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Plasma Diagnostic Techniques
Mass Spectrometry and Retarding Field Analysers

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Learning Objectives

A mass spectrometer is made up of three distinct regions:

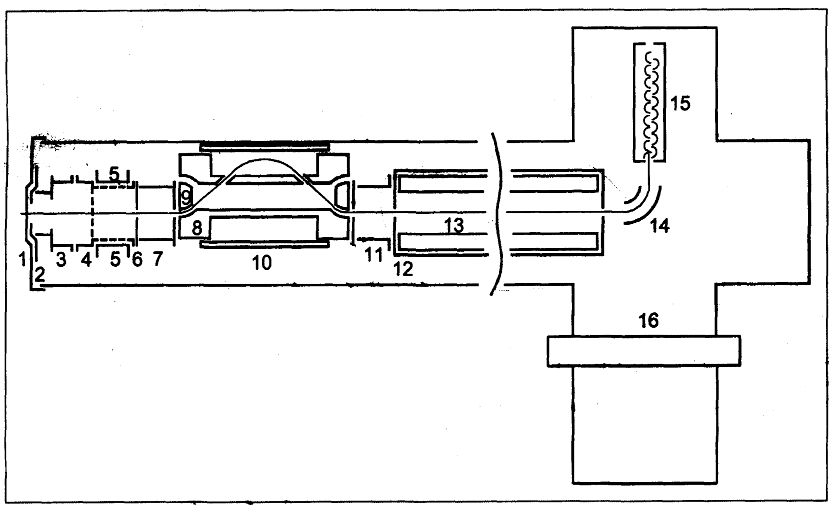
- The ionisation chamber
- The analyser
- The detection system

By the end of this lecture you should understand how each of these regions operate and why they are necessary.

You will also be able to recommend which type should be used for different diagnostic purposes.

Mass spectrometry

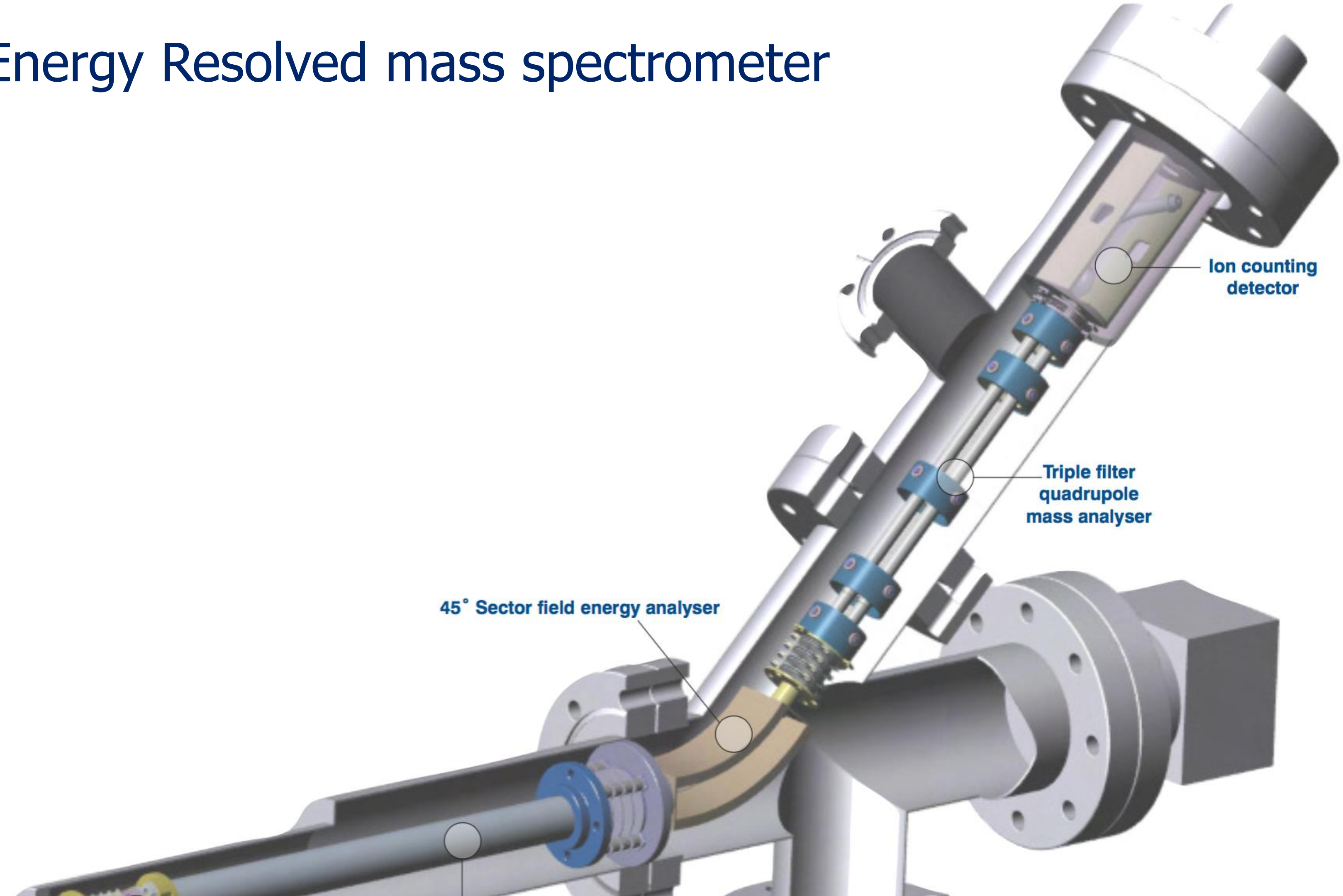
- neutral particles and ions
- energy distribution functions
  - + non-intrusive
  - + direct
  - – complicated in detail
  - – external measurement
  - – reactive gases

