

Extending the Limits of Detection into the PPT Range with a QMS



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Introduction

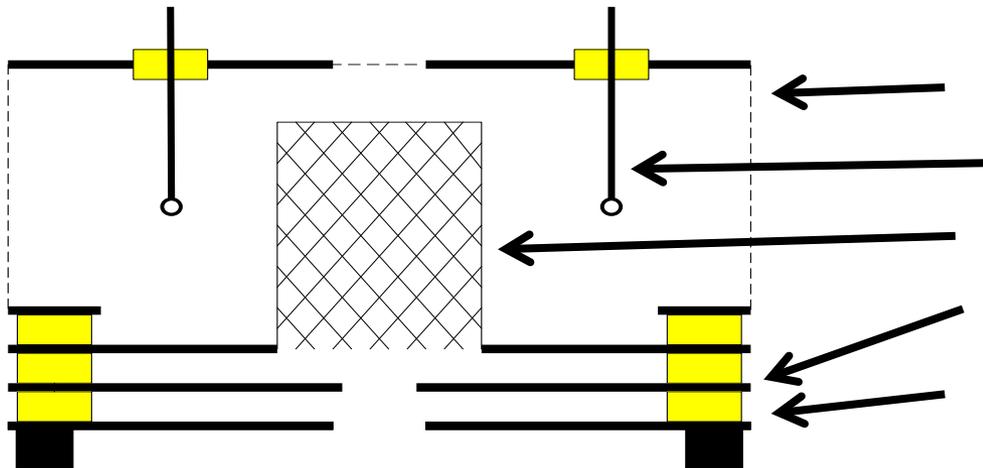
- Quadrupole Mass Spectrometers (QMS) are used in many process applications from fuel cells to semiconductor manufacturing and from environmental monitoring to high energy physics.
- In recent years, QMS has increasingly been used for process monitoring in a wide range of vacuum processing techniques requiring detection of low-level contaminants.
- Many modern designed residual gas analysers do have the sensitivity to detect sub-ppm level contaminants. However, the background signal from the RGA itself and interference from bulk gases can make the detection of ppm levels of some contaminants difficult in reality.

Introduction (cont'd)

- For applications operating at high pressure above 10^{-4} mbar, background contribution can be substantially reduced with the use of a closed ion source (CIS).
- The closed ion source extends the detection level in to the ppb range and combined with MKS V-lens[™] technology in to the sub 10 ppb range.
- To increase the limit of detection further the sampling of the analysis gas needs to be enriched. Such techniques are now available allowing detection in to the parts per trillion (ppt) range.

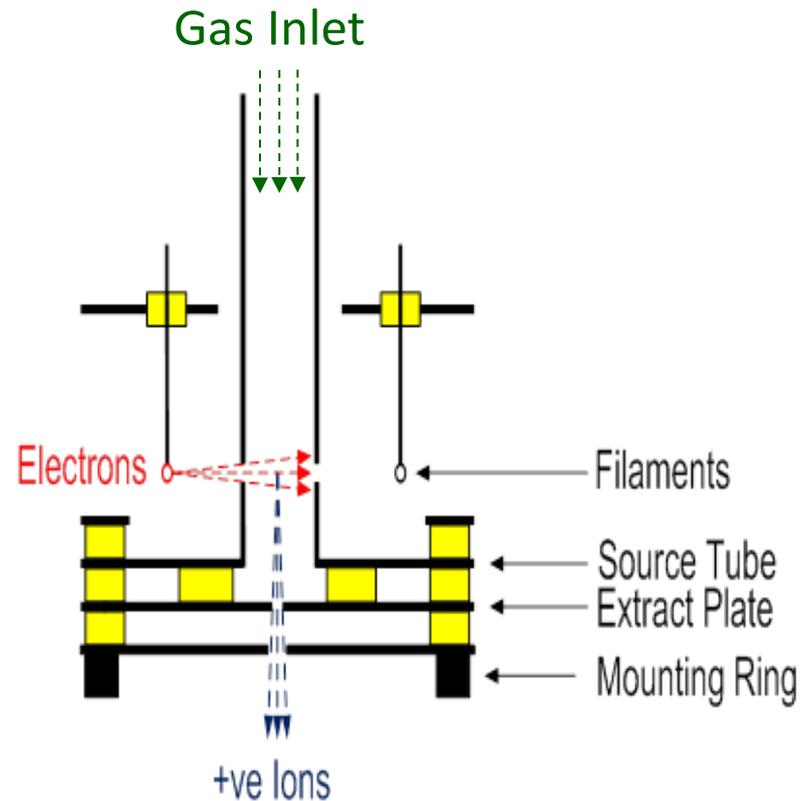
Open Ion Source

- The open ion source RGA is typically placed inside the vacuum chamber to be monitored.
- At higher pressure, above 10^{-5} mbar the source becomes non-linear, above 10^{-4} mbar the ion count reduces.
- To operate at higher process pressure, the RGA must be fitted in a separate vacuum chamber and sample gas leaked in.

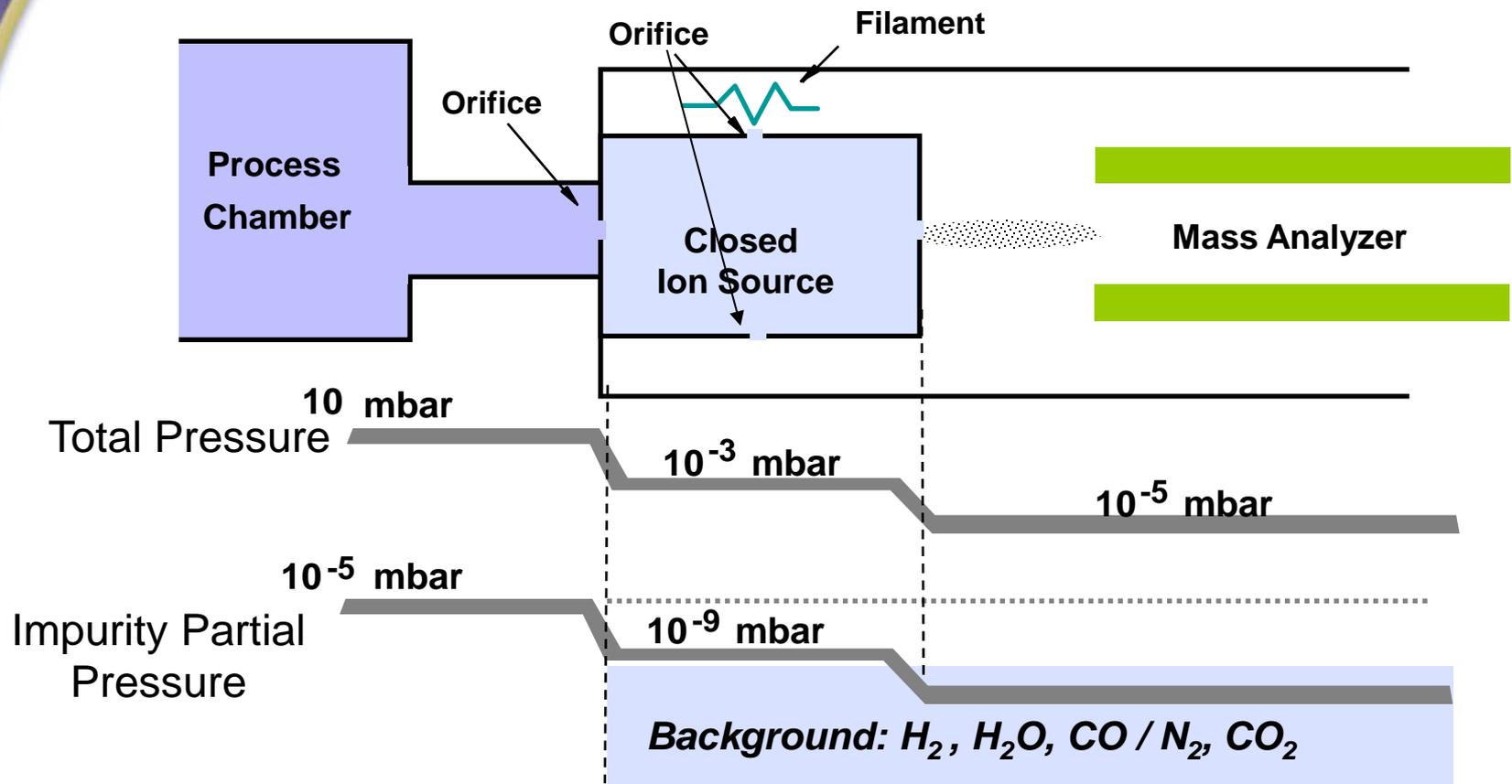


Closed Ion Source

- The closed ion source (CIS) mass spectrometer samples gas from an external chamber.
- The pressure in the source is much higher than a standard open ion source RGA, typically 1×10^{-3} mbar.
- The higher partial pressures of trace gases increases the sensitivity compared to RGA background.

