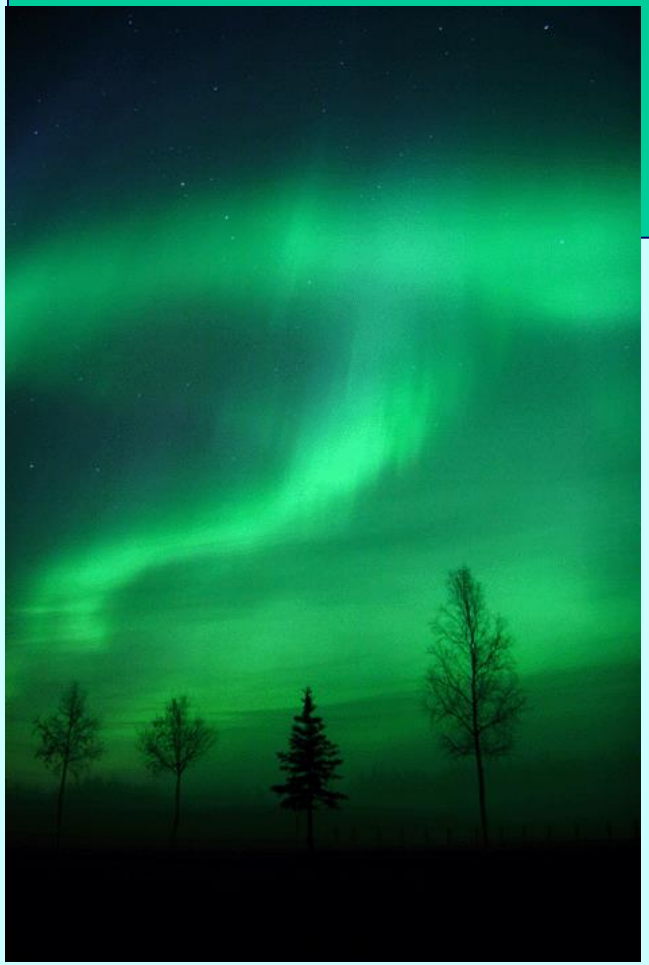
aurora technology consultants limited

gas vacuum plasma



Sensitivity enhancements for atmospheric sampling mass spectroscopy

Initial results from a collaborative development project, supported by Innovate UK, to couple a plasma based ion source to an RGA.

rob.grant@auroratechnologyconsultants.com

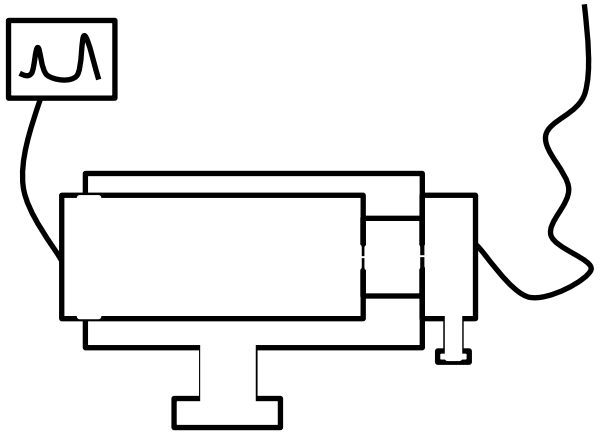
Overview

- Brief overview of conventional atmospheric sampling mass spectrometer systems
  - What are the issues?
- Goals for this project
- Overview of the test rig
- Results from using a secondary electron impact ion source
  - Focus voltage map for max transmission into the RGA
  - Optical measurements of an electron impact ion source
- Overview of the plasma ion source
- Initial results from the plasma ion source
  - Soft, cold, low energy ionisation
- Conclusions and next steps

Conventional atmospheric sampling systems

Trade-off of spectral simplicity v sensitivity

- Capillary inlet to ~0.1mb
  - Rough pumped; ensure molecular flow through next stage of differential pumping
- Orifice/sinter drops pressure by another 2-3 orders of magnitude
  - Molecular flow minimises fractionation
- Ion source operates in the range 1.0 10^{-4} to 1.0 10^{-3}mb
  - An uplift over the background vacuum of ~100
- Mass spectrometer typically operates at a pressure of ~5.0 10^{-6}mb
  - Requires turbo pump etc.
  - ~0.1 ppm level detection but with multiple ionisation, fragmentation and ion source reactions
  - Can reduce the effects of the above at the cost of sensitivity e.g. reduce electron energy