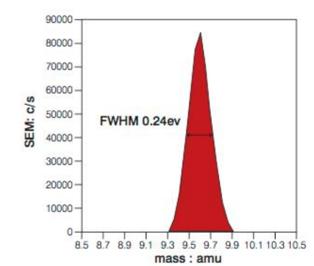


Schematical drawing of the PPM 422

1 Extraction hood
2 Grounded safety electrode
3 Entry lens (ENTRY)
4 Ionization chamber
5 Filament
6 Extraction electrode (EXTR)
7 Focus lens (FOC1)
8 Inner cylinder
9 Inflection element
10 Outer cylinder
11 Focus lens
12 Case
13 Rod system
14 Deflection unit
15 Secondary electron multiplier
16 Pumping port

Ion Energy Resolved mass spectrometer





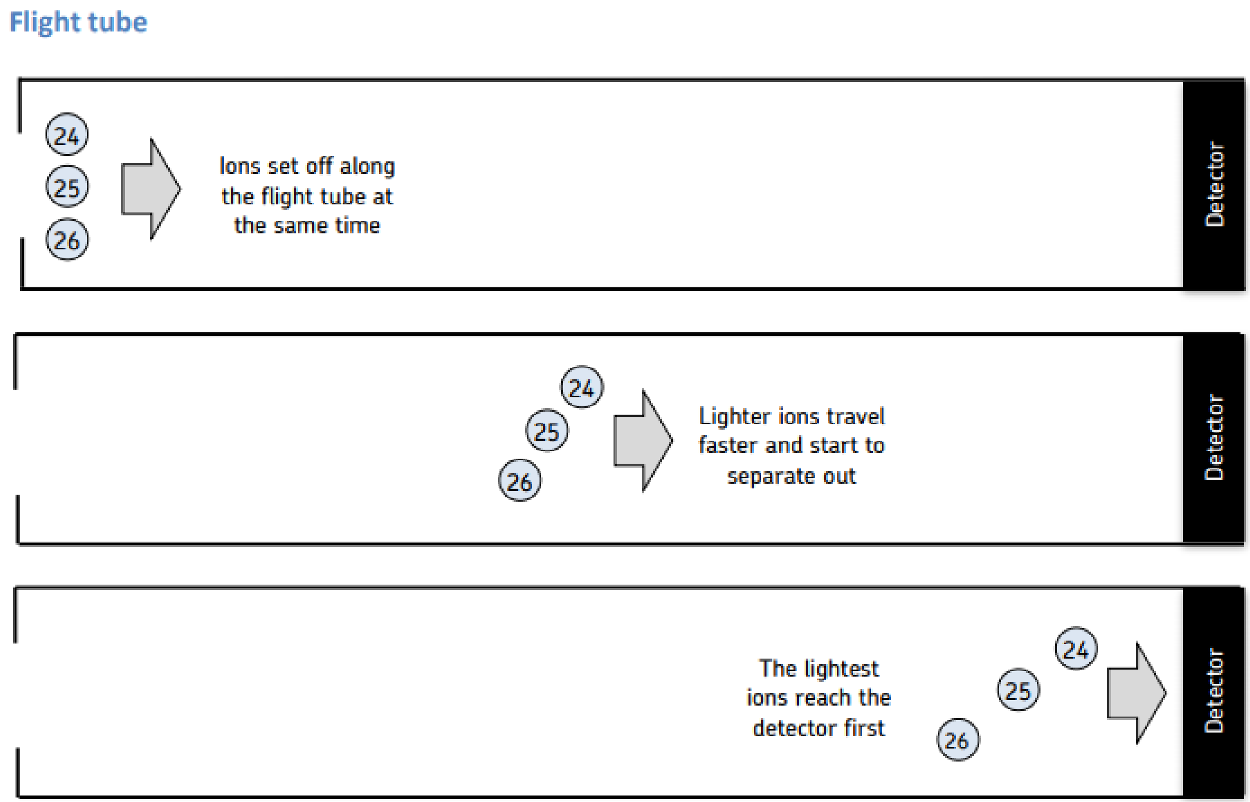
EQP Energy Resolution

http://www.hidenanalytical.com/wp-content/uploads/2016/06/EQP-plasma-ion-mass_energy-analyser-brochure.pdf

Time of Flight Mass spectrometry

A very well known example of mass spectrometry, so much so you probably covered this in school!

- The analyser portion for this mass spectrometry is very simple.
- Allow the charged particles to drift along a flight tube.
- The ions will be detected at the end separated by their mass-charge ratio.



http://filestore.aqa.org.uk/resources/chemistry/AQA-7404-7405-SG-TOFMS.PDF

Ionisation Chamber

- In order for the particles to experience the electrical field they must be charged.
- Many of the species we are interested in may be charged already, however, for the neutral species we need to ionise them.

