Design and Use of Portable and Compact Sampling Systems for Mass Spectrometers.

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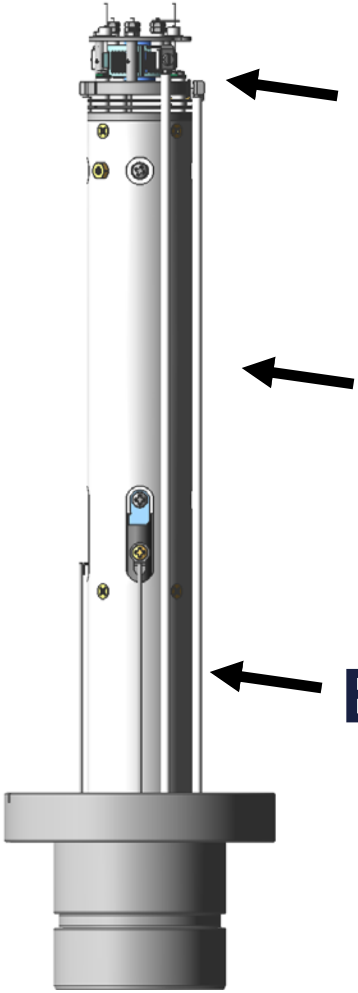
Outline

- Quick Review of PPA(RGA) Operation
- Instrumentation for Process Gas Analysis (Major application is semiconductor process monitoring)
- Non-semiconductor Instrumentation Examples
- Multi-Gas Leak Detectors.
- Not Going to Review Helium Leak Detectors
- High Pressure PPA(RGA) Alternative for mtorr Applications
- GC/MS for TIC’s, TIM’s, and CWA – HAPSITE ER.
- PPA/RGA Mass Spectrometer Specs and Analytical Figures of Merit.

Linear Quad PPA/RGA



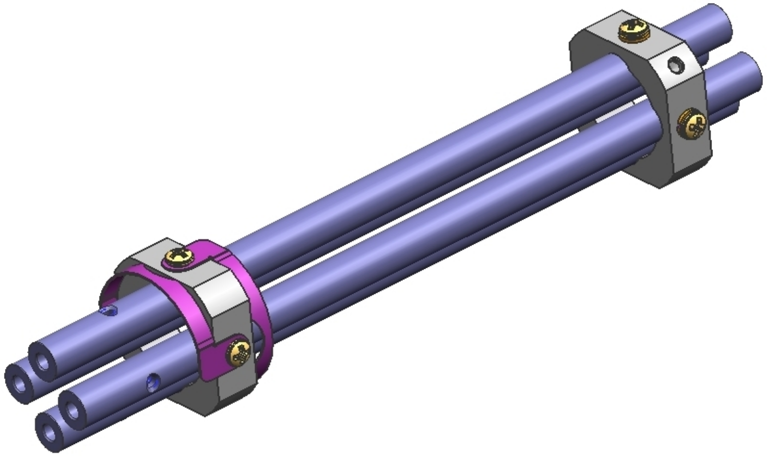
Ion Source

Linear Quad

EM/FC or FC

Open

Closed



PPA/RGA Background

- Most are linear quadrupole based and are usually limited to a maximum operating pressure of ~1E-5 torr.
  - Max pressure limit result of space charge in the ion source.
  - Collisions can limit the max operating pressure if the mean free path < ion path through the instrument.
- If P < 1E-5 torr the PPA can be directly immersed and the minimum detectable partial pressure (MDPP) is defined using sensitivity (S) and background noise (σ).

$$MDPP = \frac{\sigma}{S} \qquad Sensitivity = \frac{Ion \quad Current}{Partial \quad Pressure}$$

- Problem: no good definition for noise!

Detection limits for Sampling Systems
MDC not MDPP

- For simple pressure reduction systems the detection limit can be estimated by dividing the MDPP by the amount of pressure reduction.

- For most high pressure sampling the level of background vacuum gasses in the pumping/sampling system determines detection limits.

Fluid Dynamics

- Viscous flow does not fractionate the sample but molecular flow does – it's predictable (~$1/\sqrt{M}$). Transition flow also fractionates the sample but in a less predictable way.

- Errors in gas composition measurement can be avoided by keeping the flow into and out of the analyzer in the same flow regime.

- Viscous Flow: Mean free path is small compared to the characteristic dimension, $d/\lambda > 100$
- Molecular Flow: Mean free path is large compared to the characteristic dimension, $d/\lambda < 1$
- Transition Flow: Mean free path is similar to the characteristic dimension, $1 < d/\lambda < 100$

One Stage Pressure Reduction

- Reducing the pressure of an air sample from 1 atm to 1E-5 torr using an 80 l/s pump would require an orifice diameter >3 µm.
- This example of sampling is viscous in and molecular out.

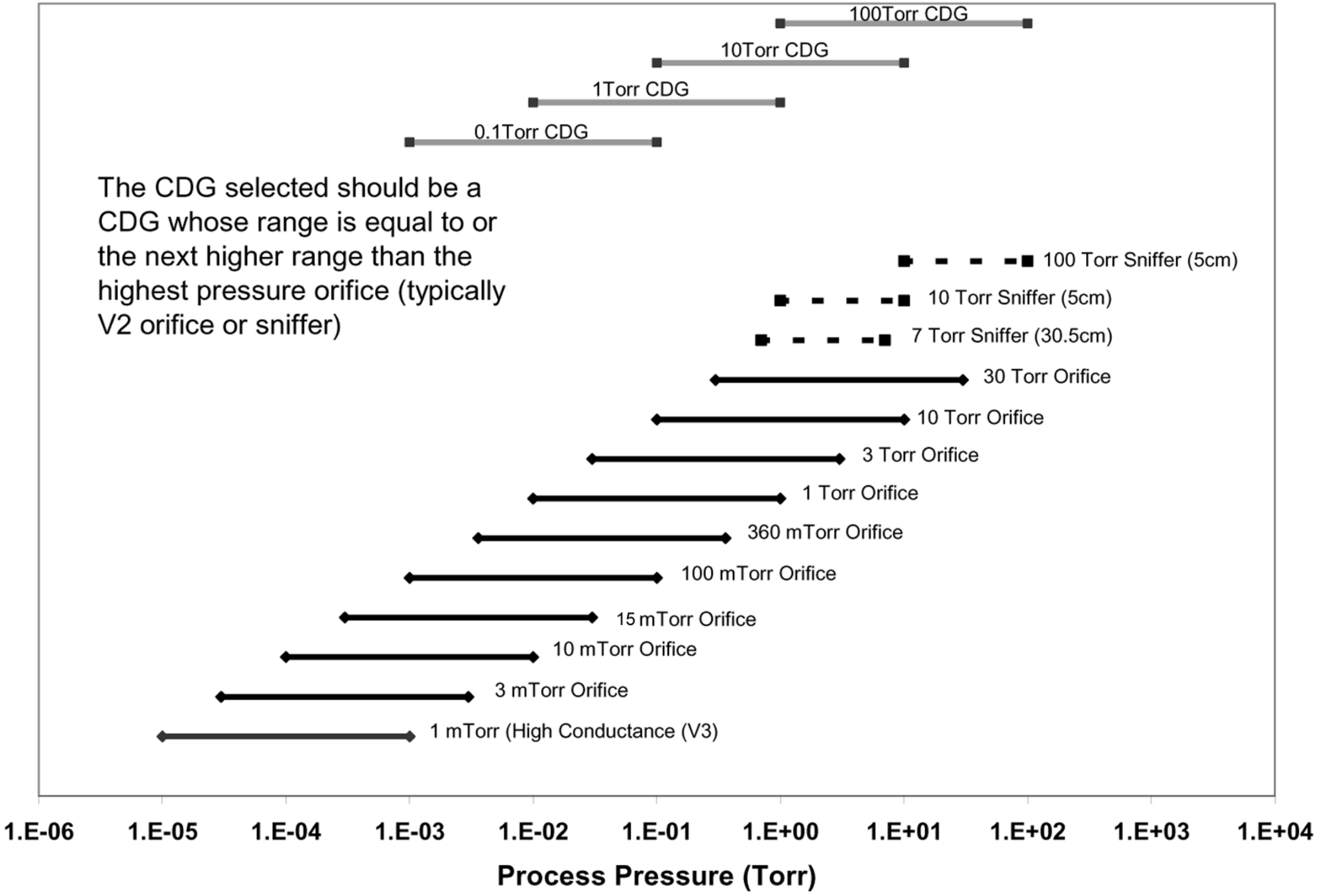
  Example: 50/50 He/Ar. The He/Ar ratio inside the analyzer would be $1.0(4/40)^{0.5} = 0.32$ (not really, more later)

  - Small orifices can clog easily.
  - Diffusion limited sampling. Diffusion time ~ P and ~$1/L^2$.