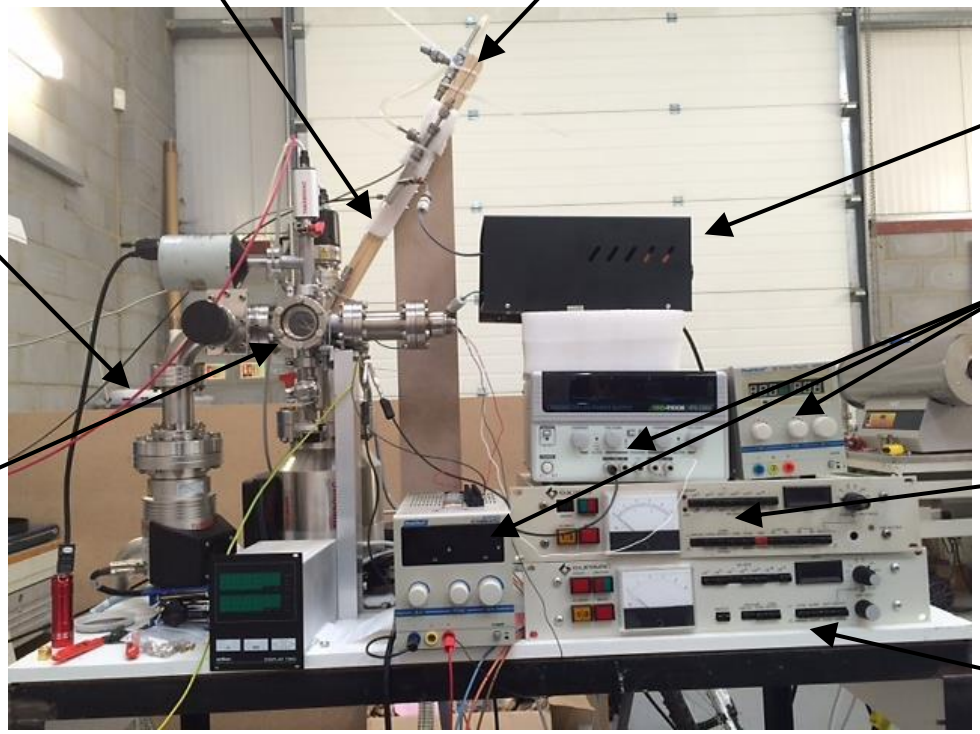
Goals for the project

- Demonstrate effectiveness of secondary plasma ionisation
  - Soft ionisation so minimal fragmentation
  - No multiple ionisation so simpler spectrum
  - Cold ionisation so no ion source reactions
  - All the above with high sensitivity
- Demonstrate a ppm level detection system that does not require electron multiplier detection and does not need a turbomolecular pumped RGA
- Demonstrate an ultra high sensitivity system suitable for single digit ppb level detection
  - For use in membrane permeation studies and high sensitivity analysis