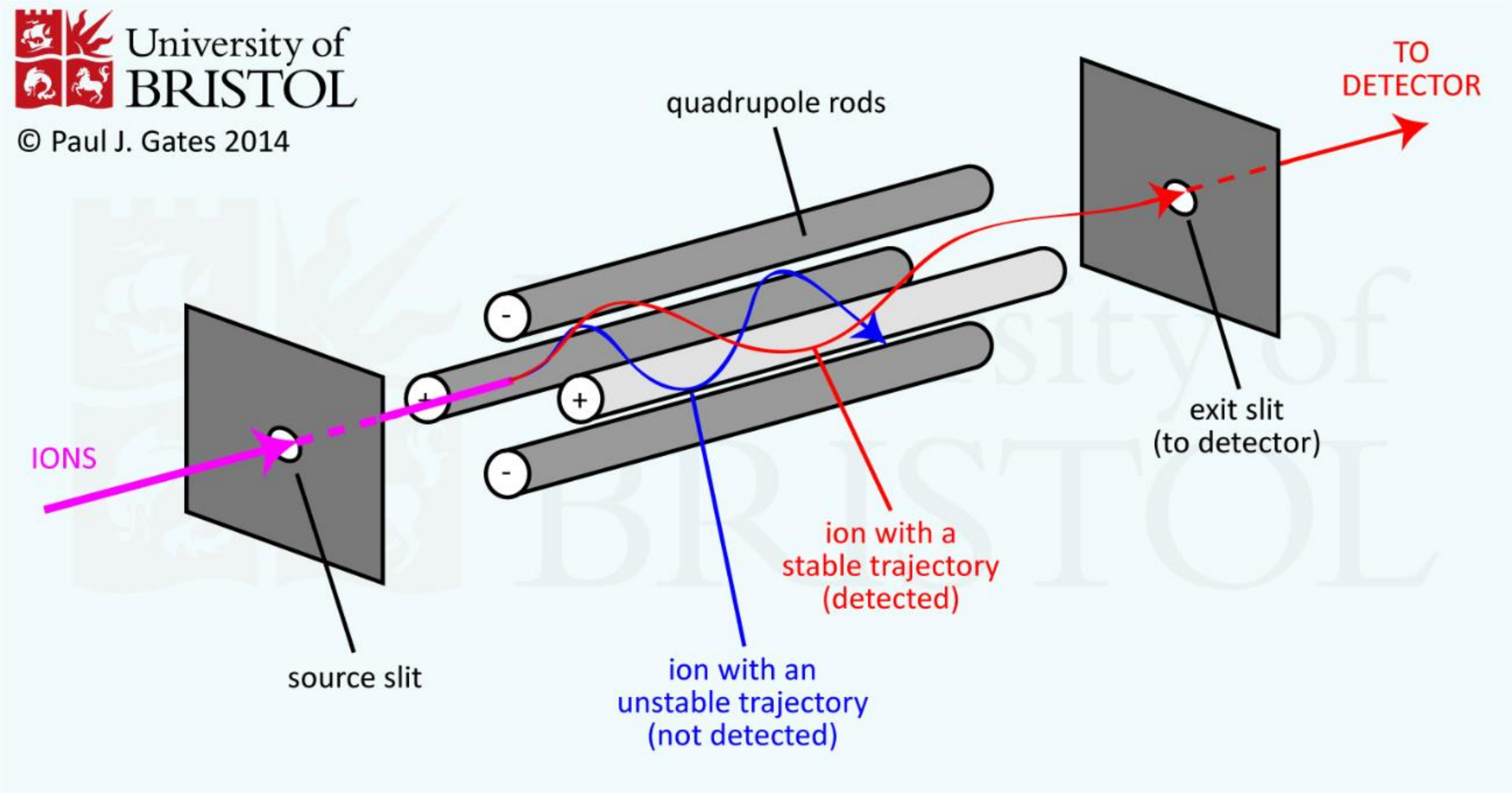
Electrical Ionisation

- Using an ‘electron gun’
- Resulting in electron impact ionisation
- $X + e^- \rightarrow X^+ + 2e^-$

Electrospray Ionisation

- A volatile ionic reagent is used
- This is injected as a fine mist into the ionisation chamber.
- Resulting in proton transfer
- $X + H^+ \rightarrow XH^+$

Quadrupole mass analyser