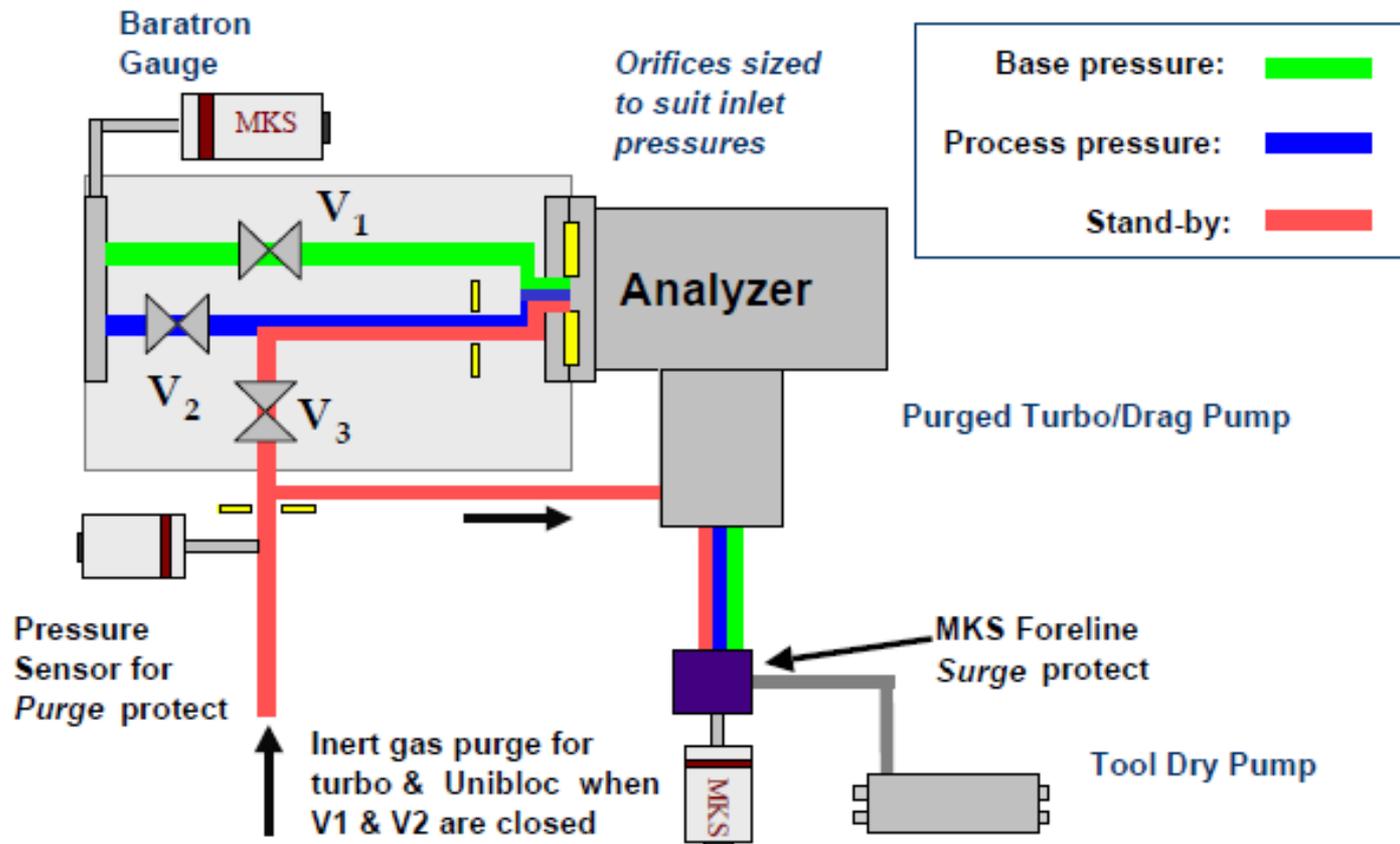


Closed Ion Source Sampling

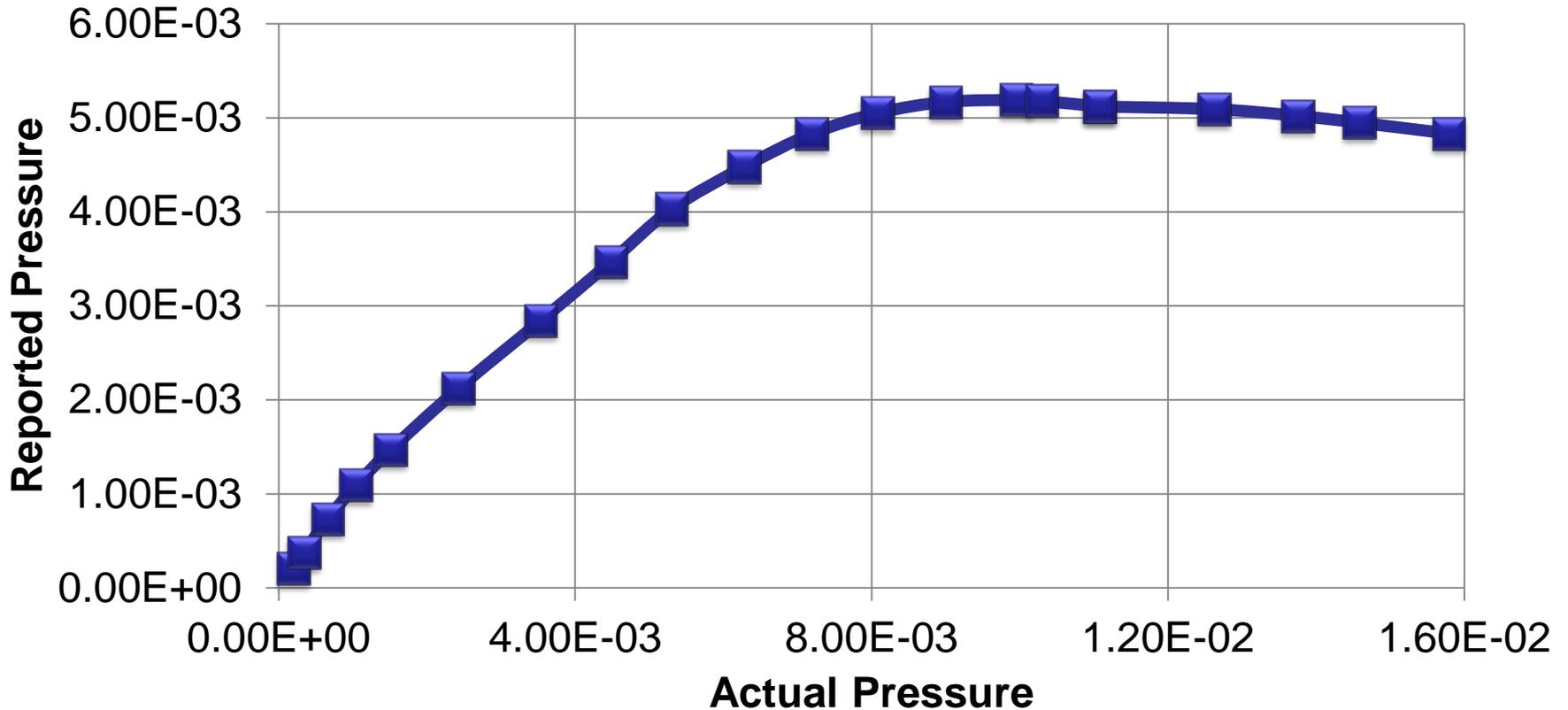


Example Sample Inlet

Three Valve UniBloc™ Configuration for CVD & Etch

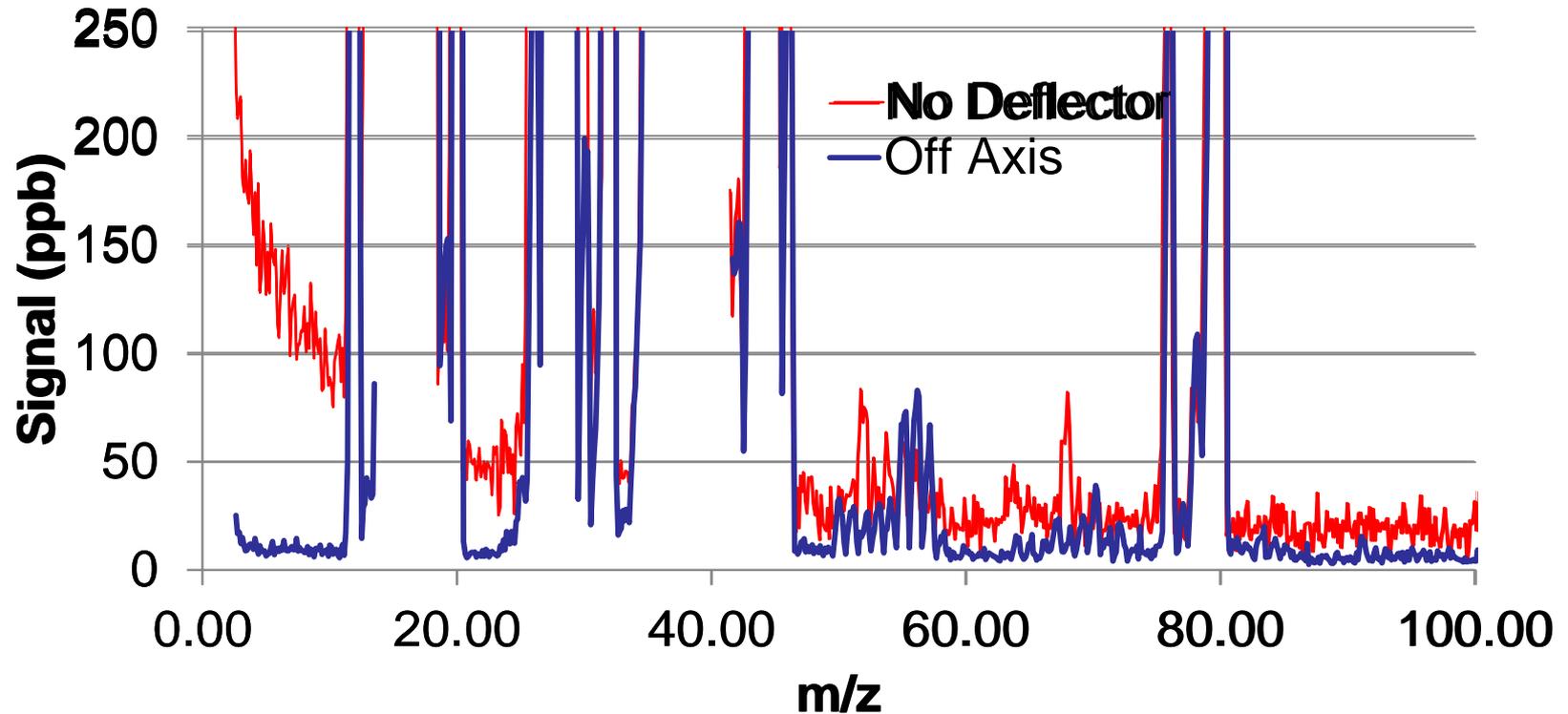