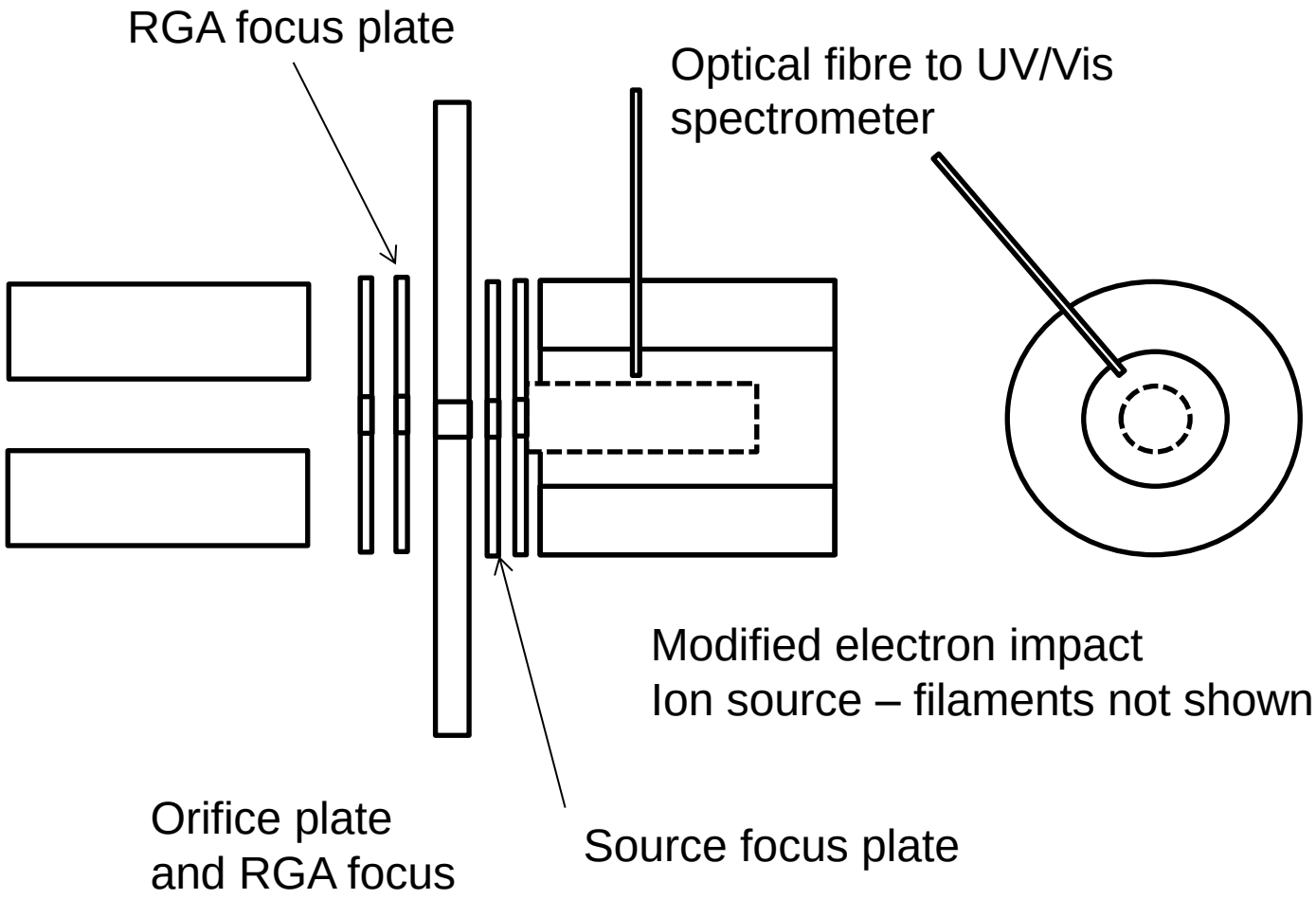
Test Rig

- The test rig was based around a VG Quadrupoles Supavac RGA
  - 100 amu, Faraday detector, manual instrument
- A high vacuum chamber housing the RGA
  - Pumped by a 300l/s turbo with a “normal” operating vacuum of 5.0 10^{-5}mb
  - Supavac RGA with the ion source removed
- A low vacuum chamber housing the ion source
  - Typical operating pressure for the plasma source in the range 0.1 to 1mb
  - Initially the ion source was a standard electron impact source driven by a set of Supavac electronics to set up focus voltages
  - Standard source replaced by plasma source later in project
  - Optical fibre for UV/Vis spectrocsopy
- Chambers connected by a 1.0mm orifice plate
  - Gives a differential pressure of ~1,000