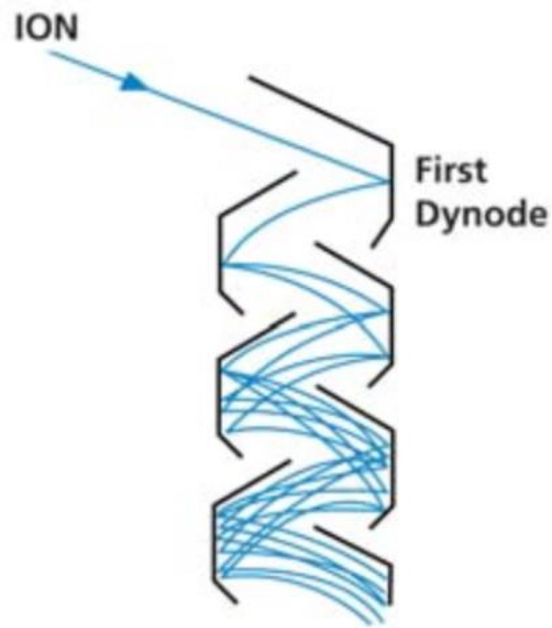


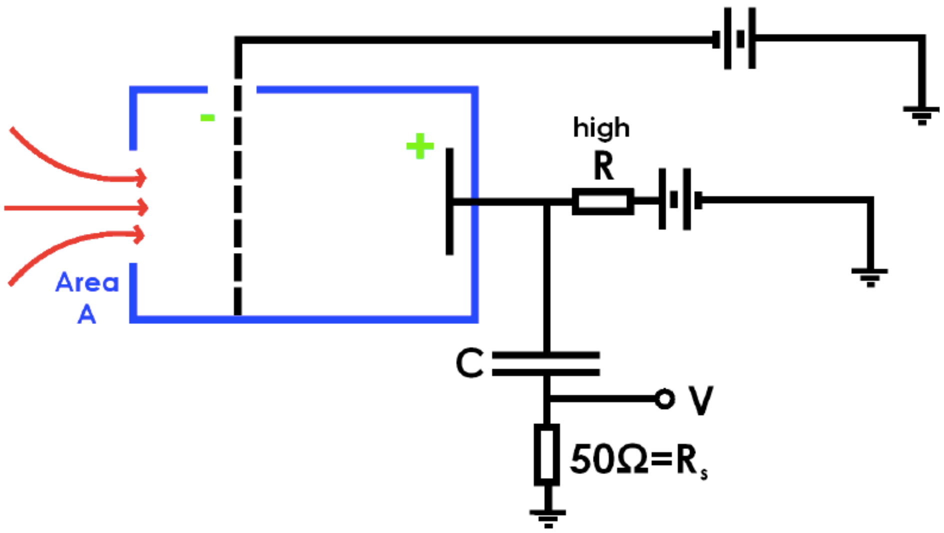
http://www.chm.bris.ac.uk/ms/quadrupole.xhtml

Detectors

- <u>Secondary electron multiplier (SEM):</u> Series of dynodes, secondary electrons emitted when charged particles strike the surface. Electron gain at each successive dynode. The cascading process results in gains up to 10^8 being achieved with ~21 dynodes.