Effect of Source Pressure



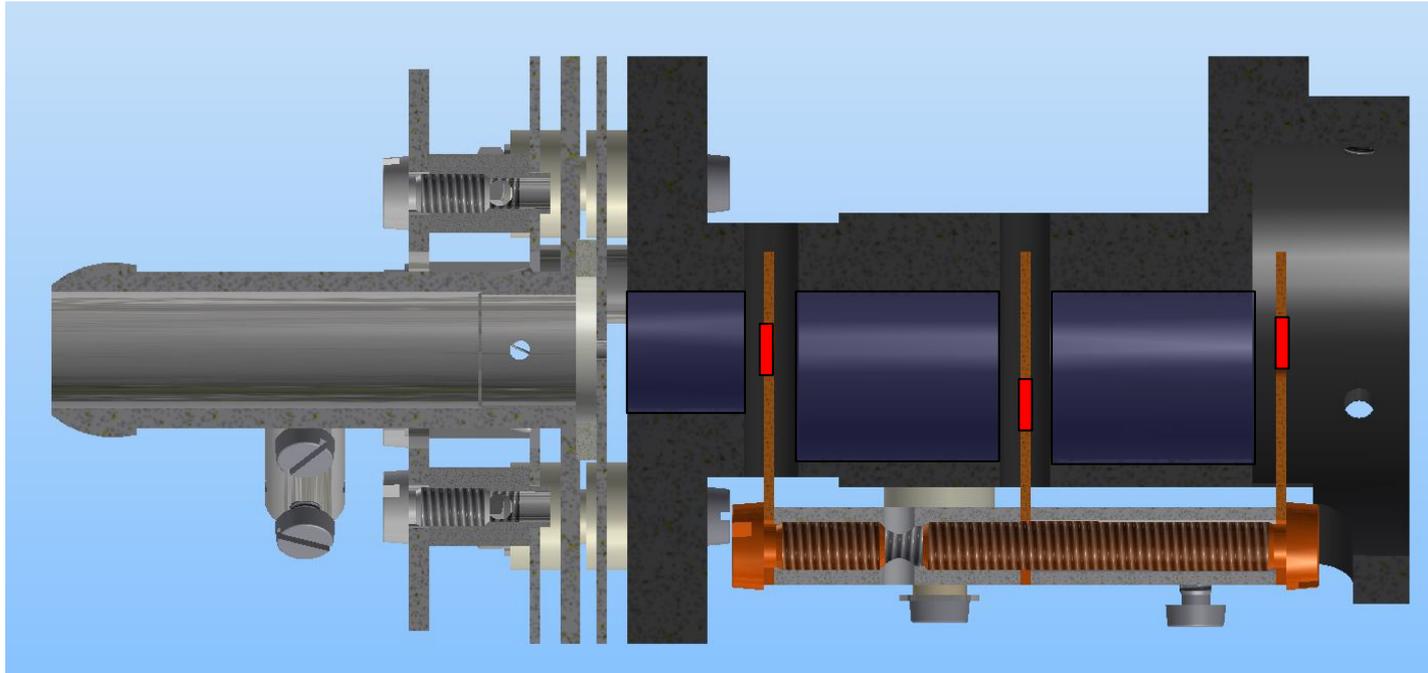
As source pressure is increased, response becomes non-linear and eventually starts to drop, this is known as roll over.

