.
 - Gain is typically 10^3 (10^2 for a channel plate)

Minimum detectable pressure
 10^{-14} Torr to 10^{-13} Torr



Residual Gas Analysis

Detector Pros and Cons:

Faraday Cup :

- Lower cost
- Indestructible
- Accurate

BUT :

- Detection limit 10^{-11} Torr
- Measurement relatively slow near detection limit

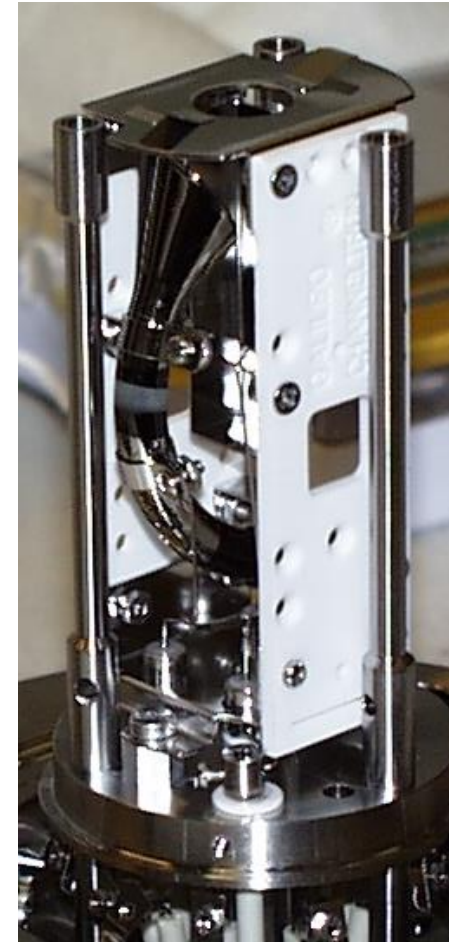
Residual Gas Analysis

SEM / SCEM :

- Detection limit 10^{-14} - 10^{-13} Torr with analogue detection
- Faster measurement

BUT :

- Expensive/Expendable/Sensitivity species dependent
- Sensitivity time / application dependent
- Typical maximum pressure of 10^{-5} - 10^{-6} Torr



Residual Gas Analysis

Resolution :

- The ability to separate /resolve ions of different m/e ratios
- All definitions directly / indirectly relate peak width to height