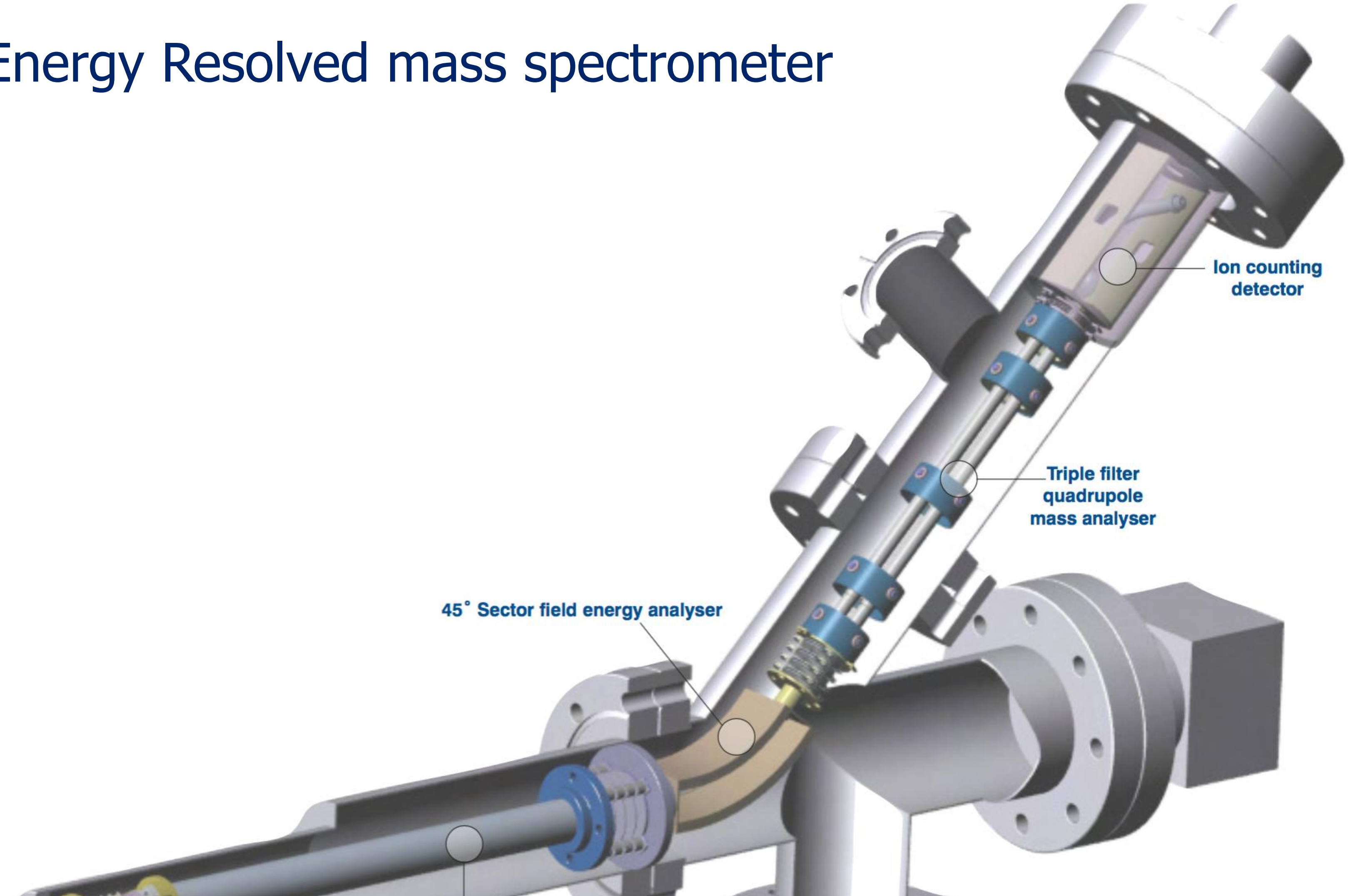
- <u>Faraday cup:</u> Flux of ions can be measured by first removing the electrons using a negatively charged grid and by measuring the current flow from an anode.