Reduction of low mass noise using V-lens



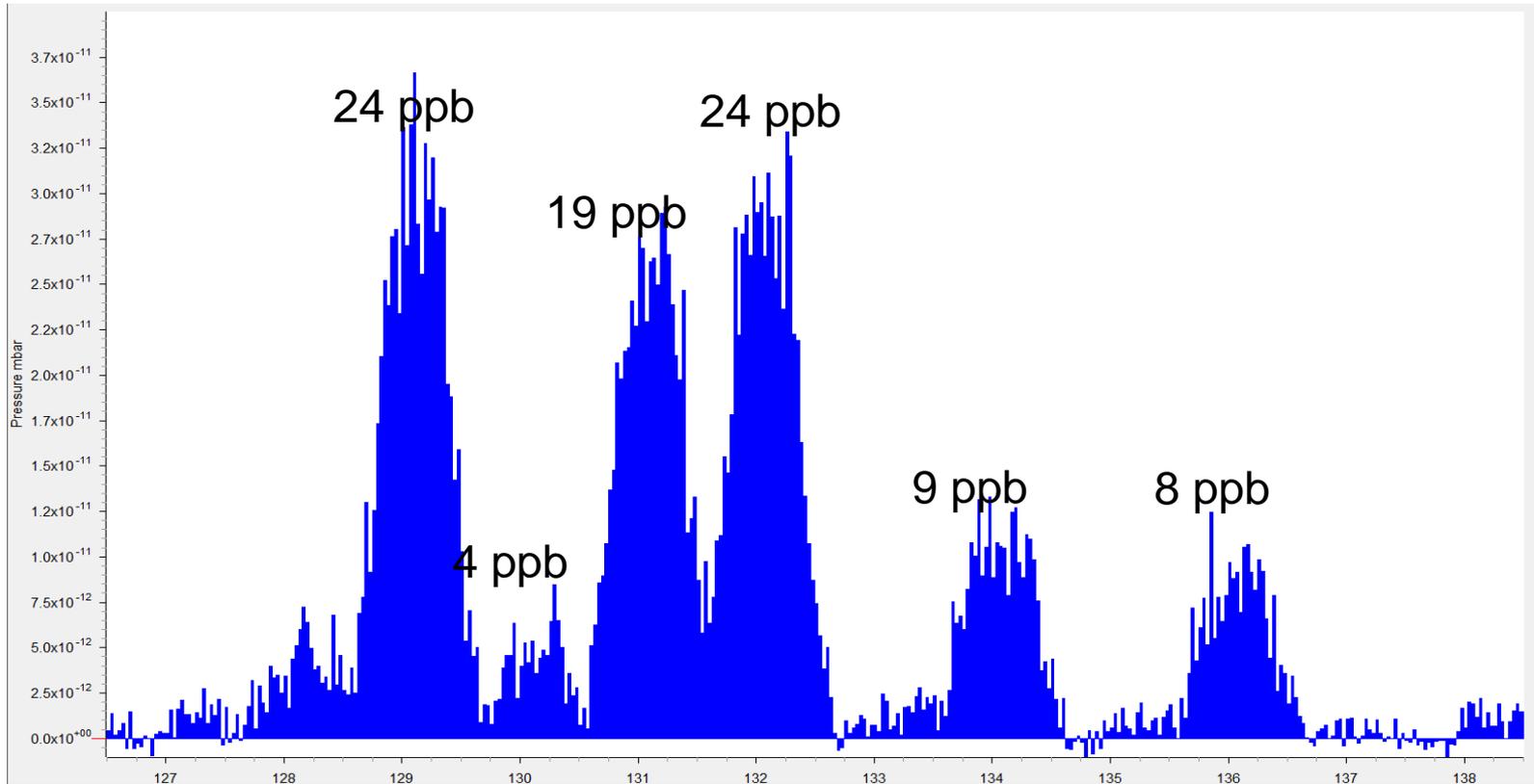
- The high pressure source allows the production of metastable neutrals, this is especially bad with Argon.

Removal of Line of Sight



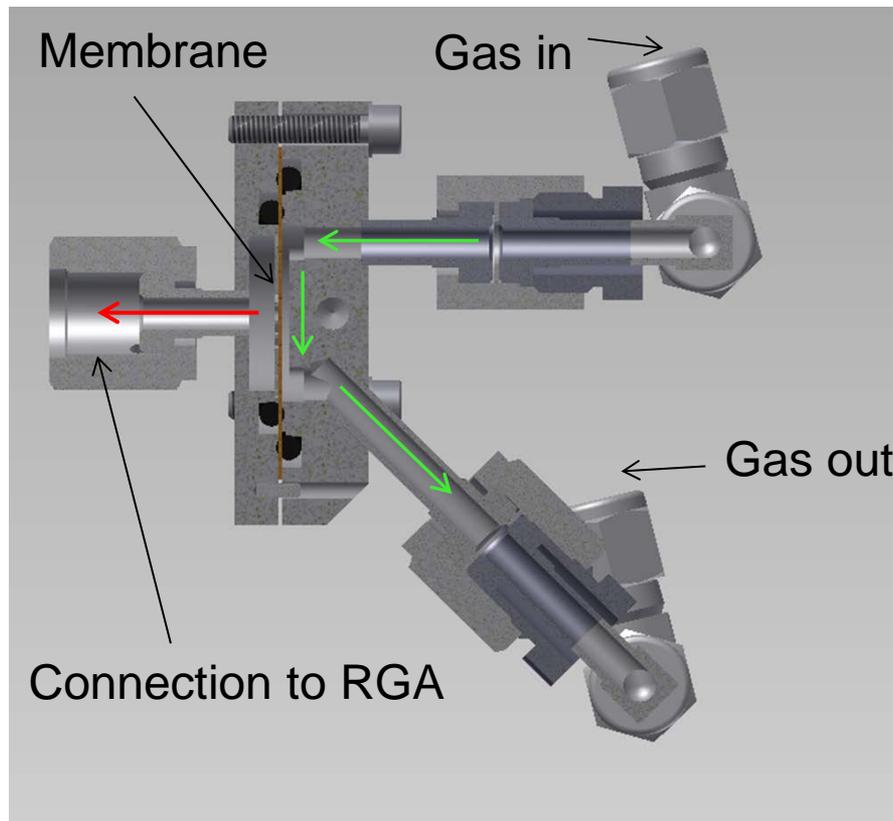
- Removal of line of sight reduced the effect of metastable neutrals completely giving a non-gas dependant baseline.
- The improved ion optics also increased system sensitivity

Best Sensitivity of System



Sampling from a chamber at 1×10^{-3} mbar of air with a Vision 2000P-XD™ xenon concentration of 90 ppb, dwell time 1.2 seconds per data point, multiplier gain 3000.

Further Reductions in Limit of Detection by Sample Enrichment



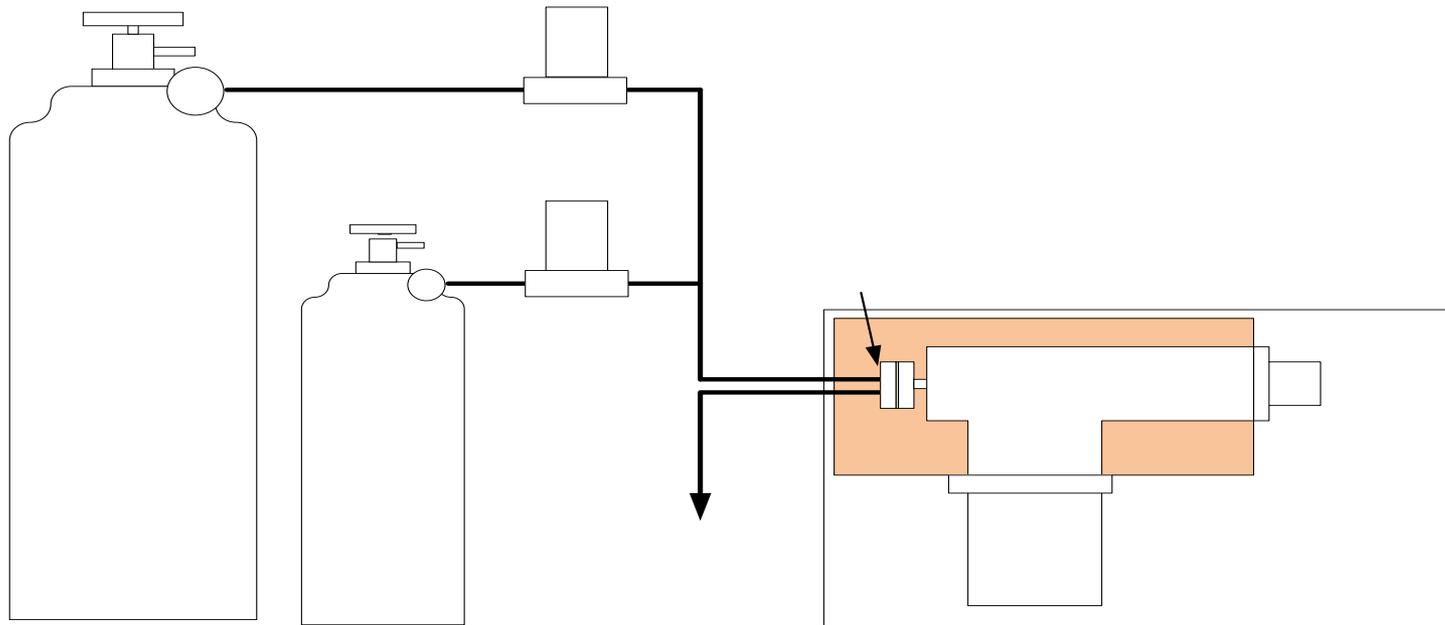
- A membrane inlet system was built for sample enrichment.
- Sample gas was passed over a polydimethylsiloxane membrane at about 50 sccm.
- Various thicknesses and numbers of membranes were tested, a single 0.2mm membrane was chosen.
- The response time when switching the sample was around 10 s to reach 90% of final response.