Multiple Stage Pressure Reduction

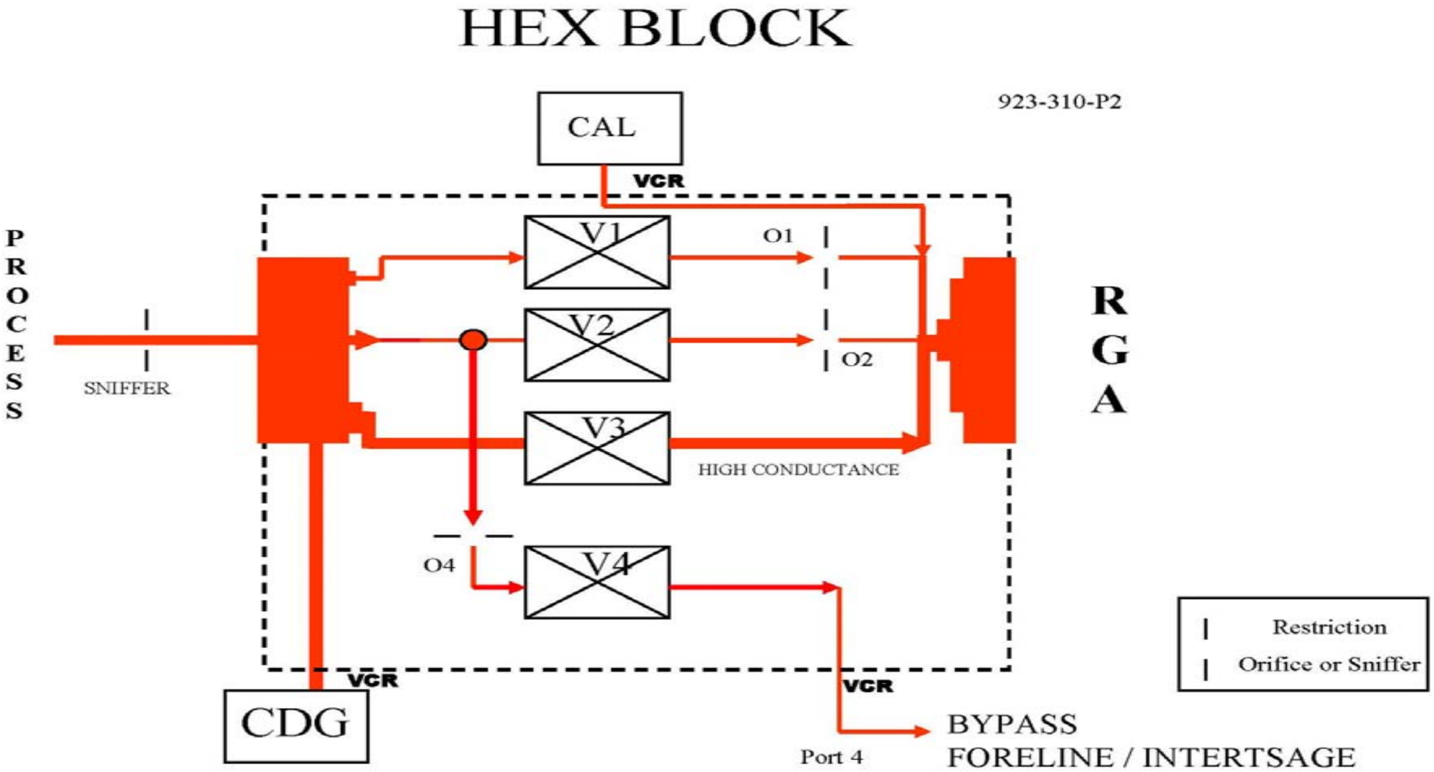
- **If process pressure is > 10 torr use a capillary (sniffer), orifice, and closed ion source.**
- **If process pressure is < 10 torr use an orifice and closed ion source**
- **Closed ion source pressure approximately 2.3E-4 torr**
- **Conductance between the closed ion source and the sensor manifold is < 1 L/s which keeps the analyzer and filament at ~ 1E-5 torr.**
- **Filament outside high pressure region to increase lifetime.**

Inlet Optimized for Target Process Pressure



The CDG selected should be a CDG whose range is equal to or the next higher range than the highest pressure orifice (typically V2 orifice or sniffer)

CPM Inlet System

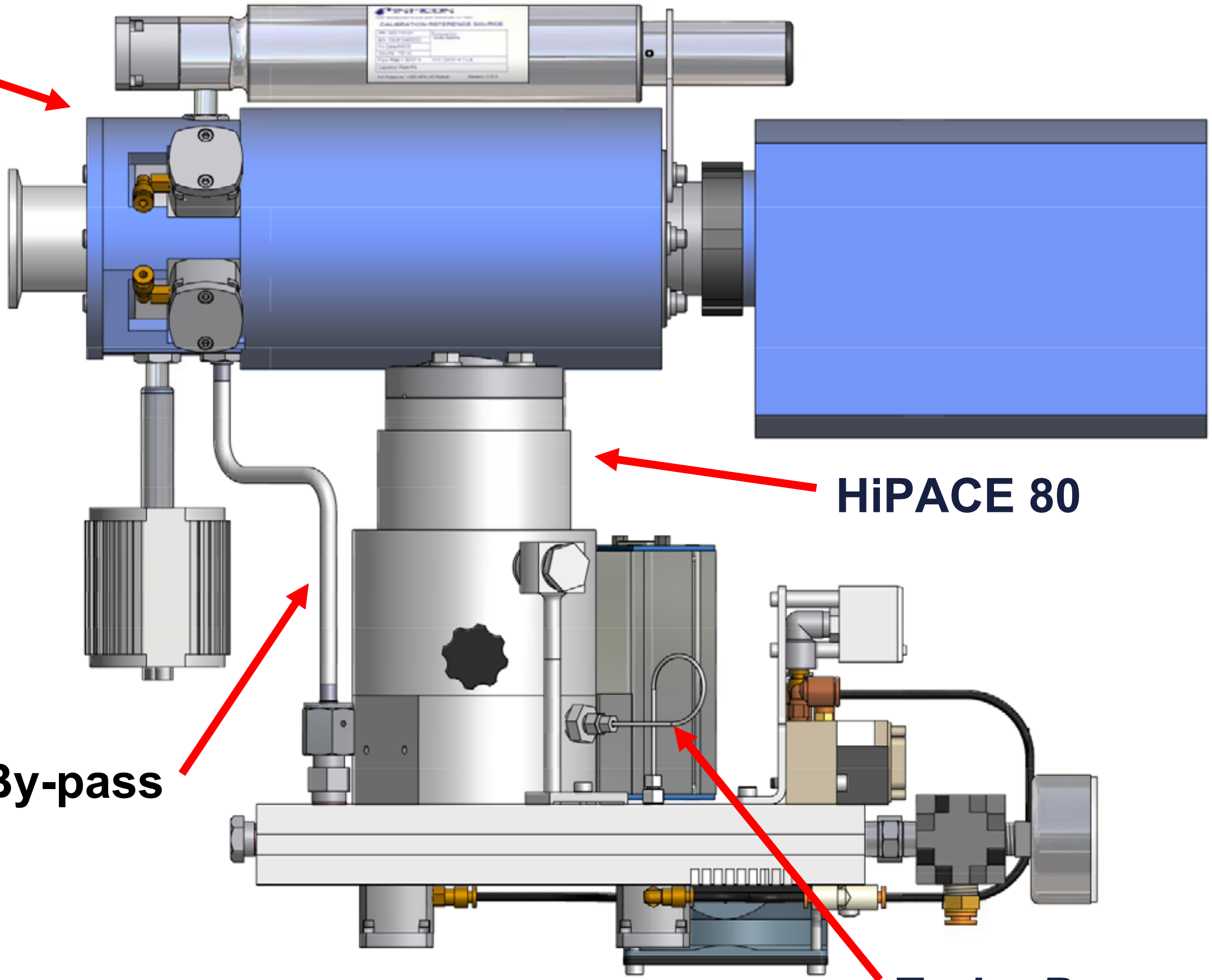


- Sniffer in choked viscous flow and orifice in molecular flow
- Bypass used to draw gas across V2 orifice to reduce response time.
- Inlet of sniffer can be placed very close to the wafer to further reduce response time.

HexBlock™

- Compact size.
- Minimizes sample path length. Important for “naughty gasses”
- Minimizes dead volume and diffusion distance (~2 cm).
- Has a calibration reference port
- CDG also attached to protect analyzer.
- Trivial to machine and low cost. (this last point is a lie).