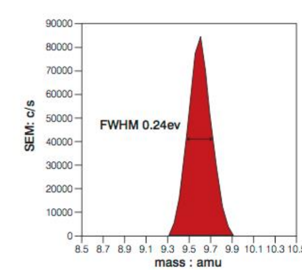




https://www.chromspec.com/pdf/e/rk123.pdf

Ion Energy Resolved mass spectrometer





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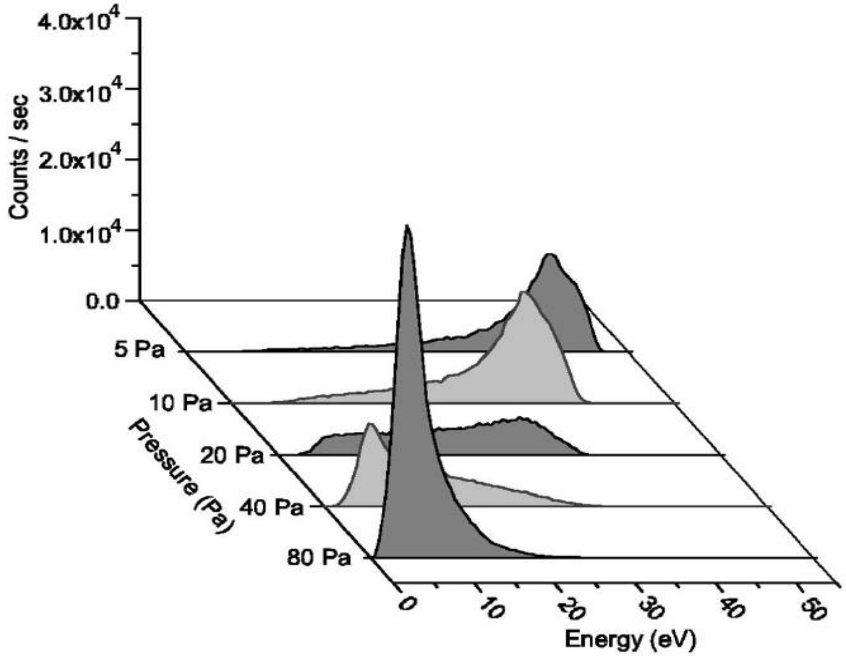
http://www.hidenanalytical.com/wp-content/uploads/2016/06/EQP-plasma-ion-mass_energy-analyser-brochure.pdf

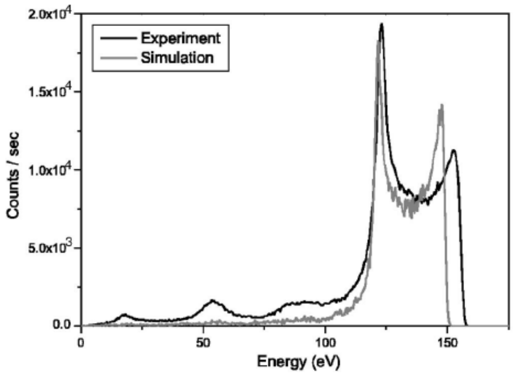
Ion energy distribution functions

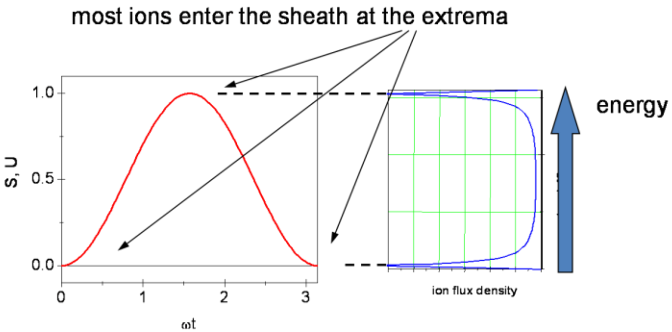
- The ion energy distribution function (IEDF) is a crucial parameter for surface treatment.
- Surface treatment is governed by the synergy of chemical reactions & physical ion bombardment.
- The IEDF determines the surface process selectivity.
- The IEDF can exhibit complex structures dependent on the sheath dynamics & collision processes.
- The simplest case is a monoenergetic peak at the time average sheath potential. This occurs when ions cross the sheath collisionless & respond due to their inertia to the average field only.
- With increased pressure collisions shift the IEDF towards lower energies.



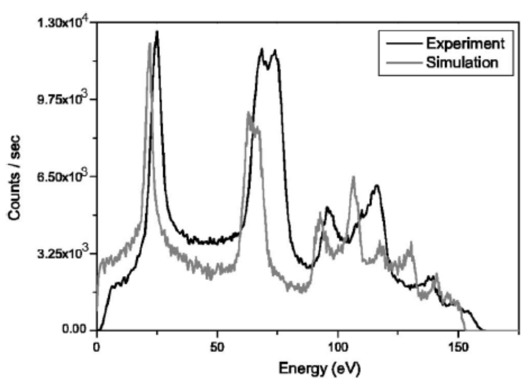
D O'Connell, et al., Phys. Plasmas ***14****, 103510 (2007)*