Test Rig

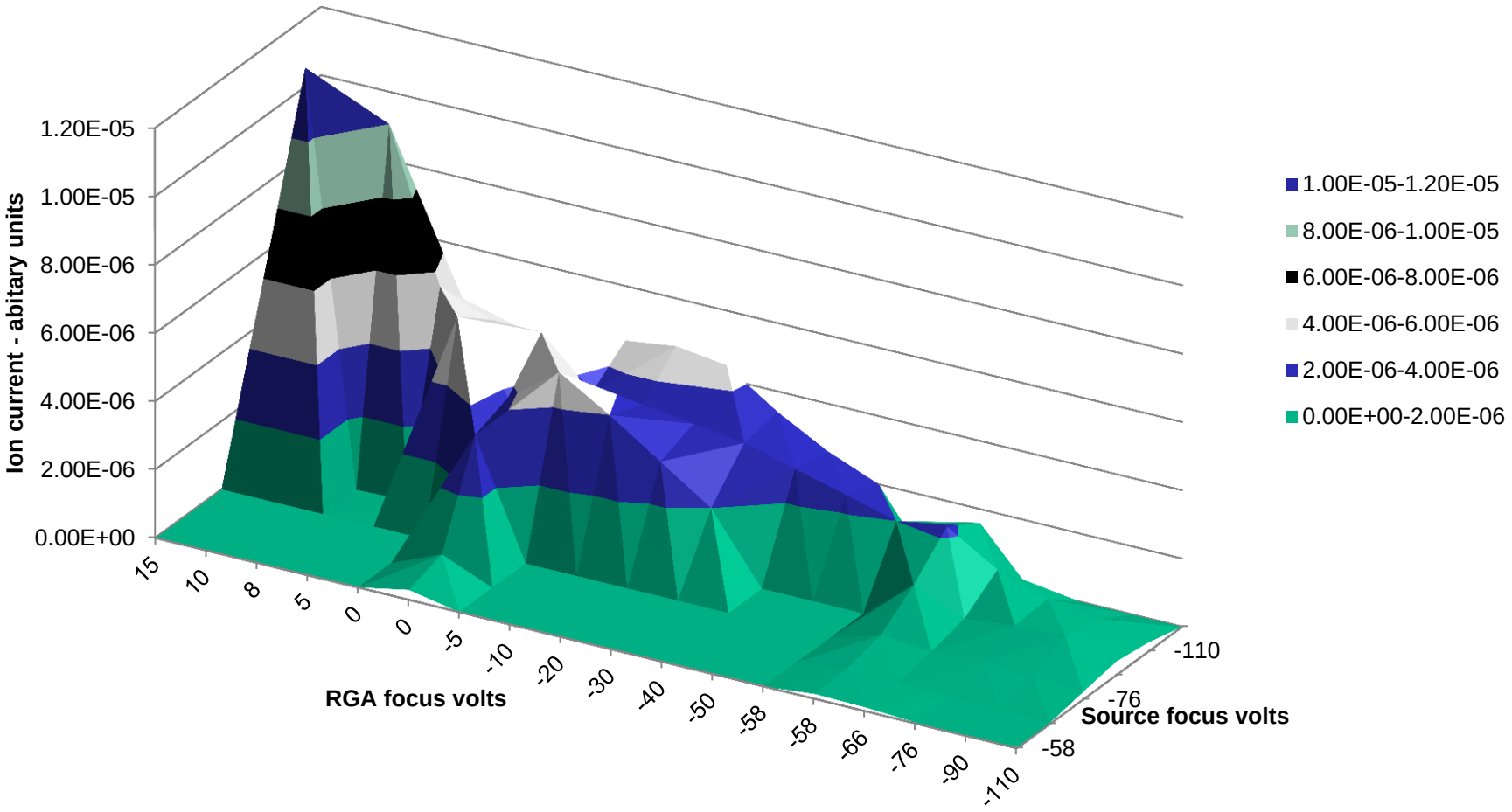

Transfer tube for excited species
Primary plasma
In Situ optical fibre to UV/Vis spectrometer
High voltage RF PSU for primary plasma.
Benchtop PSUs for focus voltages etc.
2nd Supavac controller to drive electron impact source