CPM for Process Monitoring



Calibration reference

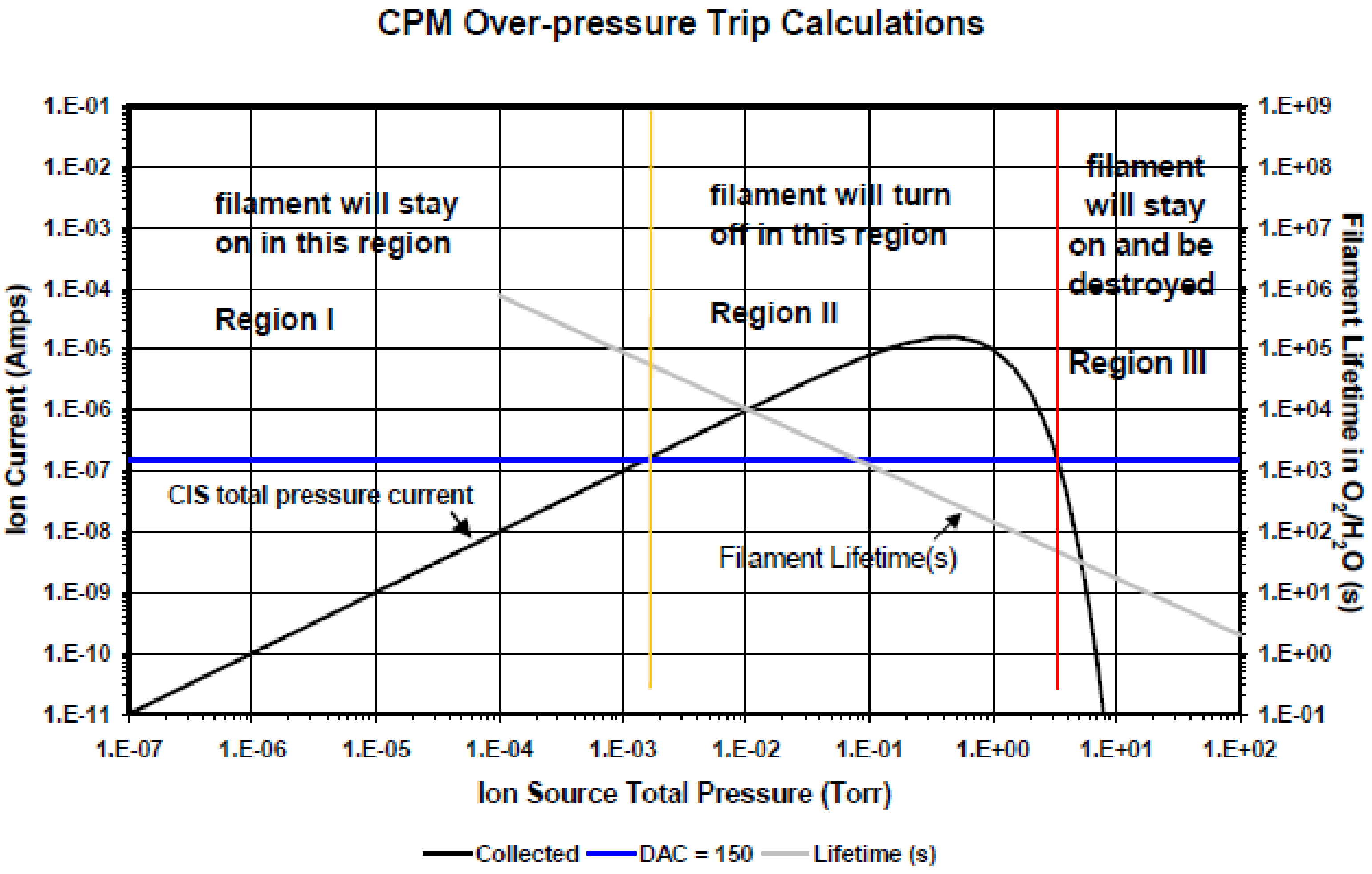
HexBlock™

HiPACE 80

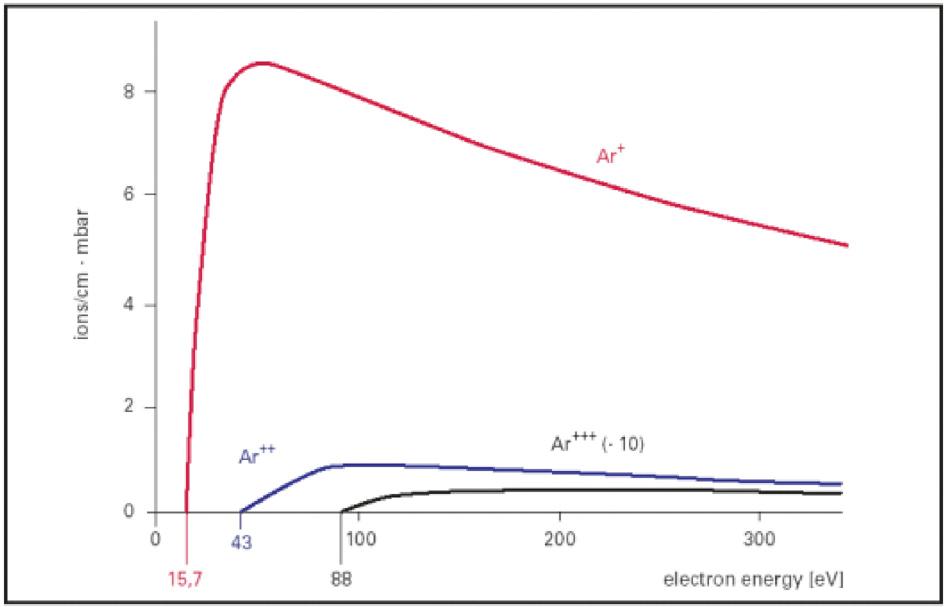
By-pass

Turbo Purge

HexBlock Gauge for Filament Protection



Lowering Electron Energy to Reduce Background Interference from Doubly Charged Ions



- •CPM has “high emission” setting (70 eV) for low pressure analyses and “low emission” (40 eV) for monitoring process pressures. This prevents 36Ar^{2+} from interfering with H20^{+} @18 *m/z*
- •Closed ion sources can be operated with only 10 eV electron energy for some applications.

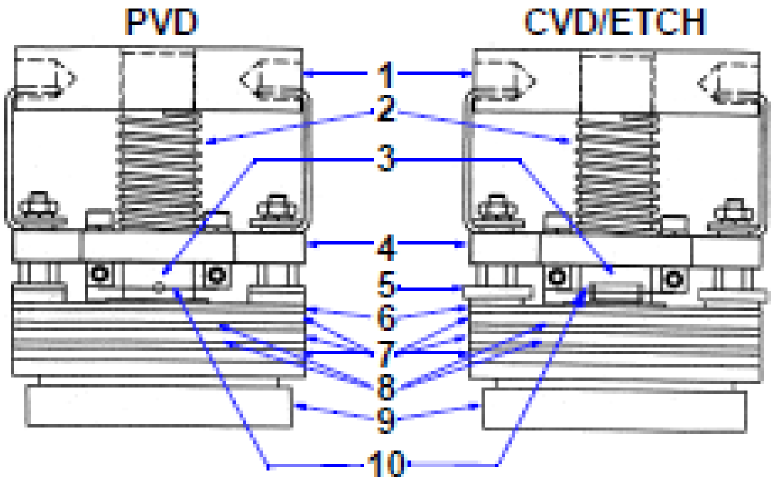
Filament Material for Closed Ion Sources: Tungsten *vs.* Yttria coated Iridium

- **Tungsten is most common for PVD and CVD applications.**
  - **PVD: Tungsten produces less artifacts (e.g. CO and CO_2)**
  - **CVD: Best resistance to corrosive halogen gasses (e.g. Cl_2 and F_2)**

- **Yttria coated Iridium is better for air sampling or other applications with high levels of water or oxygen.**
  - **Problem – reactions in coating can generate CO and CO_2.**
  - **Yt/Ir now available for INFICON CPM sources.**

- **For applications with high water and halogens...buy some extra sources.**

PVD Ion Source (really, really closed)



1 Sealing Disk
2 Spring
3 Anode Cylinder
4 Filament Block
5 Shield Washer
6 Anode Plate
7 Insulator Rings
8 Focus Plates
9 Upper Tube Ring
10 Filament

NOTE: Electron Repeller not shown (for clarity).

- **PVD source has much smaller entrance to focus electrons through but it can operate up to 10 mtorr (x160 higher than quad, CVD x23)**
- **No HexBlock, just a right angled valve.**
- **MDC limited by background gases in the inlet, closed source, and analyzer chamber.**
- **CVD closed ion source is pumped through a 0.7 L/s orifice.**
- **The PVD source has at 0.1 L/s orifice but the anode is pumped by the process (>100’s L/s) which lowers MDC.**
- **Limitation: max pressure of 10 mtorr.**