IEDF with finite ion inertia



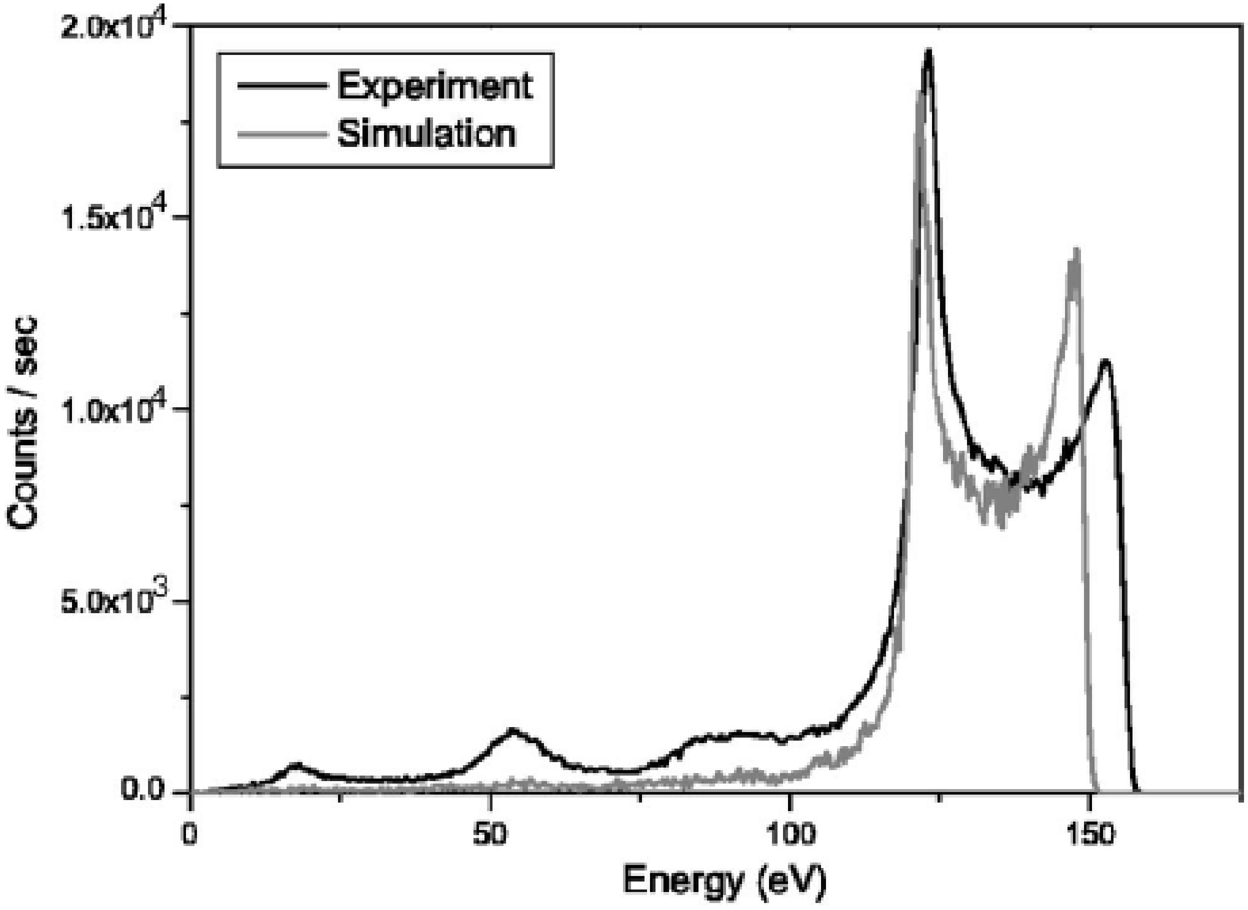


P. Benoit-Cattin, L.A. Bernard, J. Appl. Phys. 39, 5723 (1968)



- The sheath dynamics influences the IEDF due to finite ion inertia. The critical parameter is the ion transit time through the sheath.
- The typical shape of collisionless ions is a saddle shape structure with 2 maxima around the time averaged sheath potential.
- More ions enter the sheath at the extrema of the sheath potential because the sheath movement is slowest.
- Lower energy peaks represent ions created in the sheath or ions that underwent collisions

*D O'Connell, et al., Phys. Plasmas **14**, 103510 (2007)*



Question: What is the average sheath potential the ions, in the above figure, experience as they traverse the sheath?

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Measuring the production of H^- ions

Mass spectrometry is frequently used as a diagnostic technique in plasma physics (some mass spectrometers actually use a plasma in order to operate…).

- The production of H^- ions is crucial for future neutral beam injectors in order to reach the heating powers necessary for fusion to occur.
- The graph shown opposite uses mass spectrometry to measure the production of negative ions via surface interactions.
- The high energy peak is shown due to the creation of ions on the surface which do not undergo collisions.
- Whilst the low energy tail corresponding to the ions which lose energy via collisions en route to the mass spectrometers aperture.