Low vacuum chamber
Supavac RGA Controller

Secondary ion source detail



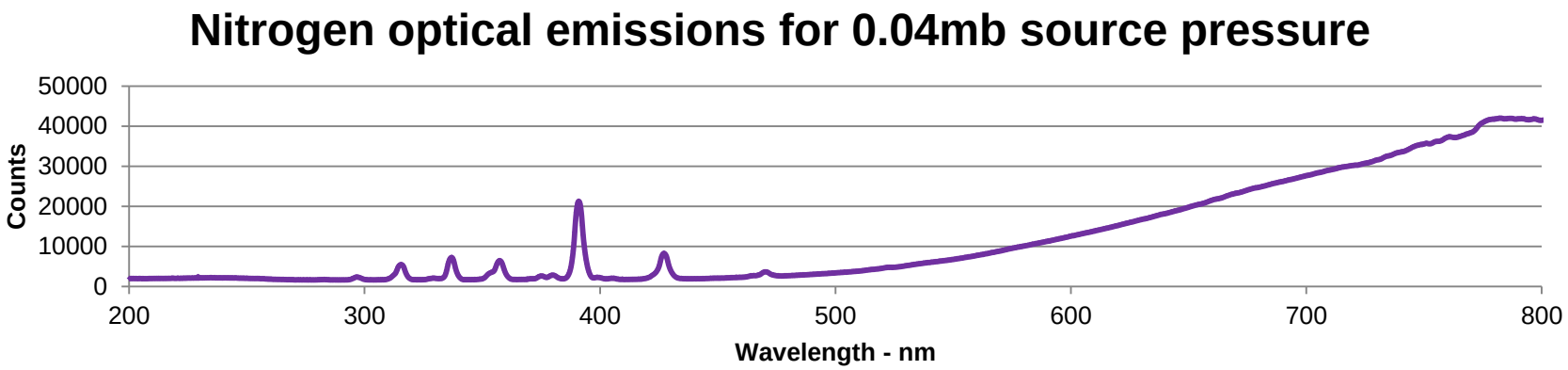
Secondary ion source focus map

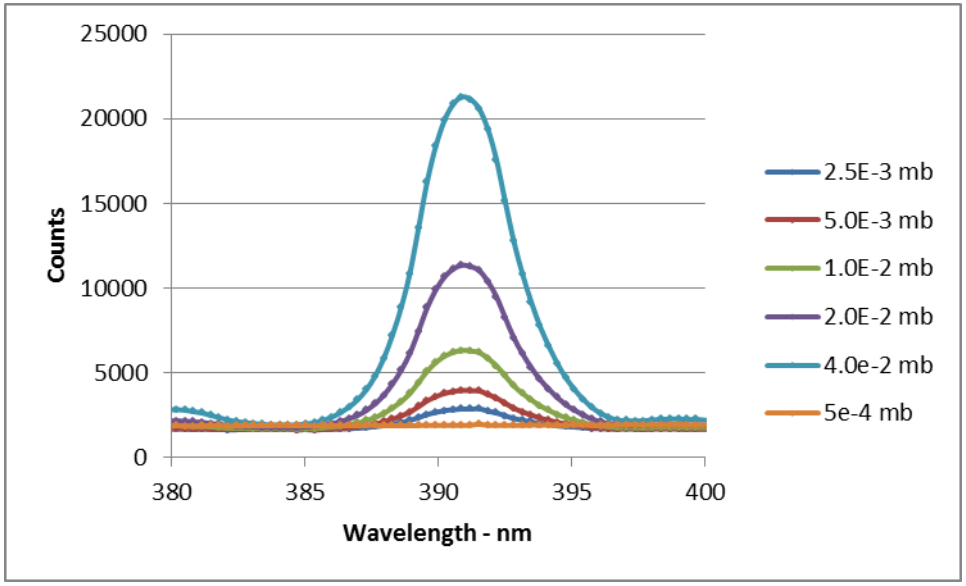
Establish the optimum values of focus voltage for max. transmission