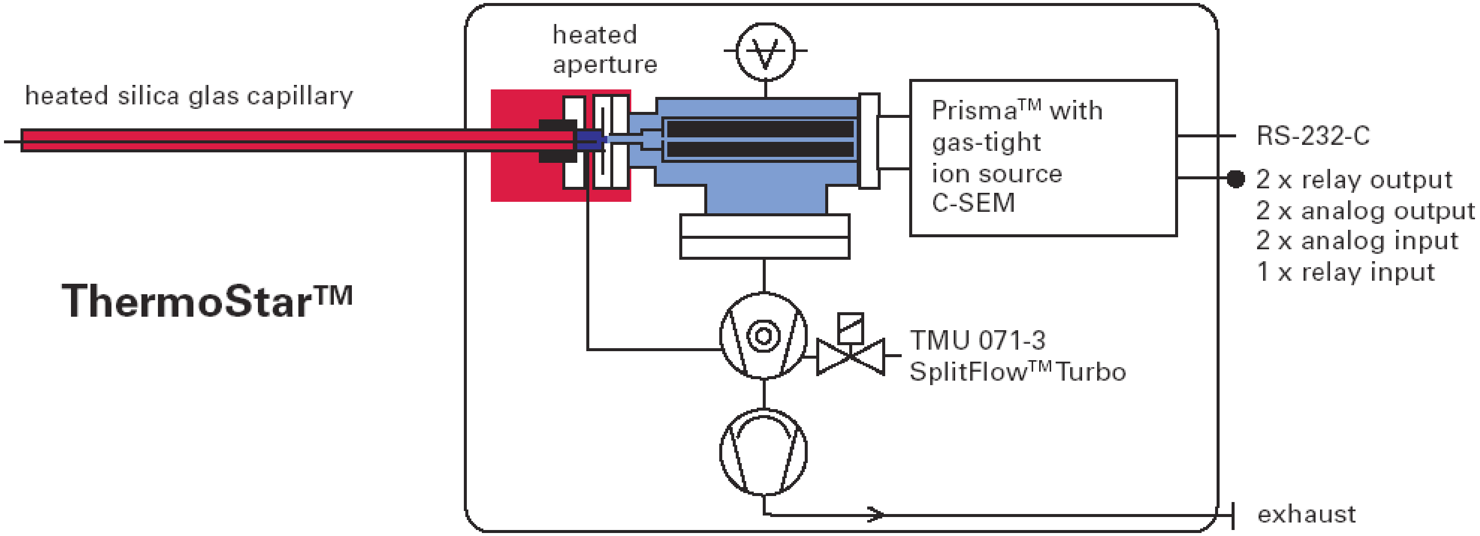
Pfeiffer Crossbeam Ion Source (Prisma+ and QMG)

- Used to sample molecular beams or pseudo-molecular beams
- Operates like an open ion source but contamination of the anode can be mitigated by directing the gas trough the center of ionization region.
- Magnets can be added to improve focusing of the electrons into the ionization region.
- Out gassing of the source also lower than normal open ion source and this has proven useful in other applications.

Pfeiffer’s OmniStar and ThermoStar

- Mostly used for atmospheric sampling
- Form factor well suited for bench top analysis.
- ThermoStar does not have a valve to minimize sampling surface area and is better suited for reactive gases.
- Example application: Thermal balances.
- Pfeiffer has also provided units with LN2 cryo traps and liquid membrane.
- Variable valve configuration can optimize inlet to new process pressures at the expense of more surface area and dead volume.

ThermoStar™


heated silica glas capillary

heated aperture

Prisma™ with gas-tight ion source C-SEM

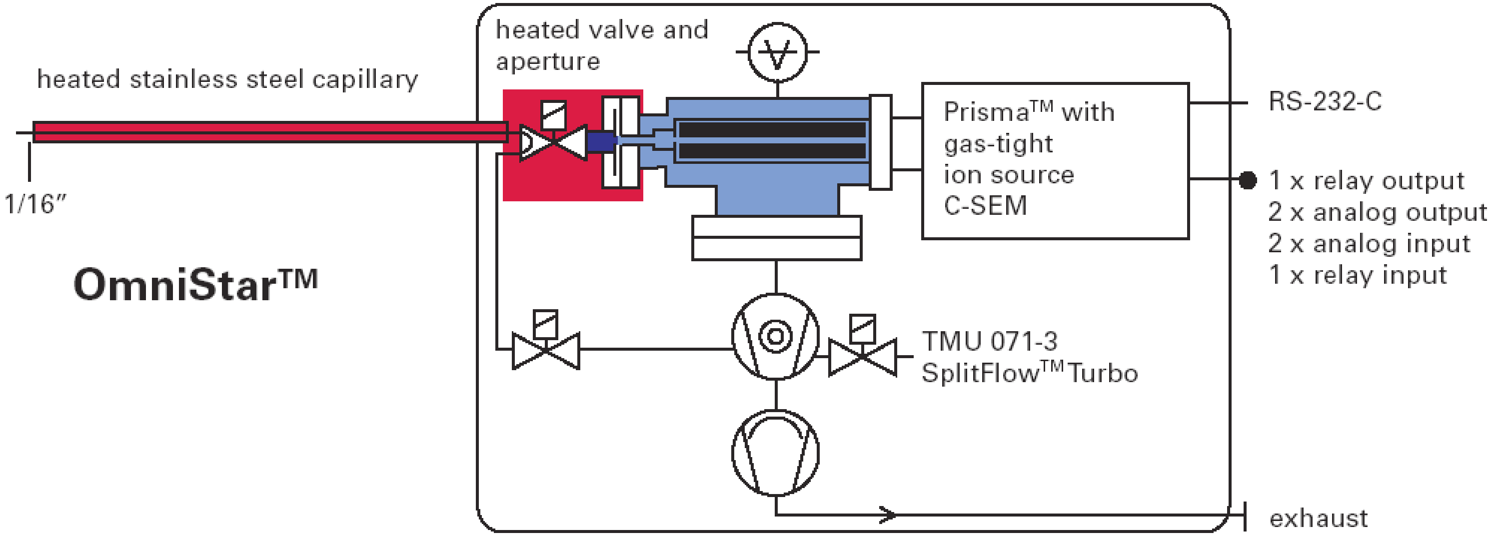
RS-232-C

- 2 x relay output
- 2 x analog output
- 2 x analog input
- 1 x relay input

TMU 071-3 SplitFlow™ Turbo

exhaust

OmniStar™


heated stainless steel capillary

1/16″

heated valve and aperture

Prisma™ with gas-tight ion source C-SEM

RS-232-C

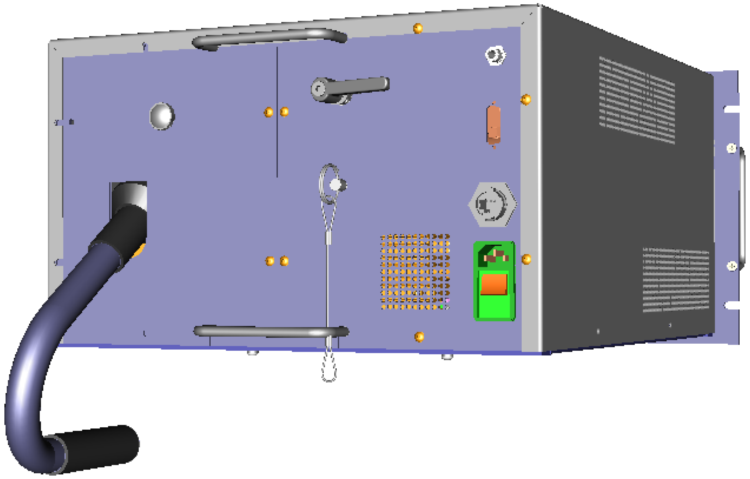
- 1 x relay output
- 2 x analog output
- 2 x analog input
- 1 x relay input

TMU 071-3 SplitFlow™ Turbo

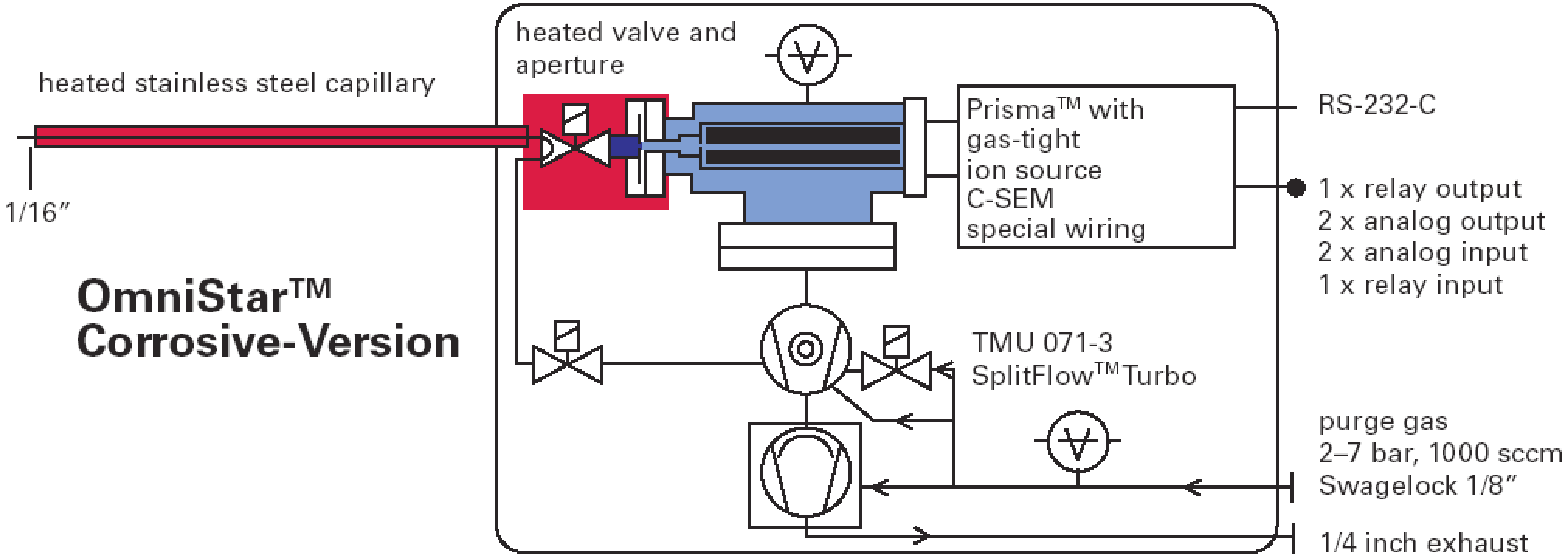
exhaust

Rack Mount Version for Mud Logging (Oil & Gas Exploration)

- Out put from a GC is feed directly into the ThermoStar.
- Sample handling and knowing where the drill tip was exactly when the sample was taken is very important.
- Analysis is better than using GC only.
- However, if you prefer a GC INFICON has acquired the micro-GC from Agilent.