- *For example:*

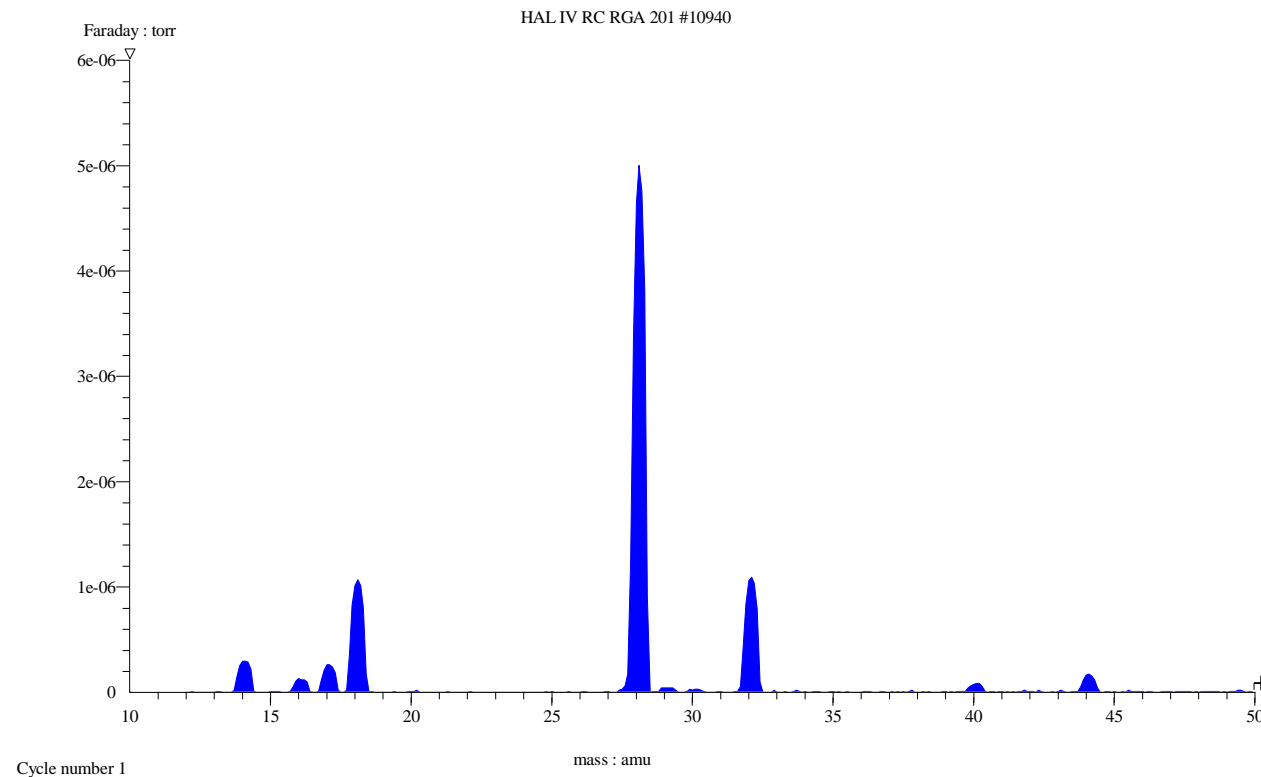
$$M / \Delta M$$

- M at 10% peak height where $\Delta M < 1$ a.m.u.
- *i.e.* For any given mass M, the peak width at 10% of the peak height, measured from the baseline, is less than 1 amu
- This may be complicated if the mass peaks of trace species occur in the peak tail of a major species e.g. the detection of m/e 27 or m/e 29 in the presence of N₂ at m/e 28.

Residual Gas Analysis

Interpretation and Cracking Patterns:

- RGA data can be presented as a profile of mass / charge peaks. e.g. the RGA of Air :



Residual Gas Analysis

Cracking Patterns:

- Cracking arises during ionisation when the high energy electrons used not only ionise species but fragment them. For CO:



This fragmentation can be used to differentiate isobaric species:

$^{12}\text{C}^{16}\text{O}$ from $^{14}\text{N}_2$ for example.

$^{14}\text{N}_2$ has peaks at $m/e = 28$ ($^{14}\text{N}_2^+$) and $m/e = 14$ ($^{14}\text{N}^+$) from:

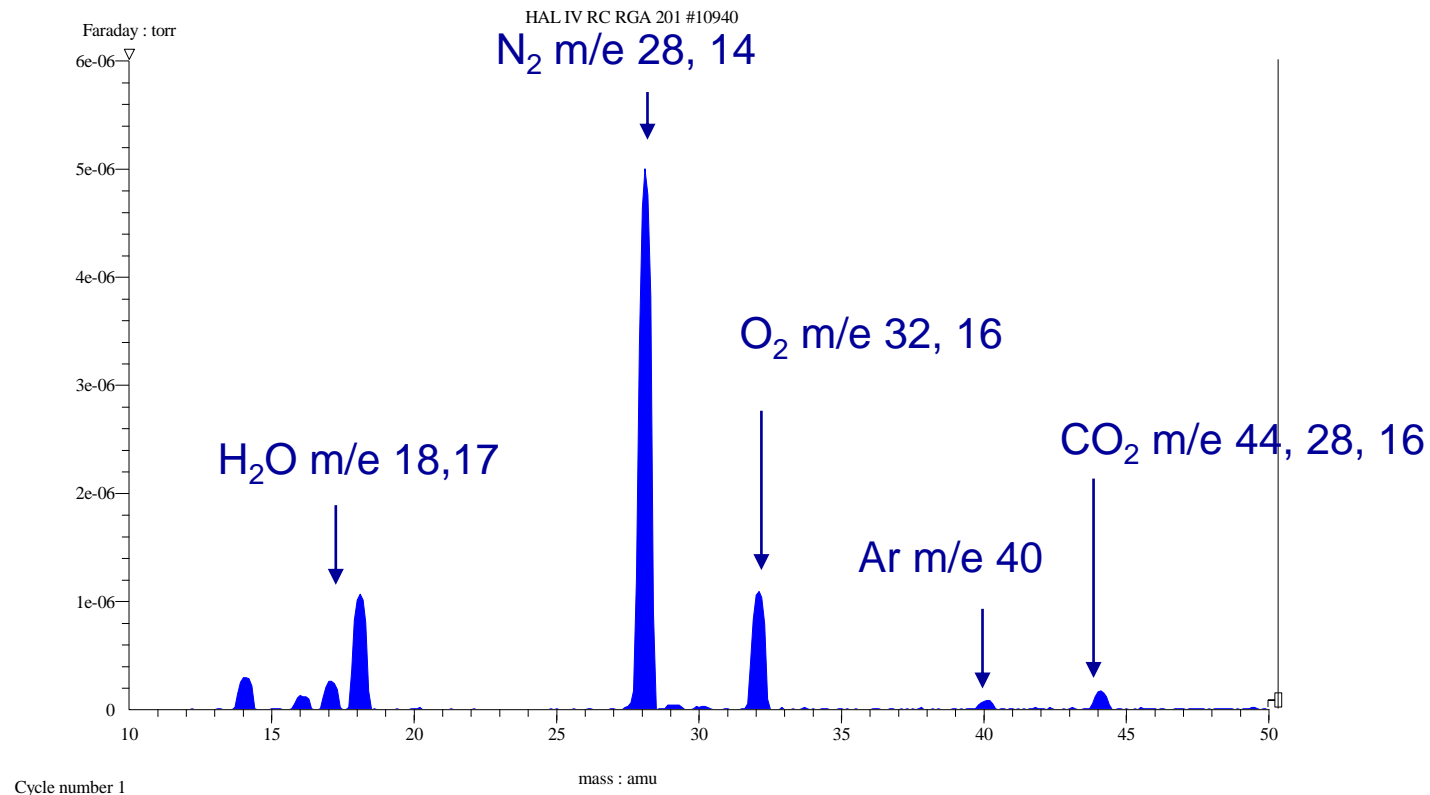


Note: CO/ N_2 are ISOBARIC \Rightarrow the same mass but different composition

Residual Gas Analysis

Interpretation and Cracking Patterns:

- Using Cracking Patterns it is possible to identify all species
- NOTE: The cracking pattern is directly related to the energy of the electrons used i.e. Under normal conditions the Cracking pattern is characteristic of a species



Residual Gas Analysis

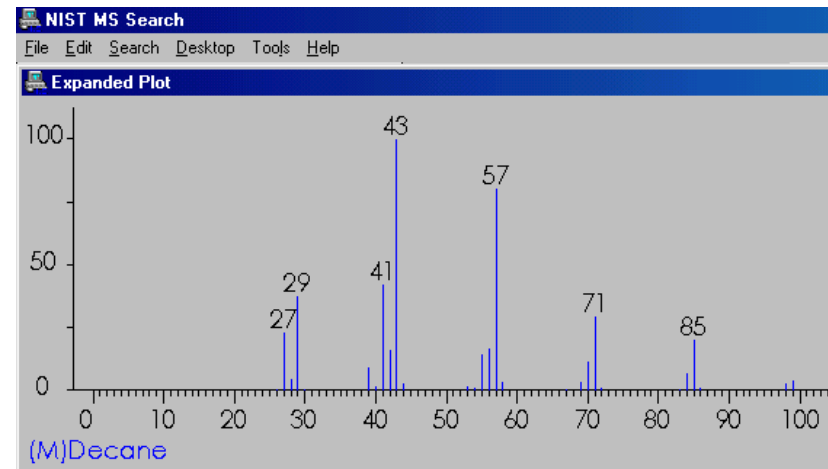
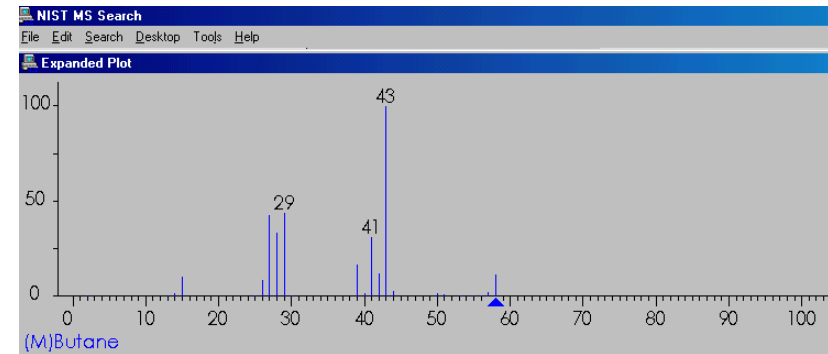
Interpretation and Cracking Patterns:

- Cracking pattern example – Linear Hydrocarbons
- Decane ($C_{10}H_{22}$) and Butane (C_4H_{10}) show similarities – why?

Both compounds show
Clusters of Peaks at:

m/z 57
m/z 43
m/z 29

⇒ Loss of unit of mass 14

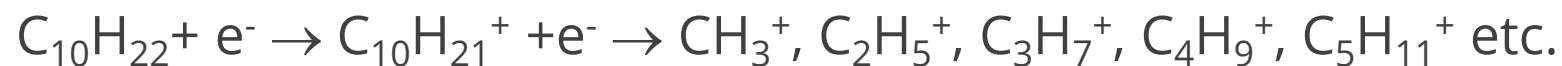


Residual Gas Analysis

Interpretation and Cracking Patterns:

Cracking pattern example

The mass 14 unit \Rightarrow loss of alkyl-type species CH_2 i.e.



And



\Rightarrow FRAGMENTATION – Bond cleavage AND Ionisation.

Residual Gas Analysis

Interpretation:

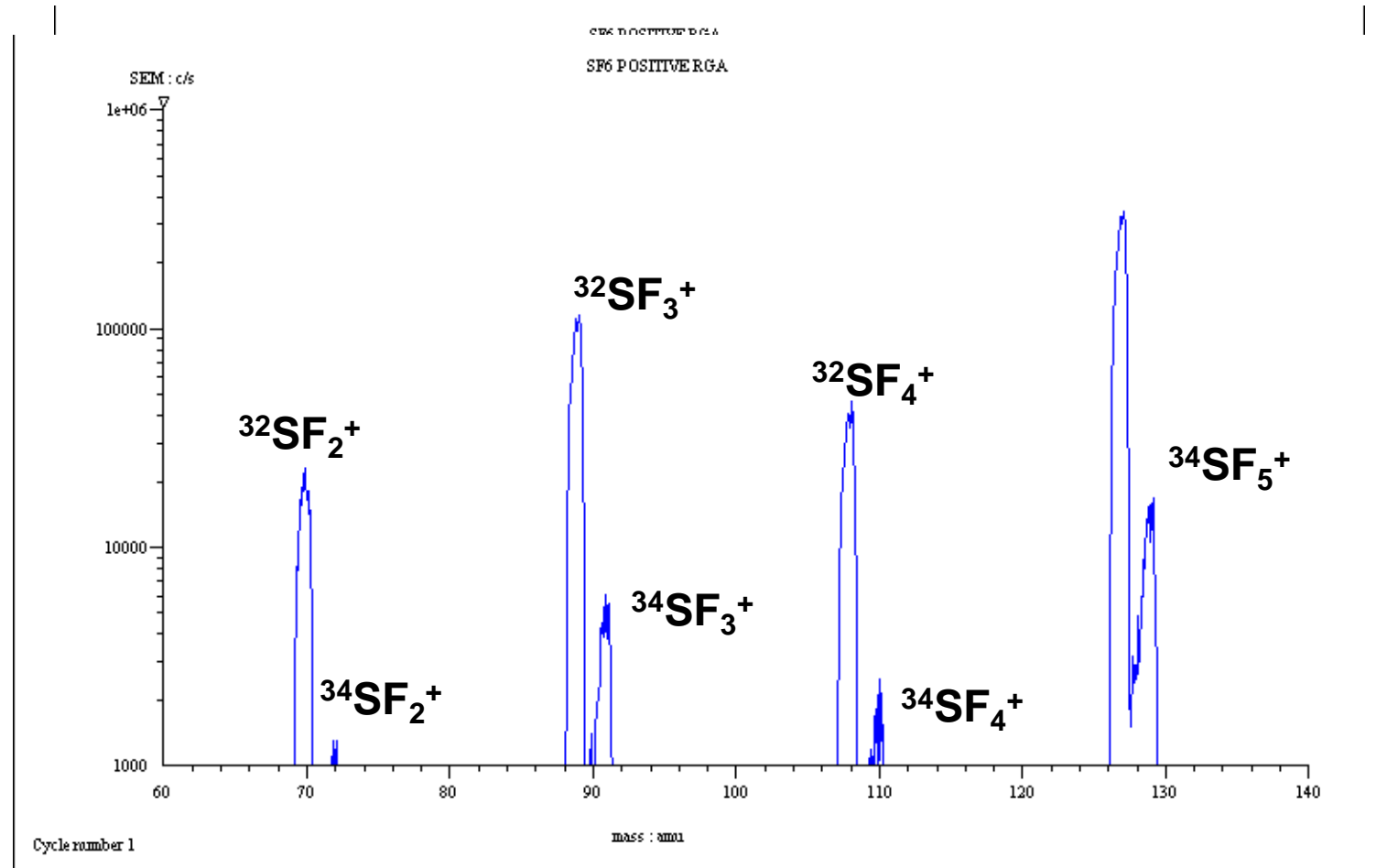
- Isotopic Abundance.
- Many species exist as several naturally occurring isotopes:

| Atom | Isotopes and relative abundances |
|-------------|--|
| Carbon | $^{12}\text{C} - 100, ^{13}\text{C} - 1.1$ |
| Nitrogen | $^{14}\text{N} - 100, ^{15}\text{N} - 0.4$ |
| Oxygen | $^{16}\text{O} - 100, ^{18}\text{O} - 0.2$ |
| Fluorine | Monoisotopic |
| Chlorine | $^{35}\text{Cl} - 100, ^{37}\text{Cl} - 32.5$ |
| Bromine | $^{79}\text{Br} - 100, ^{81}\text{Br} - 98$ |
| Iodine | Monoisotopic |
| Phosphorous | Monoisotopic |
| Sulfur | $^{32}\text{S} - 100, ^{34}\text{S} - 4.4$ |
| Silicon | $^{28}\text{Si} - 100, ^{29}\text{Si} - 5.1, ^{30}\text{Si} - 3.4$ |

Residual Gas Analysis

Interpretation :

- Isotopic Abundance eg: Sulfur isotopes in the MS of SF₆



Residual Gas Analysis

Interpretation:

- General steps in interpretation of a Mass Spectrum.
 1. Look for the Molecular Ion(s)
 2. Note the general appearance of the spectrum
 3. Check spectrum for peak clusters for Isotope patterns
 4. Check for low-mass neutral fragment loss e.g. CH_2
 5. Check for characteristic low-mass fragments
 6. Compare to reference spectra

Quadrupole Mass Spectrometers

Hiden manufactures a wide range of MS systems, all tailored to specific customer applications.

Options include:

- Mass Ranges of 50, 100, 200, 300, 510, 1000 and 2500 amu
- Ioniser options including cross-beam, gold plated and platinum
- Detectors: Faraday, and electron multipliers, channelplate, channeltron, analogue current measurement and digital pulse ion counting options.
- 6mm, 9 mm or 12mm pole diameter
- Single and triple filter options
- Ethernet, USB, and serial comms.