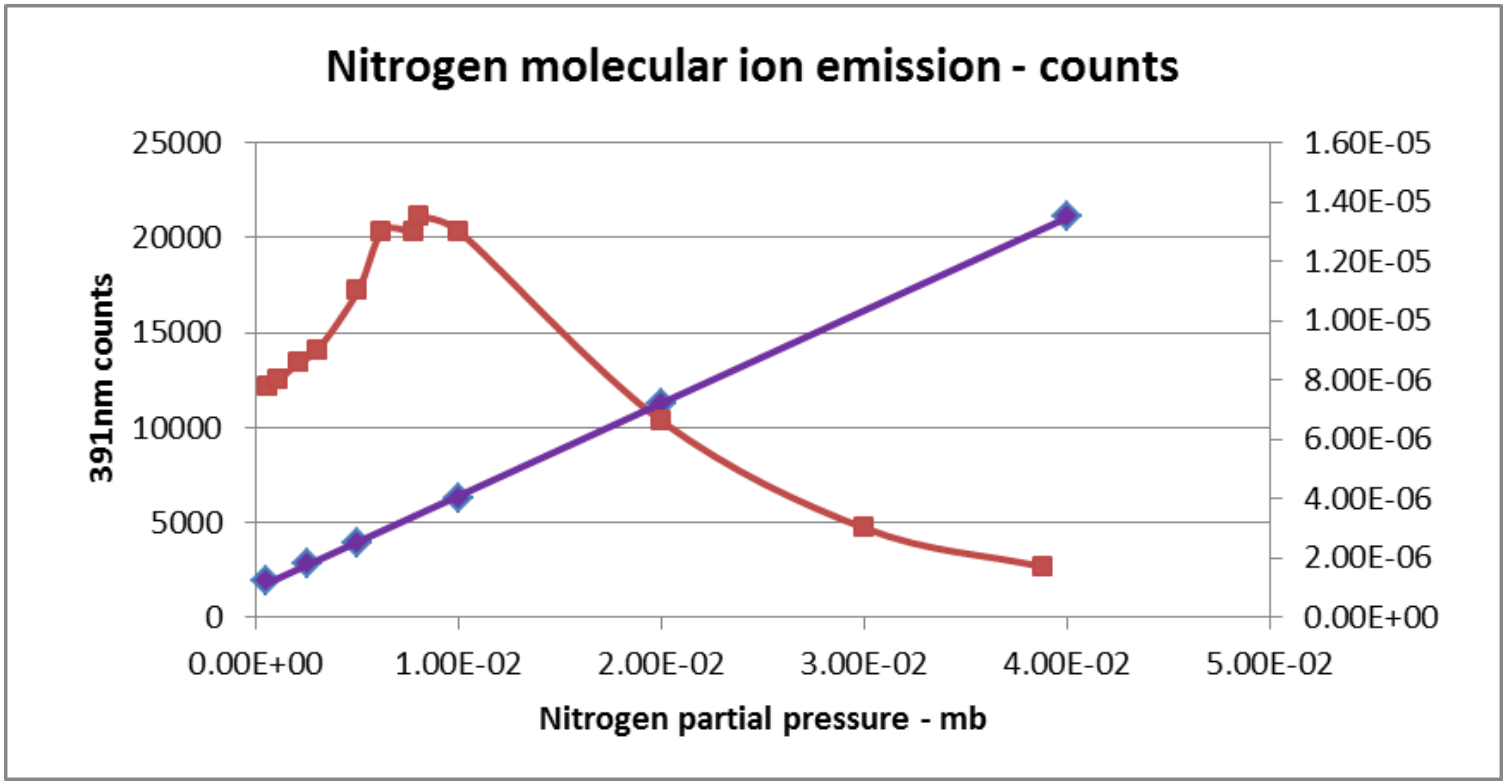
Nitrogen optical emissions

391nm molecular ion optical emissions increase with source pressure





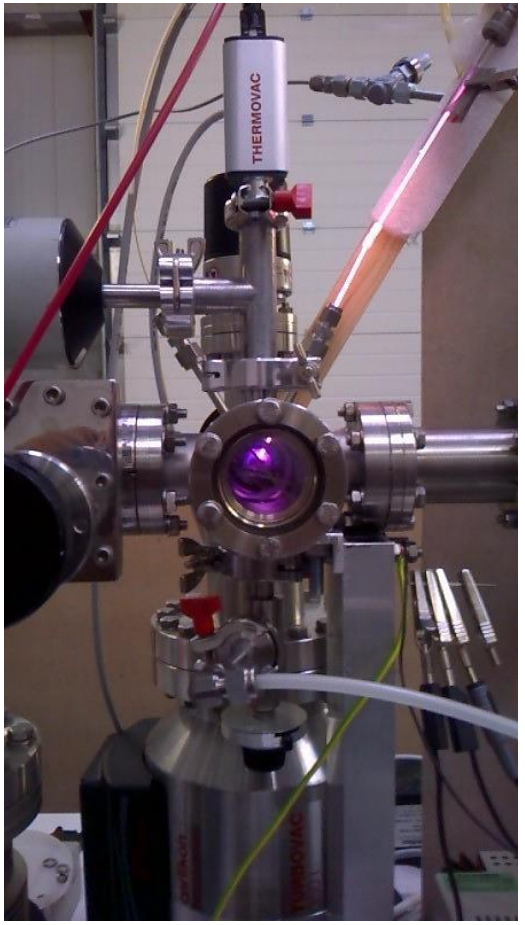
Combined optical and ion emissions




Plasma induced ionisation

Summary of plasma source results

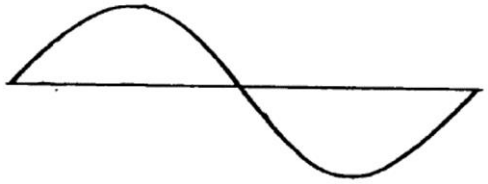
- Primary plasma is a dielectric barrier discharge running with high purity helium
- Optical emission spectrum from the primary plasma shows a clean helium spectrum
  - No back diffusion from the source region
- Source region at 0.5mb of Ne
  - Source optical spectrum is a mixture of Ne and He
  - Primary plasma shows no Ne
  - RGA shows no Ne
- Source region at 0.5mb air in argon
  - See optical spectrum from Ar, N_2 and moisture + He
  - RGA shows moisture and oxygen but no Ar or N_2
- Source region at 0.5mb 10,000ppm D_2O in argon
  - Optical spectrum shows moisture and argon
  - RGA shows just D_2O and residual H_2O



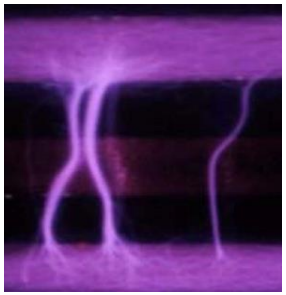
DBD plasma can be filamentary or glow

Depends on dielectric, geometry, volts, pressure and gas species

- Filamentary plasma are good for processing gas but lead to multiple ion species
  - Worse case a filament is localised and breaks through the dielectric and/or the substrate
- Even density glow discharges are usually more stable and well defined



Lifetime	1 – 20 nsec	Filament radius	50 - 100 μm
Peak current	0.1 A	Electron energy	1 – 10 eV
Electron density	10^{14}-10^{15}cm^{-3}	Gas temperature	Close to ambient, about 300 K