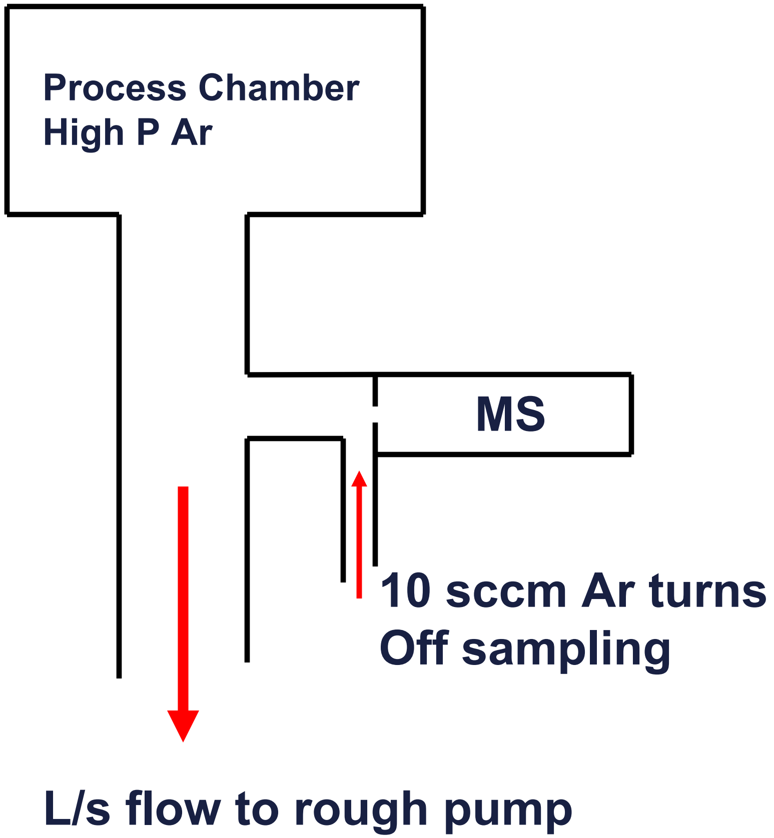
UNBLOWUPABLE



OmniStar™ Corrosive-Version

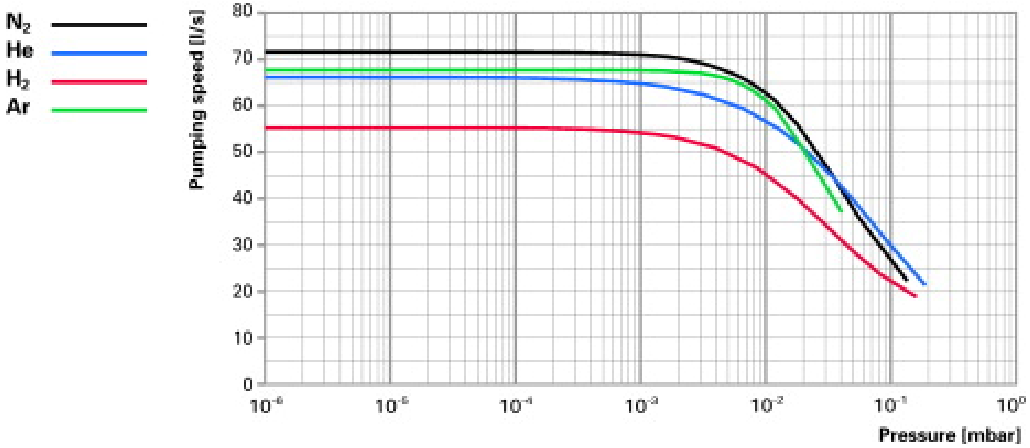
- Corrosive or flammable samples should be diluted before being exhausted by the roughing pump.

Virtual Valve



- Some Etch or CVD processes generates particles that can clog orifices and valves.
- Semiconductor process engineers are programmed not to allow anything to flow into their chambers so this has not been widely accepted.

Turbo pumps are not really “pure” molecular flow



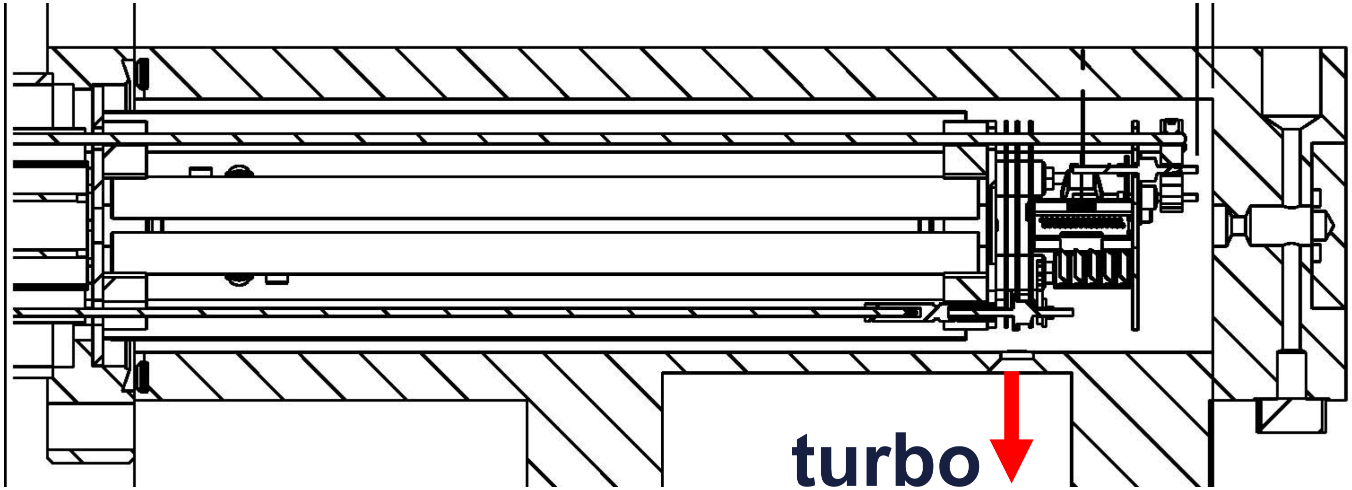
$$S_{eff} = \left(\frac{1}{S}+\frac{1}{C}\right)^{-1}$$

- Compression ratios for lighter gasses not as good – causes fractionation.
- A conductance limit between analyzer chamber and pump limits this problem. The closed ion source has this already and a conductance limit between the analyzer and the pump can allow the use of an open ion source.

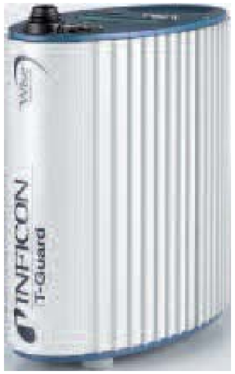
- Pumping Speed Ratio N2:H2 without conductance ~ 1.27
- Pumping Speed Ratio N2:H2 with 0.5 cm^2 orifice ~ 1.03

Open Ion Source w/ Little Fractionation

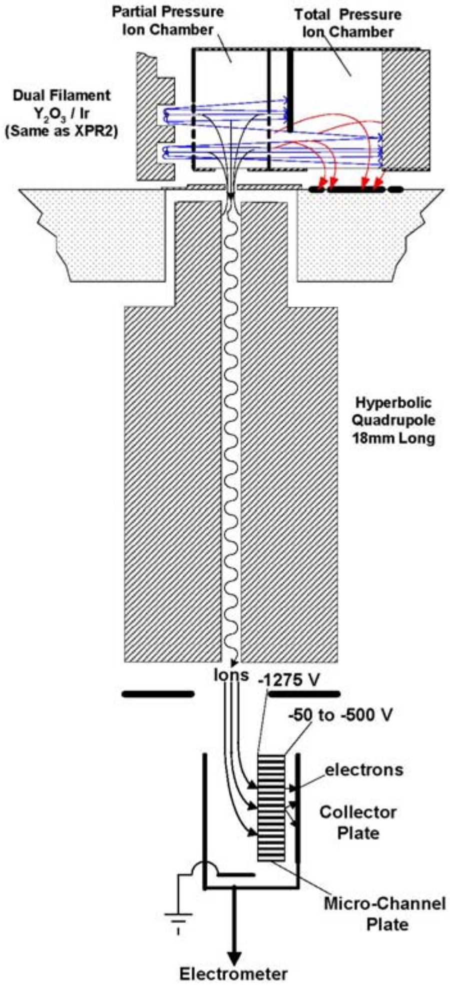
- OIS can be used for detecting non-corrosive gasses where normal vacuum gasses do not interfere.
- E3000
- PPA for multi-gas refrigerant leak detector
- High flow rate bypass minimizes response time.
- Ion source is optimized for high pressure operation ~ 2E-4 torr
- FC-only detector



Helium Leak Detectors



XPR3 : High Pressure PPA for PVD Applications



- Operates up to 20 mtorr
- Quad $r_0 < 0.015$”
- Operating Frequency ~ 13 MHz
- XPR1 released in 1996.