A Universal Solution?

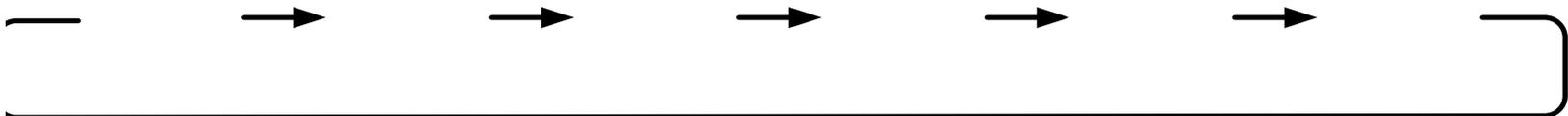
| GAS NAME | FORMULA | SILICONE PERMEABILITY COEFFICIENT (Barrer) |
|-------------------|-------------------------------|---|
| Nitrogen | N ₂ | 280 |
| Oxygen | O ₂ | 600 |
| Argon | Ar | 600 |
| Hydrogen | H ₂ | 650 |
| Helium | He | 350 |
| Methane | CH ₄ | 950 |
| Ethane | C ₂ H ₆ | 2500 |
| Carbon dioxide | CO ₂ | 3250 |
| Toluene | C ₇ H ₈ | 9130 |
| Hydrogen Sulphide | H ₂ S | 10000 |
| Benzene | C ₆ H ₆ | 10800 |
| Sulphur Dioxide | S ₂ O | 15000 |
| Water | H ₂ O | 36000 |

From: THIN SILICONE MEMBRANES-THEIR PERMEATION PROPERTIES AND SOME APPLICATIONS
 Annals of the New York Academy of Sciences, vol. 146, issue 1 Materials in , pp. 119-137
 W. L. Robb