Hidden Gas Analysers

- Rugged modular construction with precision machined radial ceramic rod supports
- Powerful processor with data buffering for true multi-tasking operation
- Ion blast free for maximum sensitivity in He leak detection
- Detection to 5×10^{-14} Torr / PPB levels
- Bench, cart or console mounted
- Fully automated operation
- Application specific gas inlets
- Corrosive gas / oil free pumping
- Multi-stream options
- Quantitative gas analysis



Appendix 1

- Table 1a gives some of the common RGA contaminants

| Name | Formula | Peak 1 | | Peak 2 | | Peak 3 | | rel sens |
|----------------------|---------------------------------|--------|-----|--------|----|--------|-----|----------|
| | | m/e | % | m/e | % | m/e | % | |
| Acetone | C ₃ H ₆ O | 43 | 100 | 58 | 33 | 15 | 20 | 3.6 |
| Air | | 28 | 100 | 32 | 27 | 14 | 6 | 1.0 |
| Ammonia | NH ₃ | 17 | 100 | 16 | 80 | 15 | 8 | 1.3 |
| Argon | Ar | 40 | 100 | 20 | 16 | 36 | 0.3 | 1.2 |
| Benzene | C ₆ H ₆ | 78 | 100 | 77 | 19 | 52 | 16 | 5.9 |
| Boron Trichloride | BCl ₃ | 81 | 100 | 58 | 33 | 15 | 20 | 1.0 |
| Carbon Dioxide | CO ₂ | 44 | 100 | 16 | 9 | 14 | 6 | 1.4 |
| Carbon Monoxide | CO | 28 | 100 | 12 | 5 | 16 | 2 | 1.05 |
| Carbon Tetrafluoride | CCl ₄ | 69 | 100 | 50 | 12 | 19 | 7 | 1.0 |
| Diborane | B ₂ H ₆ | 26 | 100 | 27 | 97 | 24 | 90 | 1.0 |
| Ethane | C ₂ H ₆ | 28 | 100 | 27 | 33 | 30 | 26 | 2.6 |
| Fomblin Oil | | 69 | 100 | 20 | 28 | 16 | 16 | 1.0 |
| Freon 12 | CCl ₂ F ₂ | 85 | 100 | 87 | 32 | 50 | 16 | 2.7 |
| Helium | He | 4 | 100 | | | | | 0.14 |
| Hydrogen | H ₂ | 2 | 100 | 1 | 2 | | | 0.44 |

Appendix 2

- Table 1b gives more common RGA contaminants

| Name | Formula | Peak 1 m/e % | Peak 2 m/e % | Peak 3 m/e % | rel sens |
|-----------------------|--------------------|-----------------|-----------------|-----------------|-------------|
| Hydrogen Chloride | HCl | 36 100 | 38 32 | 35 17 | 1.6 |
| Hydrogen Sulfide | H ₂ S | 34 100 | 32 44 | 33 42 | 2.2 |
| Krypton | Kr | 84 100 | 86 31 | 82 21 | 1.7 |
| Methane | CH ₄ | 16 100 | 15 85 | 14 16 | 1.6 |
| Methanol | CH ₃ OH | 31 100 | 32 67 | 29 65 | 1.8 |
| Neon | Ne | 20 100 | 22 10 | 21 0.3 | 0.23 |
| Nitrogen | N ₂ | 28 100 | 14 5 | 29 1 | 1.0 |
| Oxygen | O ₂ | 32 100 | 16 9 | | 0.86 |
| Phosphine | PH ₃ | 34 100 | 33 33 | 31 32 | 2.6 |
| Pump Oil | | 57 100 | 55 73 | 43 73 | 1.0 |
| Silane | SiH ₄ | 30 100 | 31 78 | 29 29 | 1.0 |
| Silicon Tetrafluoride | SiF ₄ | 85 100 | 86 5 | 28 4 | 1.0 |
| Sulfur Dioxide | SO ₂ | 64 100 | 48 50 | 32 10 | 2.1 |
| Water | H ₂ O | 18 100 | 17 21 | 16 2 | 0.9 |
| Xenon | Xe | 132 100 | 129 98 | 131 79 | 3.0 |