HAPSITE ER Chemical Identification System

- Another membrane inlet system designed to fractionate the sample.
- The membrane is used to limit air, or N2 from the GC, from getting into the analyzer.
- ER version has significant improvements to previous models.
- TIC's, TIM's and CWA's including VX.

What is a HAPSITE?

- **H**azardous **A**ir **P**ollutants on **Site**
- Person portable Gas Chromatograph/Mass Spectrometer (GC/MS)
  - Light weight
    - 42 lbs (with battery)
  - Rugged for field use
  - Easily decontaminated
  - VOC concentration range of ppm-ppt
    - Survey mode > 1ppm
  - Portable when used with battery
  - Heath risk assessment on-site without the laptop
    - AMDIS library of ~ 800 chemicals
  - Programmable for self-contained use
    - Onboard quantitative methods and integrated internal standards
  - Can also be controlled using a laptop computer
    - NIST library with a library of ~100,000 analytes

HAPSITE ER

New Keypad

802.11G wireless

New Universal interface

New HAPSITE software and Graphical User Interface (GUI)

New GC

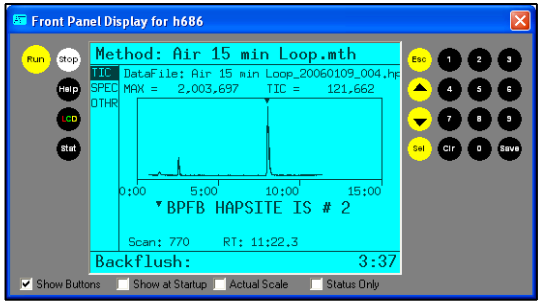
(ER) IQ software remains the same

HAPSITE ER Pumping System

- Membrane inlet with NEG pump and ion pump.
- Many improvements in sampling system were needed to detect VX. These improvements also lead to less gas consumption and lower detection limits for other chemicals.
- VX can be detected with SPME, Thermal Desorber or VIPER. VX will not, however, make it through air sampler
- Faster analysis: ER has 15 m column (old version used 30m)
- 15 GC/MS runs in 2-3 hours on 1 battery.
- NEG pump warranty is now for 200 hours of analysis time or 3 years. Engineering estimates that the NEG may last up to 1000 hours! Marketing and training units have over 500 hours and are still going strong.
- Sold over 300 ER units and have had no NEG replacements yet.
- Thermal desorbed can be used 5 analysis which takes ~ 1hr and 40 min on a single battery.

HAPSITE Major Milestones

- 1993 Idea conceived - development begins
- 1996 First analytical modules shipped
- 1998 First Headspace Sampling System
- 2001 Introduction of New GC/Concentrator System
- 2003 Situ Water Probe Released
- 2004 HAPSITE Smart Released
- 2005 HAPSITE Smart IQ V1.2 Software Released
- 2006 Version 1.3 Software Released
- 2008 HAPSITE Smart Plus
- 2008 HAPSITE ER
- 2008 HAPSITE Viper
- 2009 SPME Sampling System
- 2010 Thermal Desorber Sampling System



Front Panel Display for h686

Method: Air 15 min Loop.mth

DataFile: Air 15 min Loop_20060109_004.hp

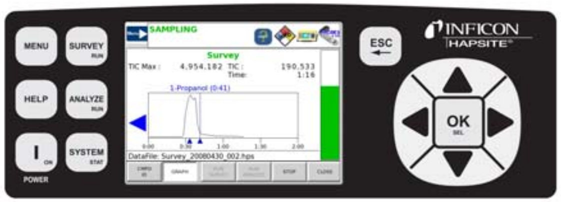
MAX = 2,003,697 TIC = 121,662

BPFB HAPSITE IS # 2

Scan: 770 RT: 11:22.3

Backflush: 3:37

☑ Show Buttons ☐ Show at Startup ☐ Actual Scale ☐ Status Only



HAPSITE ER Accessories

- Headspace Sampling system
  - Water
  - Soil/solids
  - Liquids
- SituProbe Sampling System
  - Clean water
- Detect VOCs
  - Qualitative methods
  - Quantitative methods
  - PPB to PPT range

Headspace Sampling System
H

SituProbe Sampling System

HAPSITE ER Accessories

- Solid Phase Microextraction (SPME)
- SPME fibers are used to collect the sample
  - Application specific fibers
    - Polydimethylsiloxane material
  - The analyte is collected on the SPME fiber and brought to the SPME Sampling System
  - The SPME fiber is inserted into the SPME Sampling System desorption chamber, where it is desorbed and sent to the HAPSITE ER sample pathway
    - Once the analyte is desorbed, all of the features of the ER are available for analysis
- Expands the capability of the HAPSITE ER
    - Carbon range up to C_{20} with a boiling point (BP) of up to 350°C

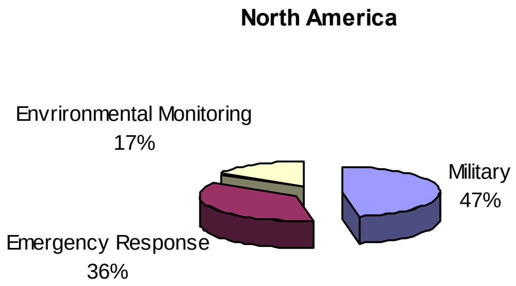
SPME Sampling System

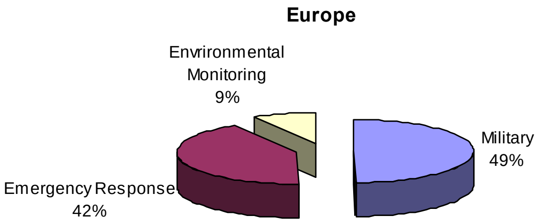
HAPSITE ER Accessories

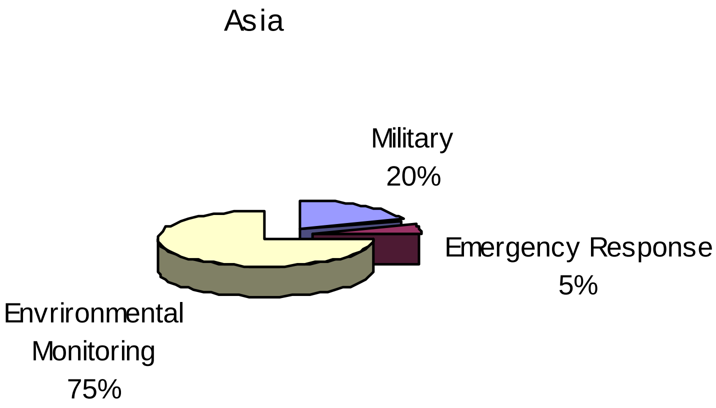
- Thermal Desorber Sampling System
  - Using an external sample pump, analytes are collected onto a thermal desorption tube
    - Thermal desorption tubes are available packed with Tenax or Carbon
  - The thermal desorption tube is inserted into the Thermal Desorber Accessory for analysis
    - Analytes are desorbed off of the TD tube and sent to the ER for analysis
      - MS (Survey) and GC/MS capability
- Qualitative and Quantitative analysis
- Trace level quantitative sampling of volatile organic compounds (VOCs) in air
- Samples can be collected from several locations simultaneously with multiple sampling pumps
  - Carbon range up to C_{17} with a boiling point (BP) of up to 300°C (air probe range is up to C_{15} with BP of up to 270° C)