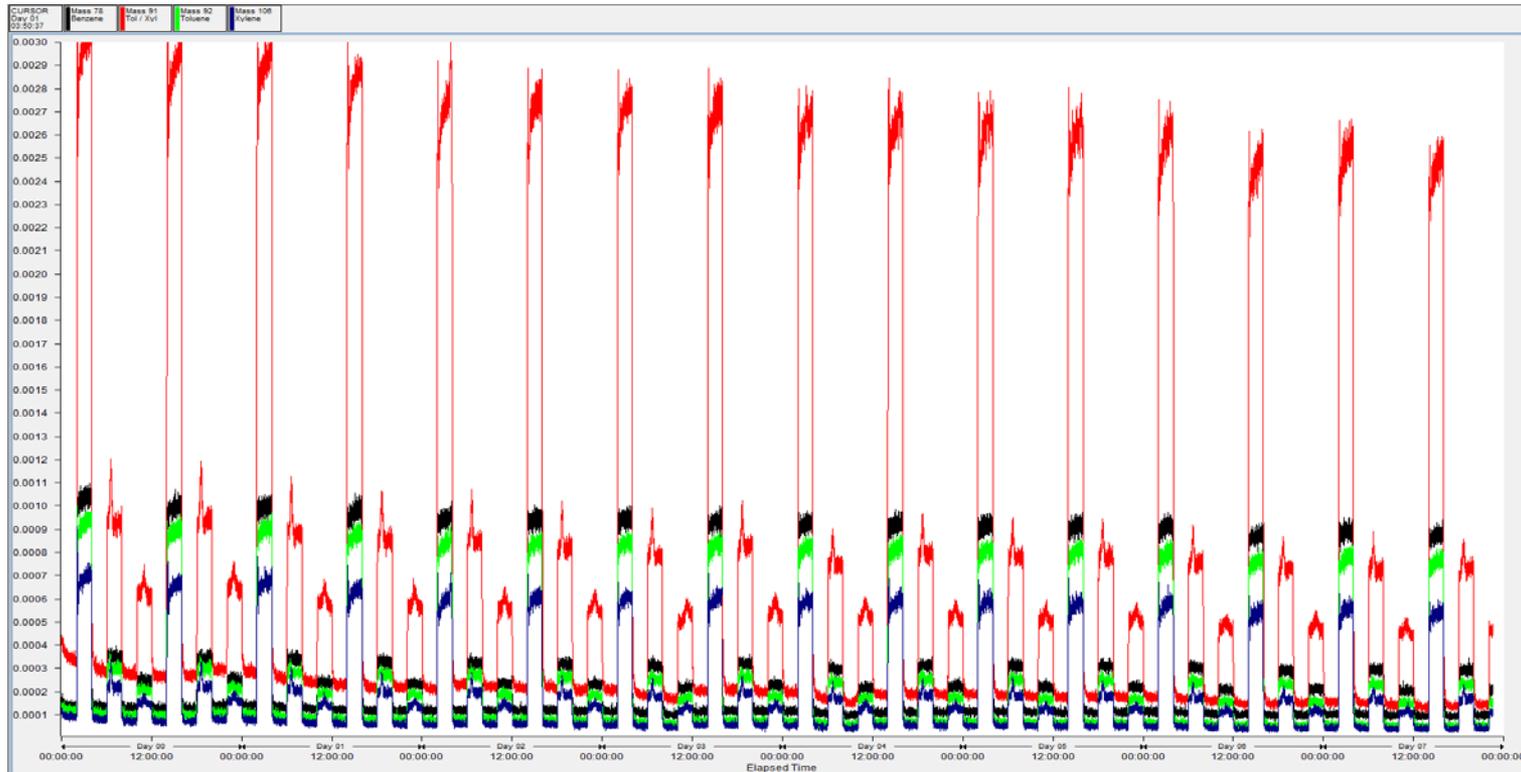
BTX in Nitrogen



The gas mix was automatically changed every 2 hours, the sequence being

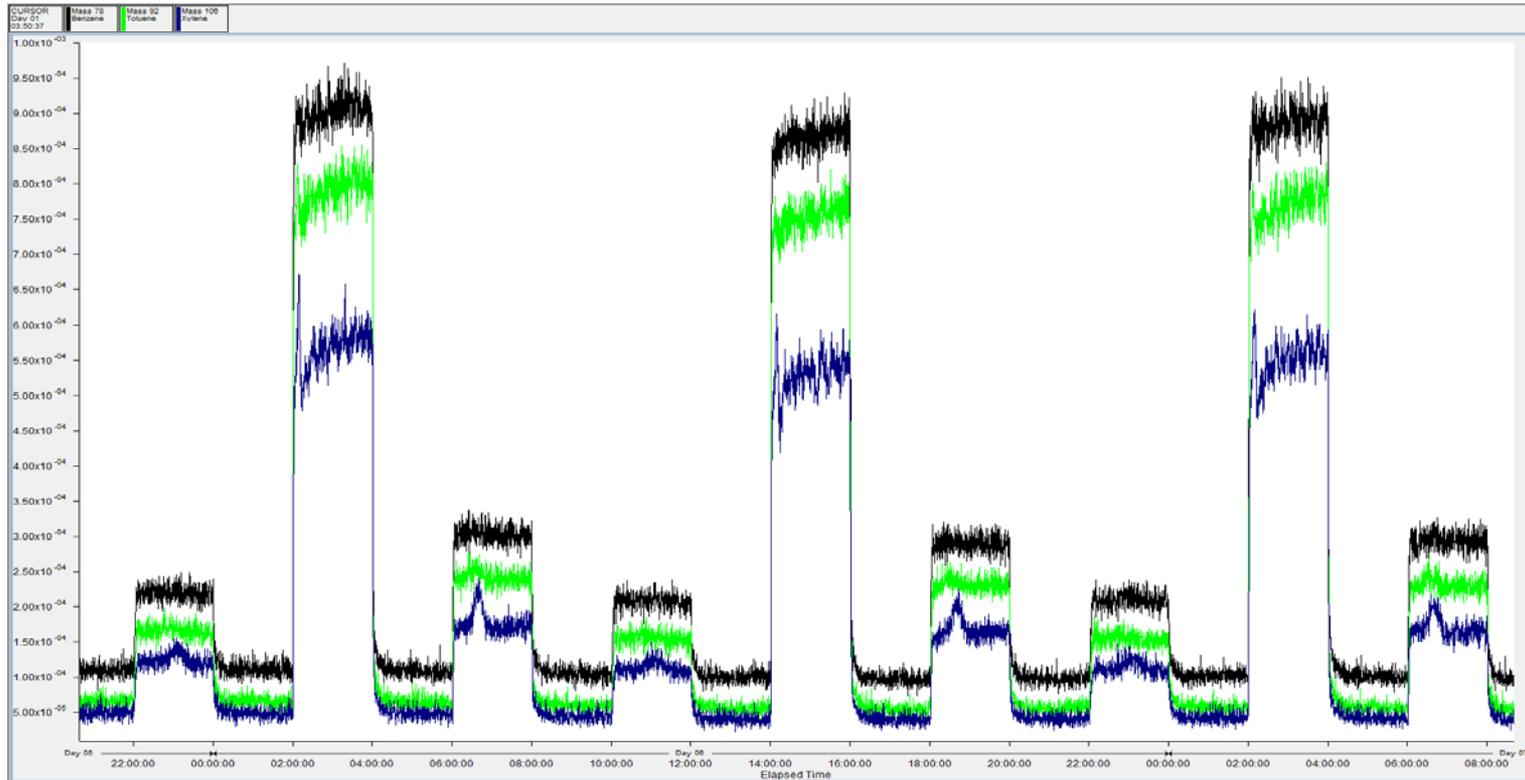


Results of 7 Day Run



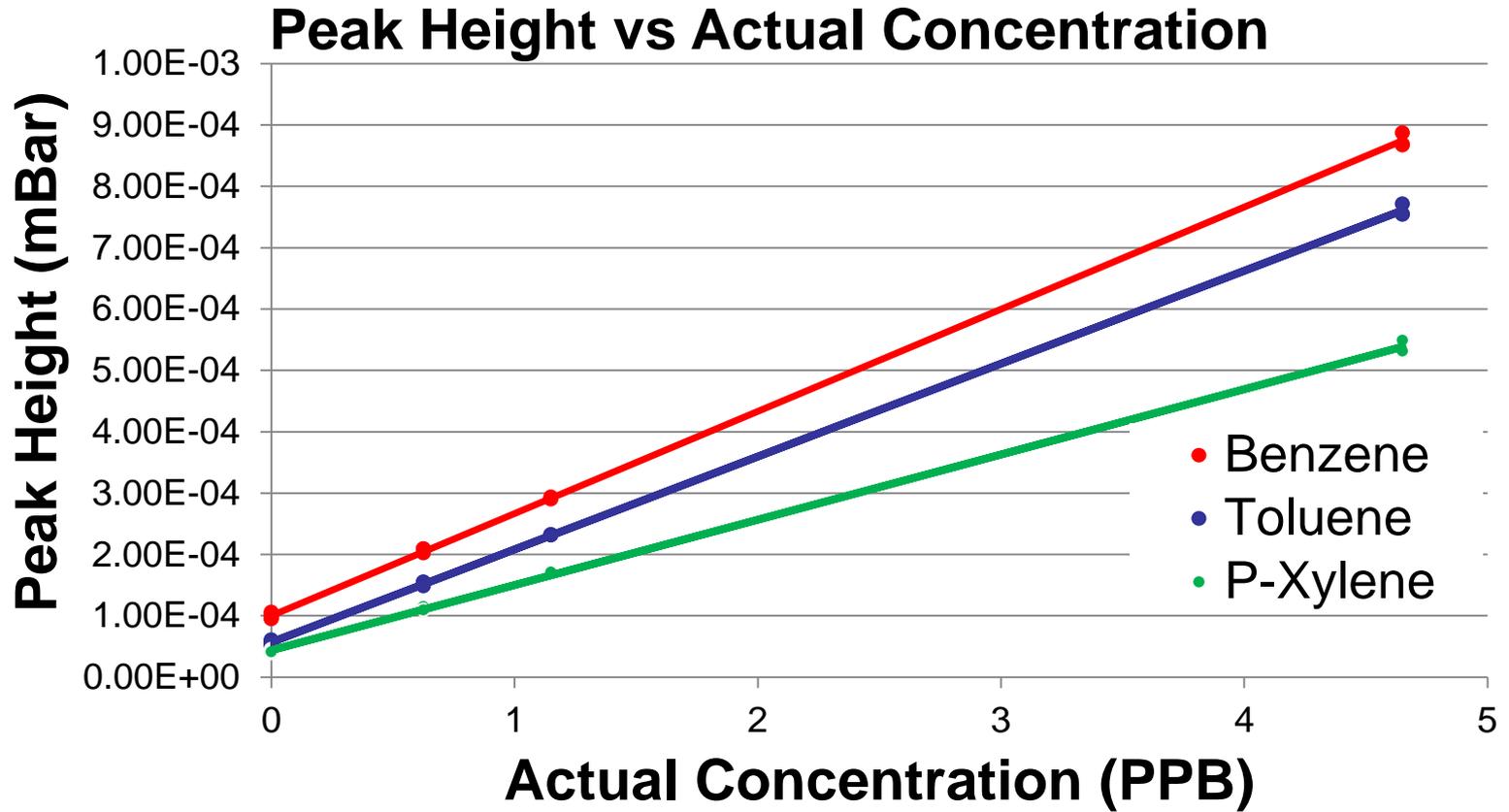
Over the 7 days the drift in sensitivity was approximately 20% but the reproducibility was good and all steps are clearly visible for all masses even when going from 0 to 630 PPT.

Data Analysis 1



The data from the last 3 cycles taking mass
 78 for Benzene (black)
 92 for Toluene (green)
 106 for P-Xylene (blue)

Data Analysis 2



Using the average of the peak heights and comparing to the actual concentrations (based on the dilution of the test gas) the system shows good linearity.

BTX Results

| | Benzene PPB | Toluene PPB | P-Xylene PPB |
|-------------------------------|--------------------|--------------------|---------------------|
| Background | 0.59 | 0.36 | 0.39 |
| Standard Deviation | 0.04 | 0.04 | 0.06 |
| 3 x Standard Deviation | 0.12 | 0.12 | 0.18 |