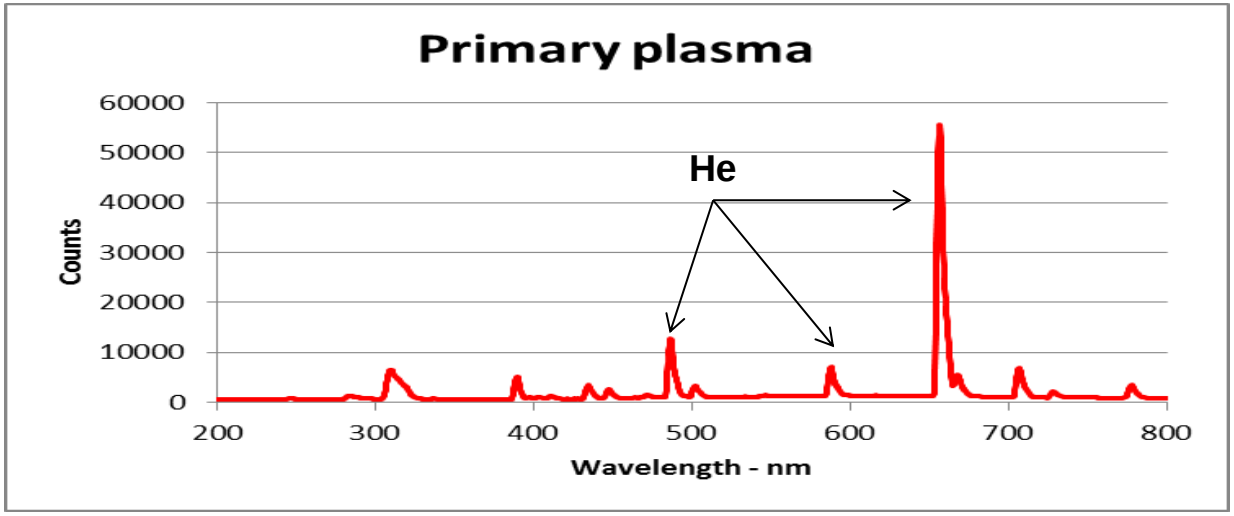


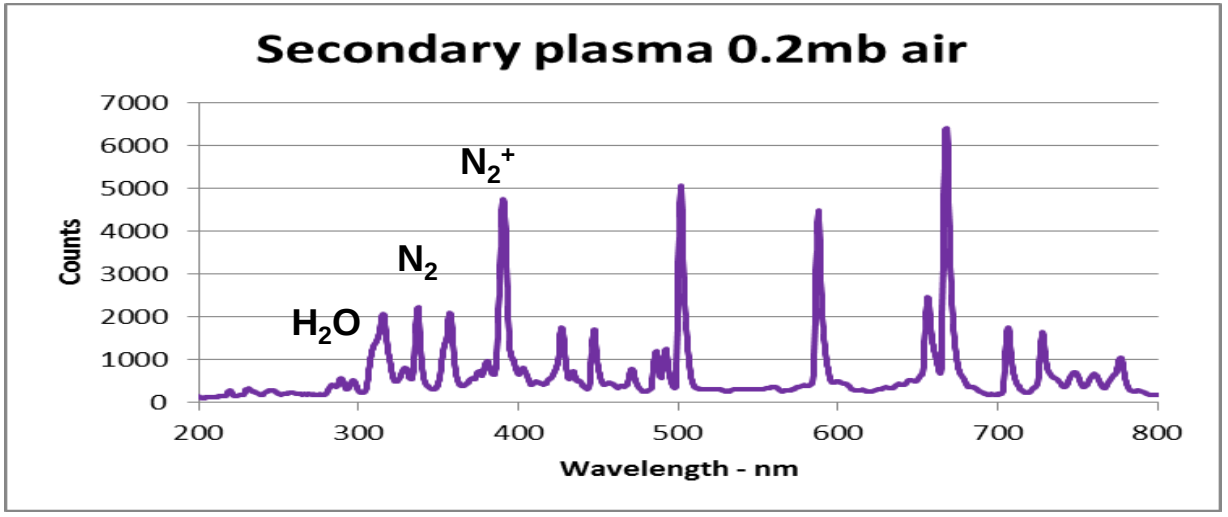
- Inert gases have long-lived excited species which can stabilise the plasma and create a glow discharge
  - Lifetime of meta-stable species greater than that of the micro-discharges
  - Sustain plasma via penning ionisation