Thermal Desorber Sampling System

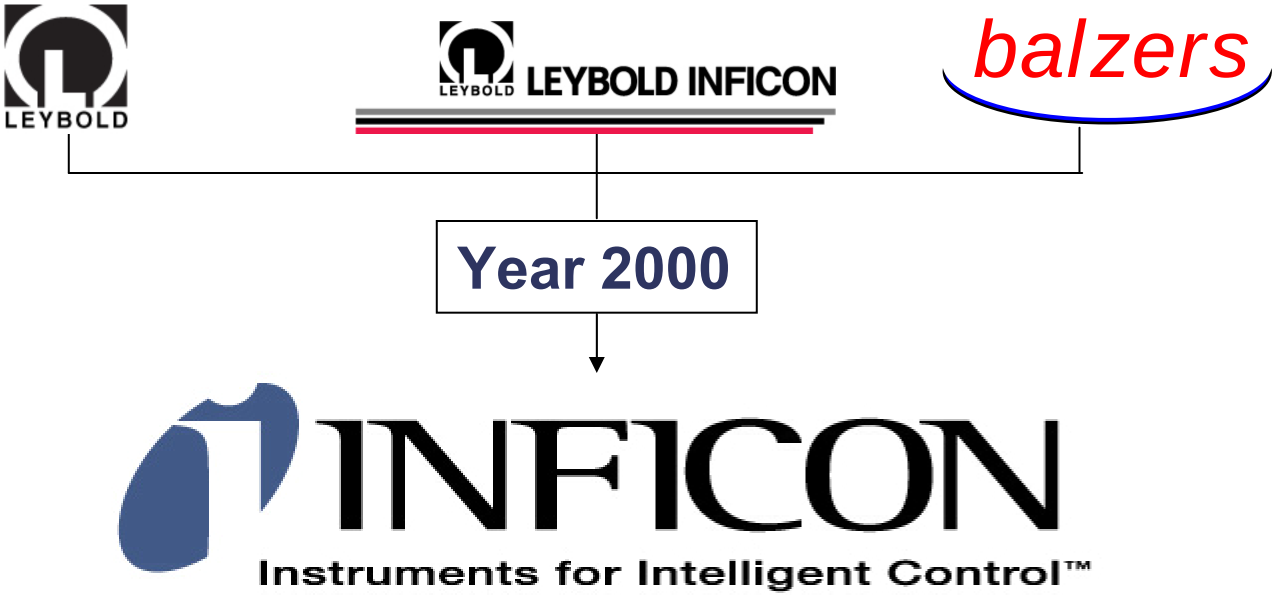
HAPSITE ER Markets







INIFICON in Business for > 40 Years



The instrument divisions of Leybold and Balzers joined together to form a new global company in 2000.

Major Manufacturing Facilities

Syracuse, NY, USA

Cologne, Germany

Balzers, Liechtenstein

RGA Specifications and Analytical Figures of Merit.

Outline

- Introduction
- Sensitivity & Linearity
- Zero Blast
- Abundance Sensitivity
- Stability
- Minimum Detectable Partial Pressure (MDPP)
- Scan Speed
- Special Considerations for UHV/XHV

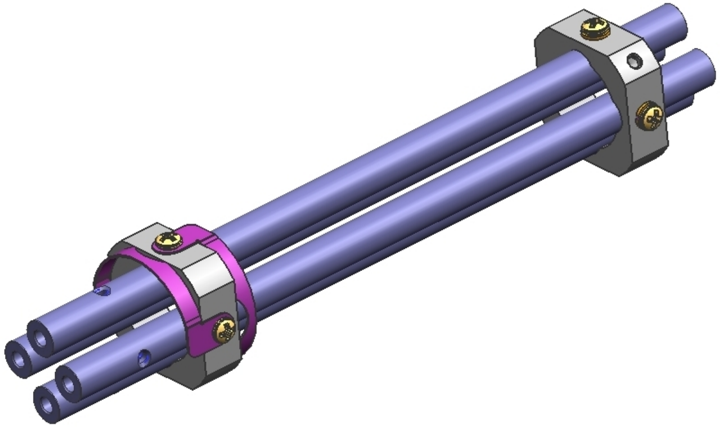
Introduction to Specifications

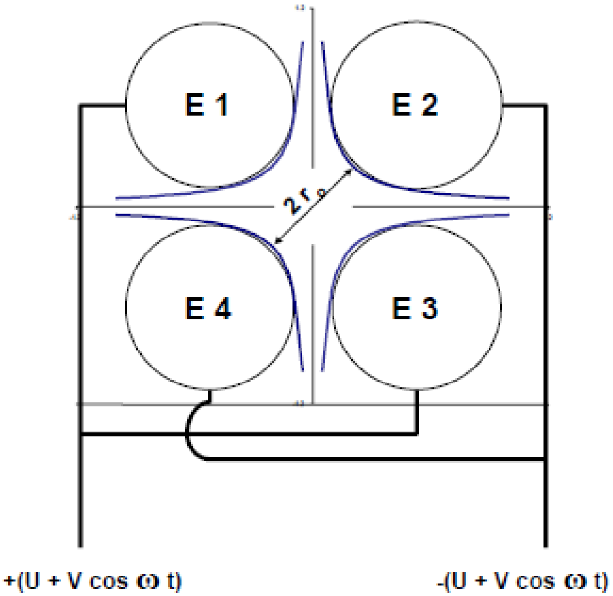
- Not everything included on an RGA spec sheet is a useful analytical figure of merit.

- Some specifications are often not well defined making it difficult to accurately compare different instruments.

Basic Requirements for High Performance RGA’s

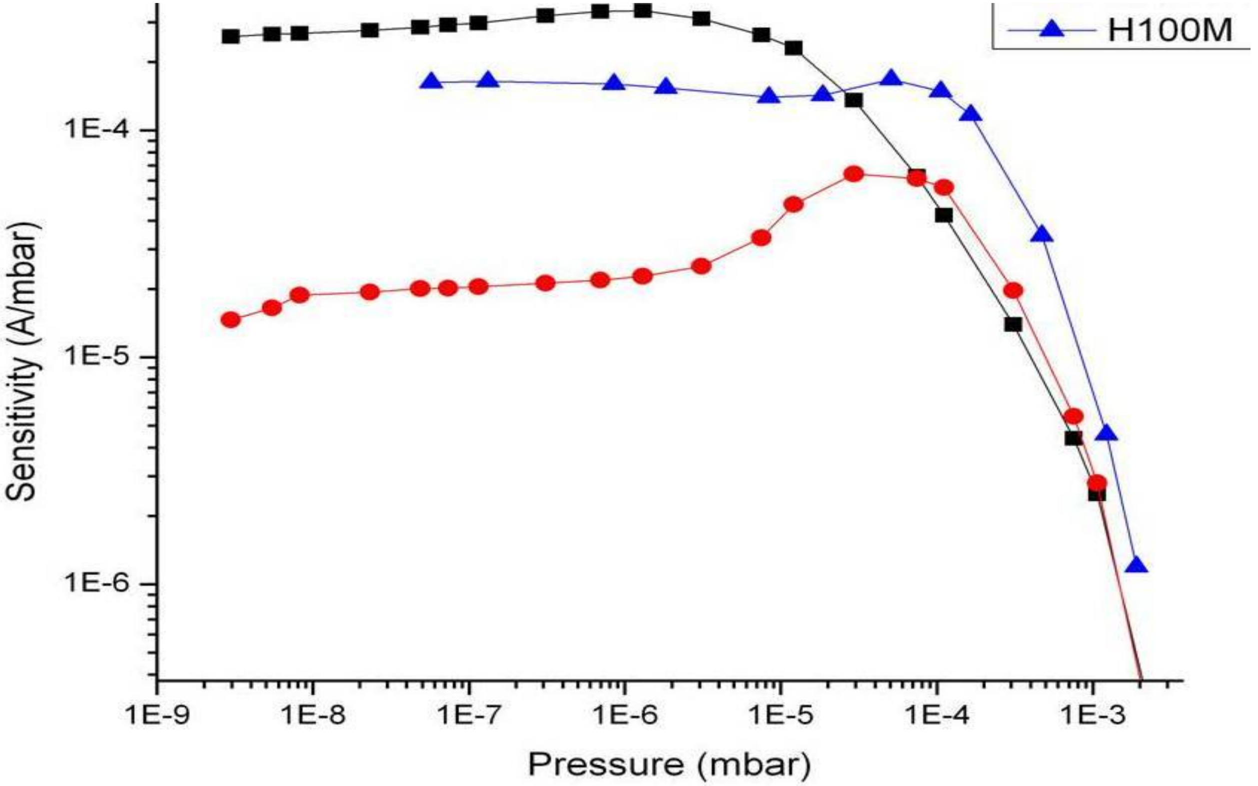
- **High precision mechanical alignment – especially for the quadrupole assembly.**
- **“Clean” components to avoid charging problems. (PACKAGED SO THEY STAY CLEAN!)**
- **Stable electronics**
  - **RF/DC power supply (high frequency → high performance)**
  - **Lens supplies**
  - **Emission Regulator**
  - **HV supply for electron multiplier**
- **Sensitive Electrometer**





Sensitivity and Linearity

$$Sensitivity = \frac{Ion \quad Current}{Partial \quad Pressure}$$



- Linearity is the analytical working curve (Sensitivity *vs.* Pressure).
- Dynamic range for intensity - MDPP to max operating pressure.
- FC mode matters – “EM Sensitivity” is a detector spec!