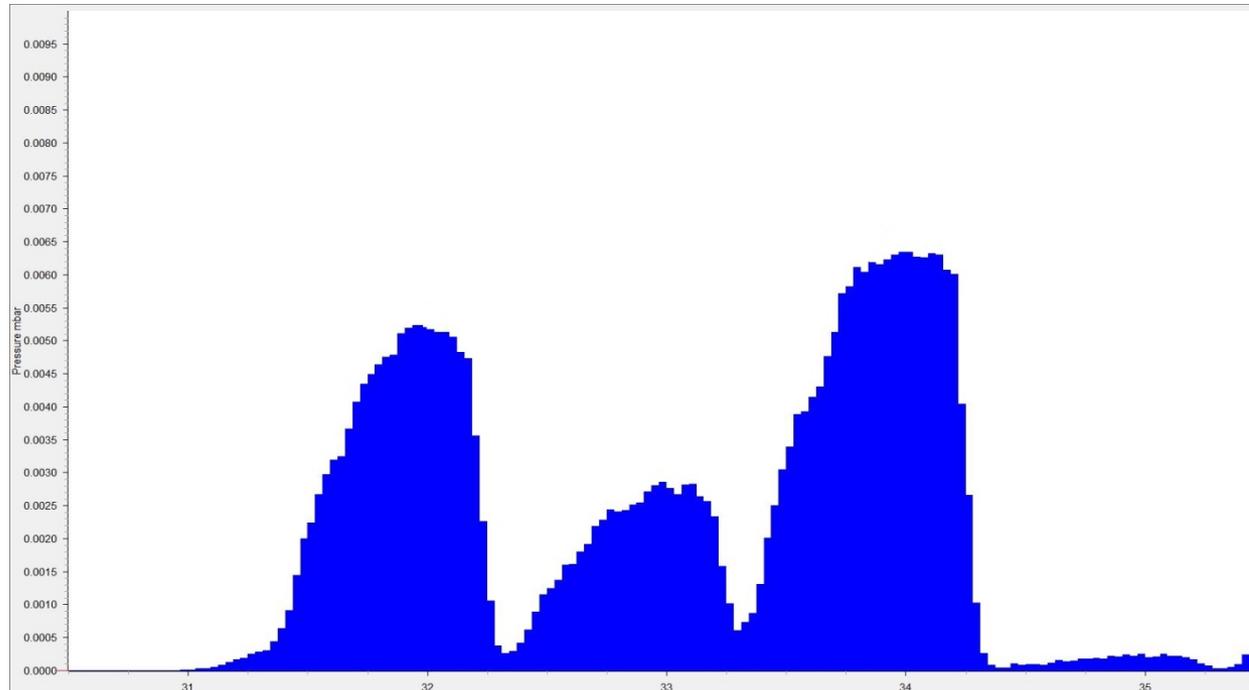
- The membrane inlet gives good stability and linearity for BTX at low concentrations with a detection limit in the 40-60 parts per trillion range.
- The most intense peak for Toluene and Xylene is m/z 91, if there was no need to differentiate these 2 compounds the limit of detection would be lower.

Coping with Interfering Peaks

- In the BTX example the interferences between the sample peaks raised the limit of detection.
- Interferences between compounds of interest and residual or matrix gases can also cause limitations in detectability.
- There are many instances of this, for example it is common to want to monitor CO in air.
 - CO has a mass of 28
 - Nitrogen also has a mass of 28
 - CO₂ with a mass of 44 also gives a fragment ion at mass 28

H₂S Detection Using Cirrus™

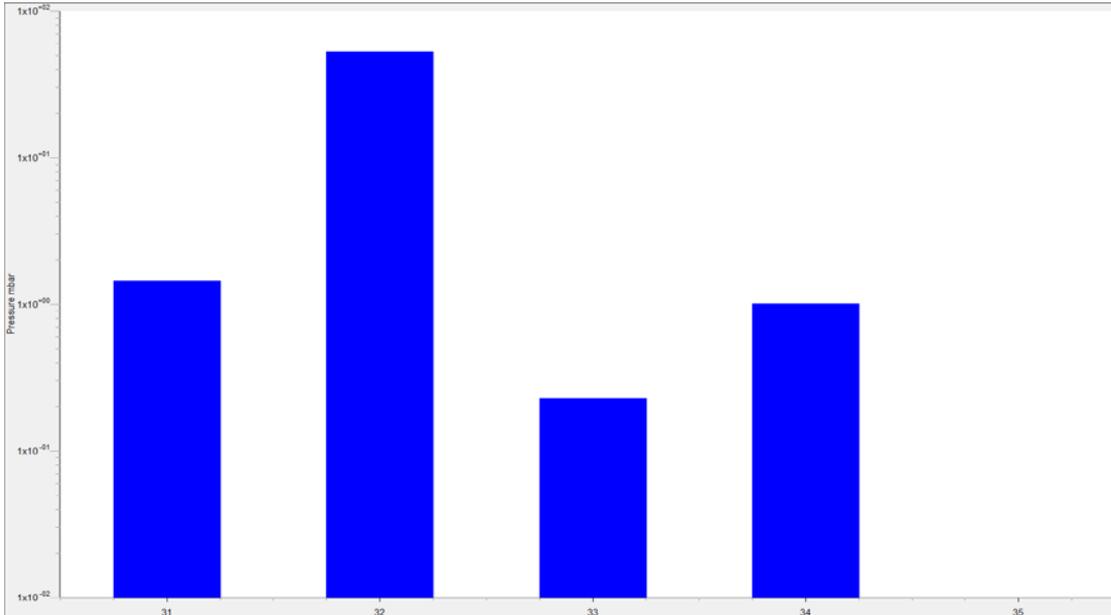
- Analog spectrum of 10 ppm H₂S in a balance of N₂



- Gives a detection limit for H₂S of 50 ppb and a precision on the 10 ppm reading of +/- 0.5 ppm with a sample time of 2 seconds

Air Spectrum Using Cirrus

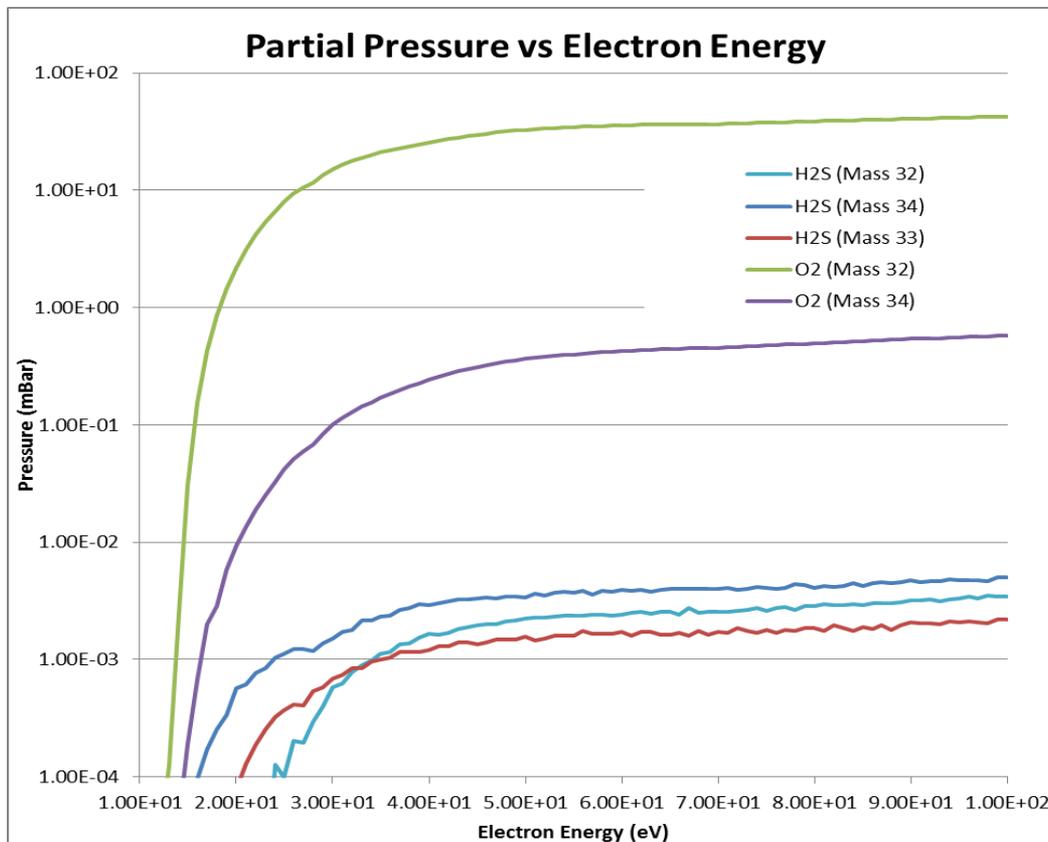
- Scanning the same peaks in air but with no H₂S



- Gives an equivalent H₂S background due to O₂ isotope at 34 amu of 2000 ppm.
- Using mass 32 and a subtraction for mass 34 would possibly improve detection limit to 50 ppm.