$$He^* + M \rightarrow He + M^+ + e$$

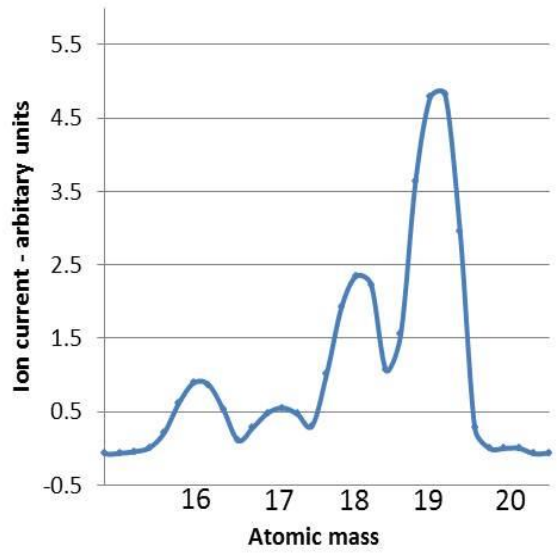
Optical emission spectra

In reality the primary plasma is ~1000 more intense than the secondary plasma

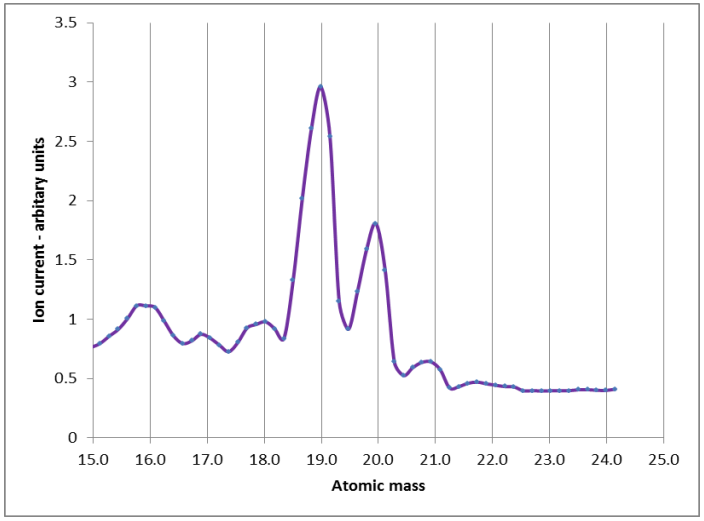




Moisture mass spectra

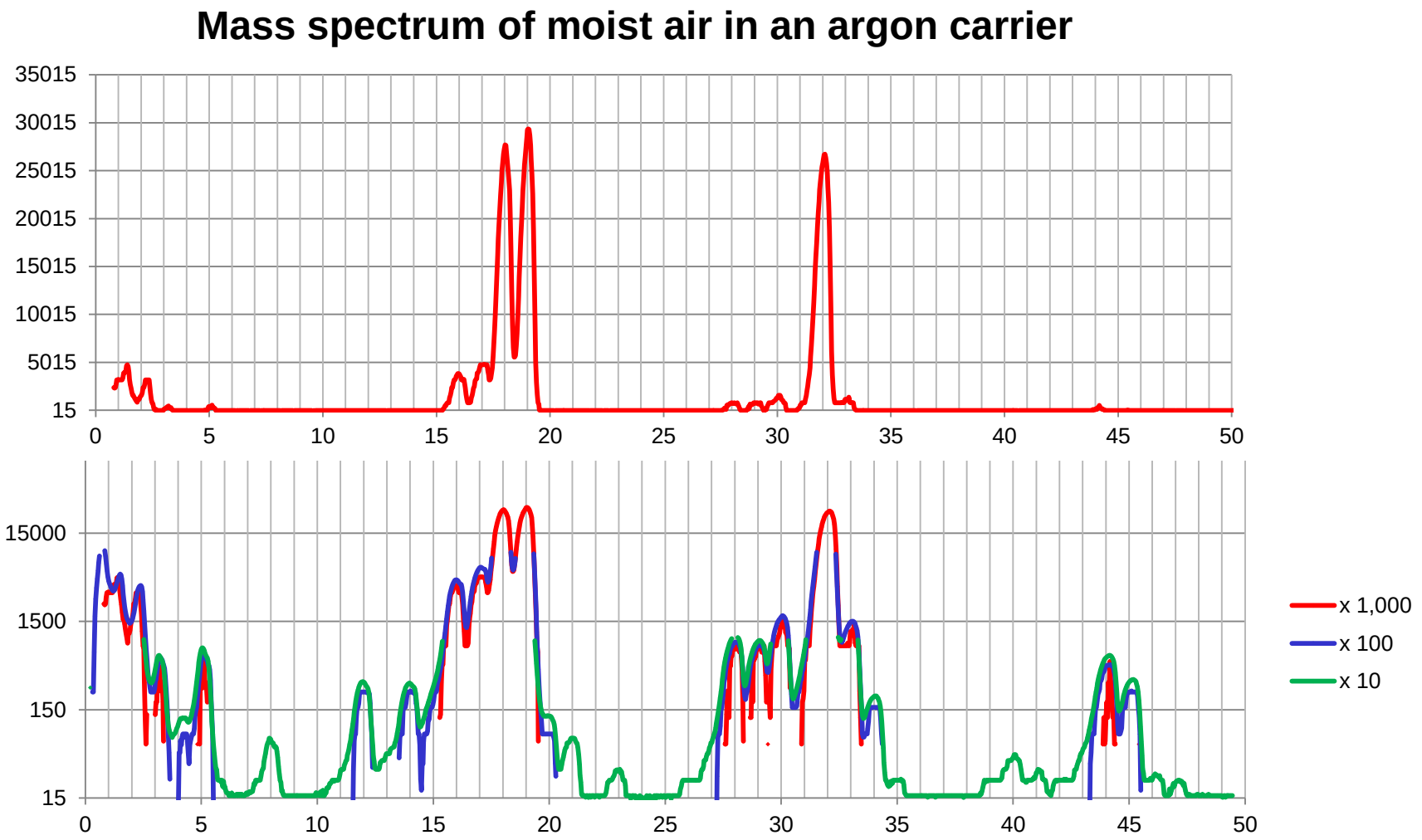


- Spectrum of air plus Ar
- 19 amu an artifact??
- No Ar peaks at 20 or 40
  - Ionisation energy must be less than 15eV
- 17 is less than 10% of 18
  - Relatively soft ionisation



- Spectrum of Ar + 10,000ppm D2O
- Minimal fragmentation to OD^+
- Immediately see mass 20 and no change to mass 19
  - Relatively cold ionisation as no isotope exchange
- Baseline is ~1 ppm D_2O

Full mass spectrum of air at 0.5mb



Conclusions & Next Steps

- We have demonstrated:-
  - Dielectric barrier discharge generates a workable plasma for secondary ionisation
  - Effective ionisation at ~0.5mb of gaseous species using secondary induced plasma ionisation
  - Ionisation is of low energy estimated to be ~13-14eV – doesn't ionise He, Ne Ar, N_2
  - Ionisation is soft – minimal fragmentation, 17 typically less than 0.1 18
  - Ionisation is cold – no isotope scrambling of D_2O, H_2O
  - ppm level detection with a faraday detector RGA operating at ~10^{-3}mb
- Next steps are to:-
  - Further optimise the sensitivity of the ion source
  - Couple to a high spec. RGA to determine the ultimate detection levels
  - Bring to market commercial instruments based around this ionisation method for low cost atmospheric analysis and high sensitivity membrane permeation measurement
- We are in the process of seeking additional funding to complete the above

Acknowledgements

Innovate UK

SS scientific
PRECISION IN VACUUM

oerlikon
leybold vacuum

SOHAM
SCIENTIFIC


Any Questions?