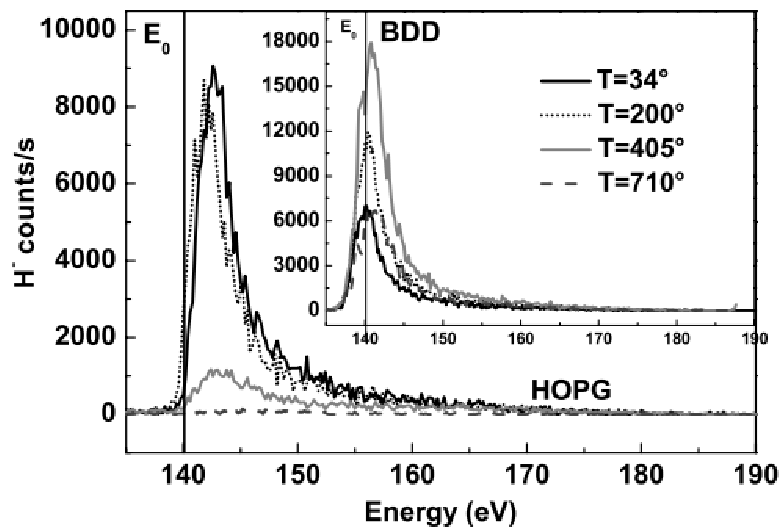


Figure 4. Negative IDFs measured on HOPG and BDD surfaces at different surface temperatures. X-axis shows negative ion energy in the plasma.

P. Kumar et al., "Enhanced negative ion yields on diamond surfaces at elevated temperatures", J. Phys. D: Appl. Phys. **44** (2011) 372002

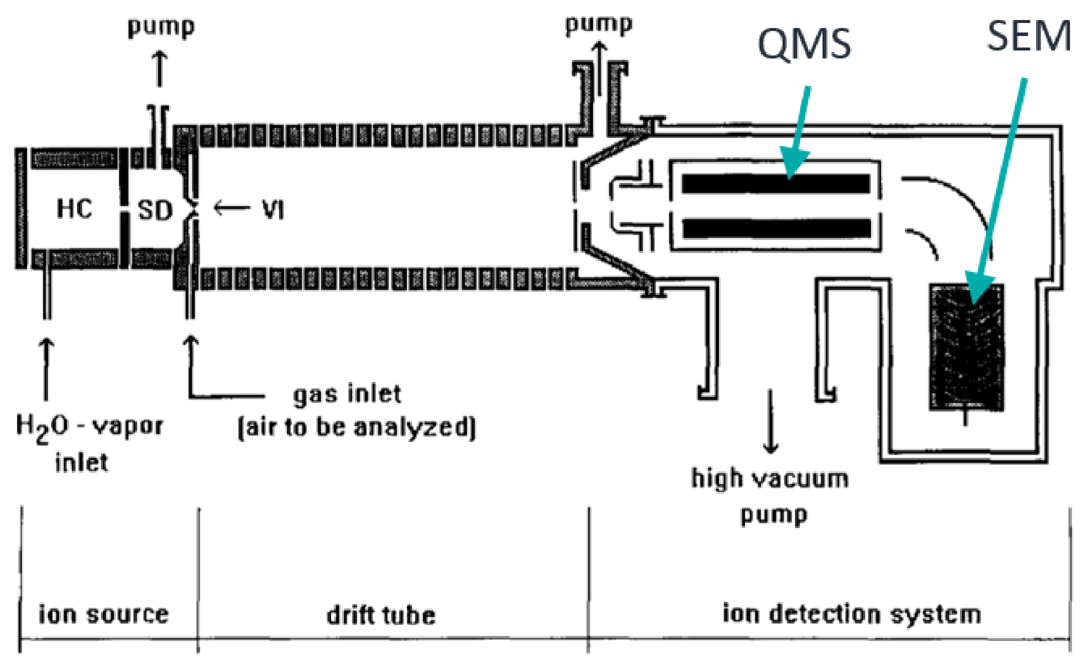
PTRMS

Another example of mass spectrometry which we use here in York is PTRMS – Proton Transfer Reaction Mass Spectrometry.

This type of mass spectrometry relies on the electrospray style of ionisation.

It is used in our own plasma group in order to determine the concentration of volatile organic compounds.

Hopefully now you can see that most of the spectrometer is similar to what has been show before!



HC –Hollow cathode, SD-Source drift region, VI-Venturi type inlet, QMS – Quadrupole mass analyser, SEM – Secondary electron multiplier

W. Lindinger, A. Hansel, and A. Jordan Int. J. Mass Spectrom., vol. 173, no. 3, pp. 191–241, 1998.

Retarding field analysers

- Retarding field analysers (RFA) are based on a similar principle as Faraday cups.
- RFA measure ion energy distribution functions by using an additional grid to scan the transmitted ion energy. This is particularly important for edge plasmas in MCF and low temperature plasmas.
- In principle a 3-grid structure is sufficient, but a 4-grid structure provides better resolution.
- Secondary electrons released at the grids can play an important role.