Effect of Electron Energy

- Measuring the peaks at lower electron energies can be effective, if monitoring NH_3 , water interference can be removed by scanning 17 eV or below.



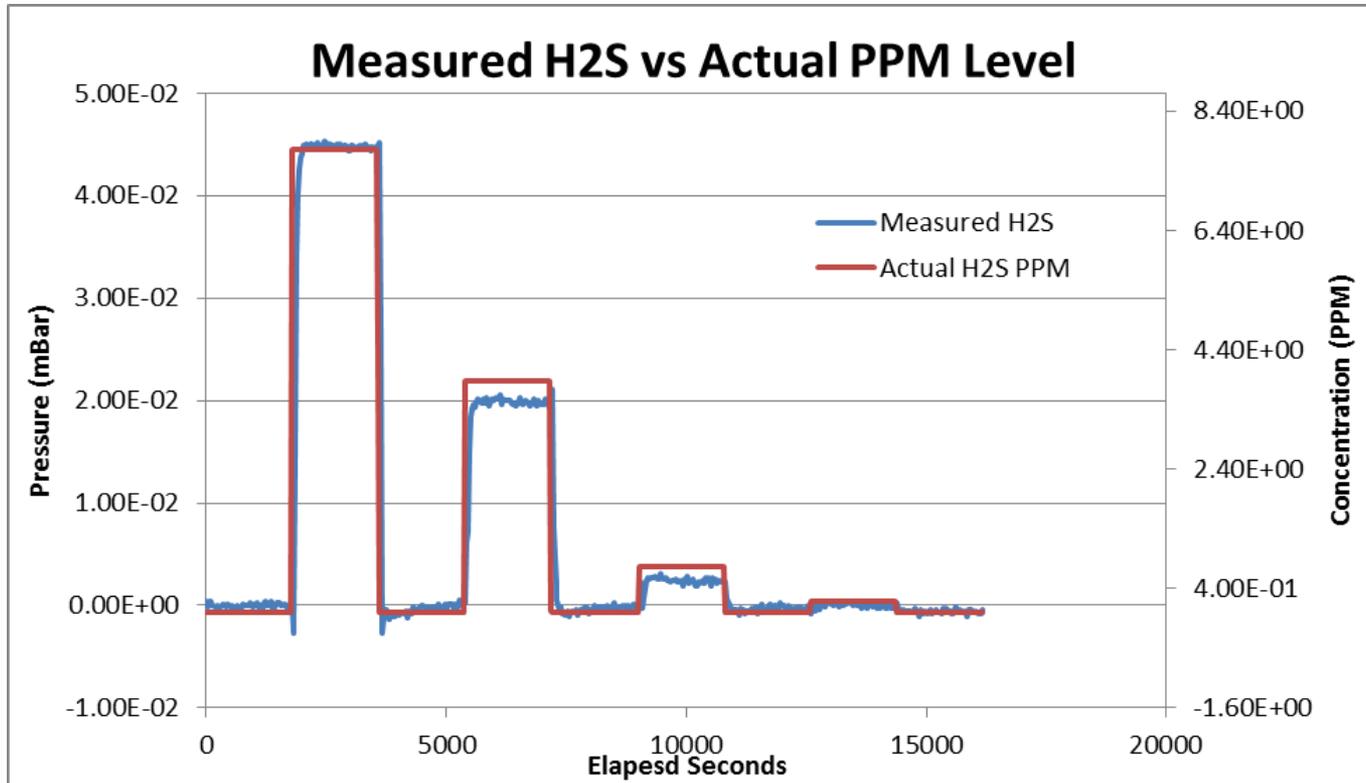
- Since oxygen is easier to ionise electron energy cannot be used to remove it's interference.
- The interference of H_2S at mass 34 can be removed by running below 25 eV

Universal Calibration Software

- Interfering peaks can be subtracted automatically with the Universal Calibration Software.
- This software allows a spectrum of each pure compound to be saved as a calibration standard.
- If all the major components are known, the overall composition can be de-convolved using simultaneous linear equations.

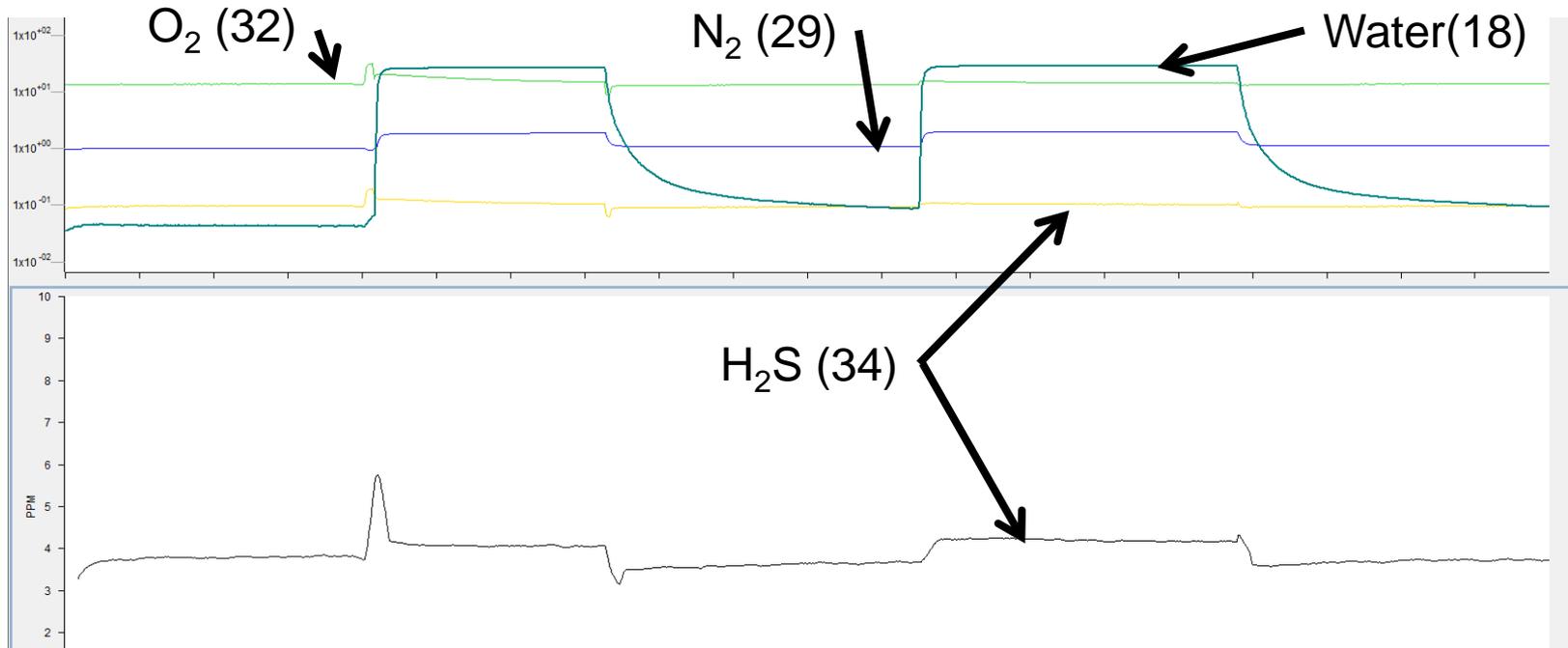
H₂S in Synthetic Air

- Measuring a 7.7, 3.3, 0.7 and 0.2 ppm H₂S in Air mix



- Results were not perfectly linear
- Implies a detection limit of around 0.5 ppm

Effect of wet and dry air



- Gas mixer switched between dry N_2 and N_2 bubbled through water.
- The effect on H_2S of several hundred times increase in water vapour is small.

Summary

- The membrane inlet allows fast enrichment of a wide range of sample molecules.
- The response time is equivalent to the standard capillary inlet.
- BTX with no interfering peaks showed an LOD as low as 40ppt.
- H₂S in air has the LOD reduced from 2000 ppm to 30 ppm using the membrane inlet, this can be lowered to less than 1 ppm with the subtraction of interfering peaks.
- The system ran reliably for 8 months without significant loss in sensitivity.