Zero Blast

$$ZB(ppm) = \frac{I_{\Delta BL(@2)}}{I_{AB}} * 1E6$$

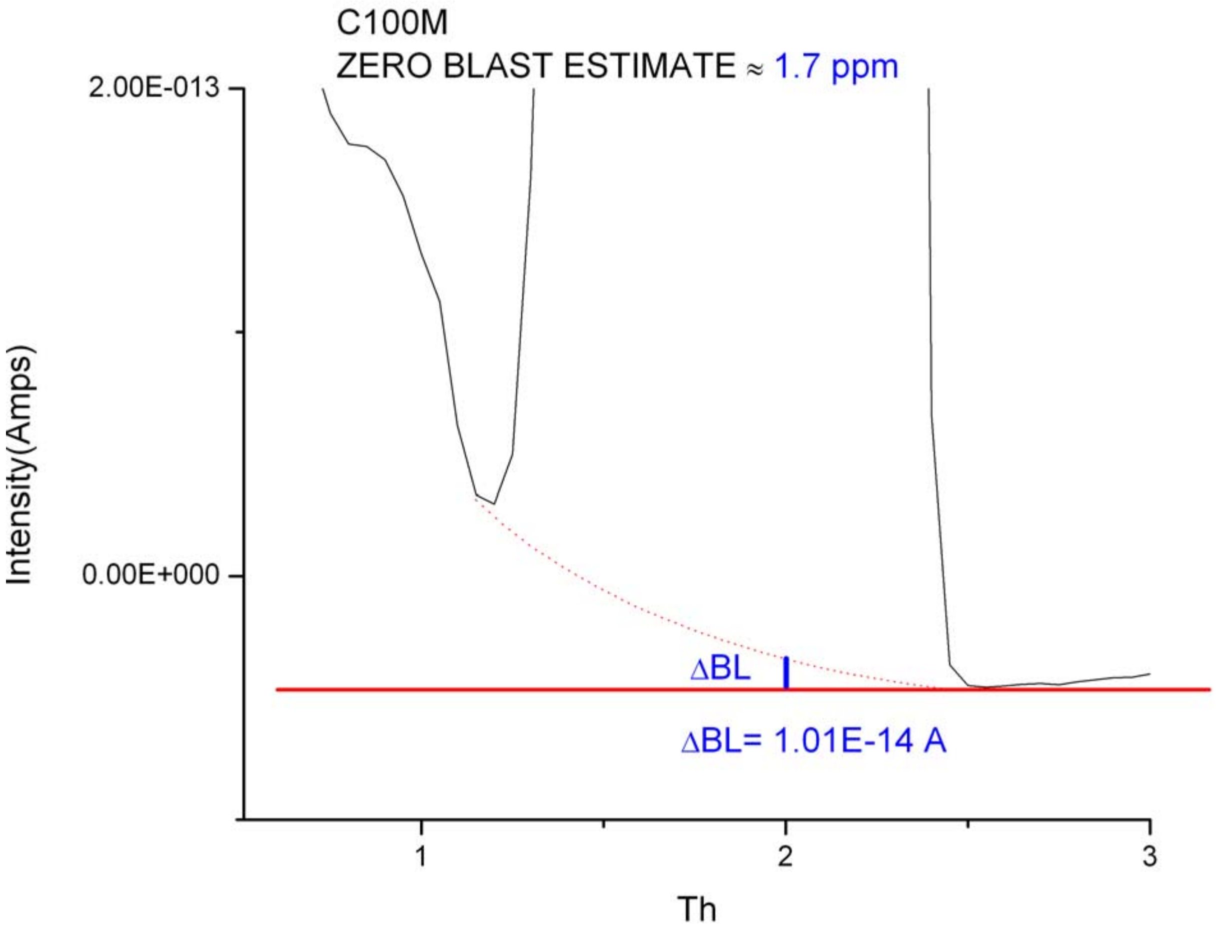
- Zero blast interference is caused by higher mass ions reaching the detector when the mass filter is set to pass low mass ions. Typically, ZB interferes with measuring low levels of hydrogen (2 m/z) in the presence of much higher amounts of nitrogen or argon. If ZB is exceptionally high it could also interfere with the measurement of helium (4 m/z).

- For a high performance RGA this is really only a high pressure issue (> 1E-5 torr)

- Often mitigated by over resolving the DC from 0-2 *m/z.*

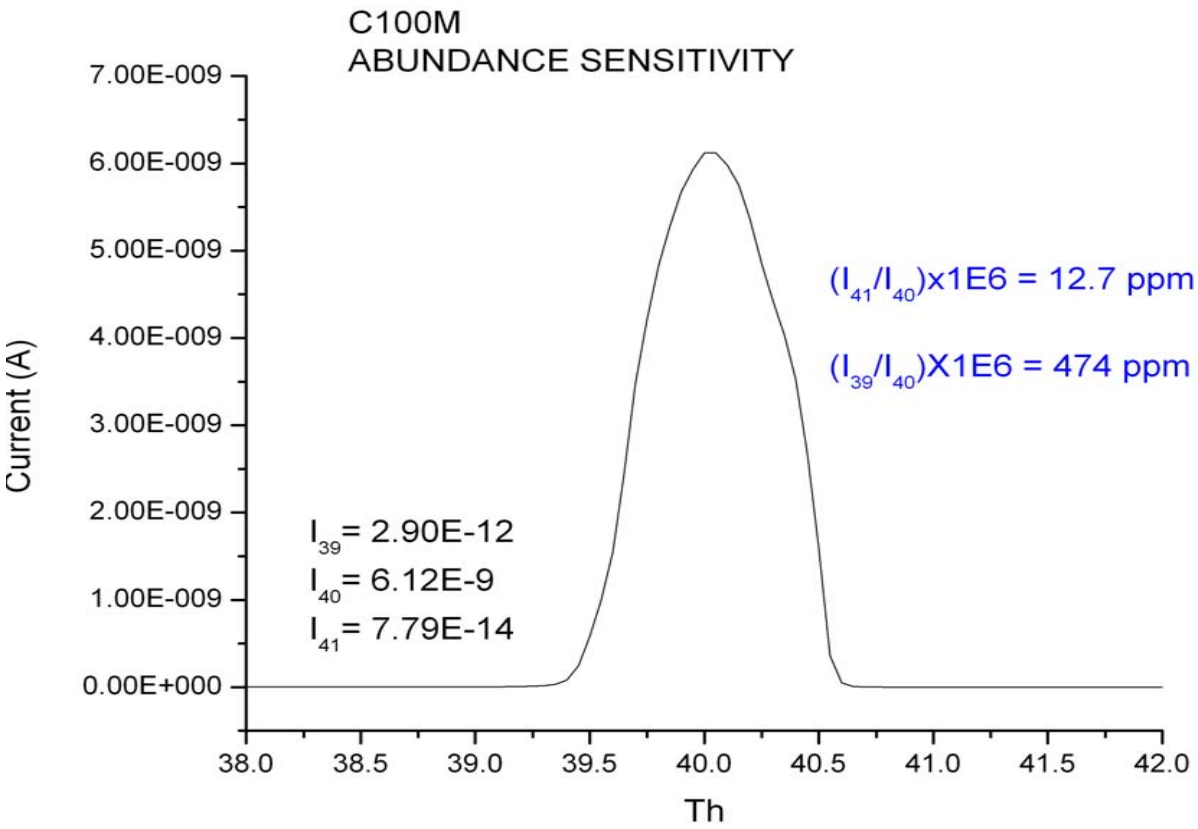
- High performance 100 amu systems have zero blast < 10 ppm. Lower performance RGA's can have zero blast > 200 ppm.

Zero Blast Example (1E-5 torr Ar)



Abundance Sensitivity

$$AB(ppm) = \frac{I_{m\pm1}}{I_m} * 1E6$$



Only relevant for a given resolution/sensitivity.

Stability

- Peak Position
  - Peak drift can be a problem especially on warm-up if the sensor changes mechanically or the electronics are not properly temperature compensated. Peaks shouldn’t move more than .1 m/z during a warm-up.
  - Long term drift can be corrected for using daily/weekly calibrations. (ref Inficon HPR)
  - Drift can also be mitigated using “Peak Lock” or something similar.
  - Especially important if you have poor peak shapes (unfortunately these usually go together).

- Peak height ratio is often used as a figure of merit but absolute peak height might be a better measurement.
  - Loss of EM gain can be recovered by increasing the voltage applied to the EM (use FC mode to check calibration).
  - Peak heights can change with ambient temperature.

- Both can sometimes change with input voltage (although that really shouldn’t happen).

Minimum Detectable Partial Pressure (MDPP)

$$MDPP = \frac{\sigma}{S}$$

- **MDPP is calculated from the measured sensitivity (S) and one standard deviation (σ) of the noise.**
- **Analytical chemists more commonly use 3σ for detection limit calculations.**
- **Problem: There does not appear to be an exact definition of how to make the noise measurement. (Ask for side-by-side demos)**
- **EM detectors can have high gains (1E6 – 1E7) but they also add noise so the MDPP is only a few orders of magnitude better – not 6 or 7 orders. (If you want high gain and low noise you can use a CuBe discrete dynode multiplier available with the QMG 700 system)**

Scan Speed

- Relatively straight forward specification just don't expect to achieve the best MDPP at the fastest scan speed.

- RGA's are most often operated in a selected peak mode for a number of reasons:
  1. Most speed, why scan the whole mass range when you are only concerned with a small number of masses.
  2. Total hydrocarbon determination can often be accomplished with an rf-only measurement.
  3. Analog scans can generate a lot of data – mostly zeros. Many customers want to store the data in quickly searchable databases. If our semi customers wanted to save analog scans for every wafer they'd need a "Goggle's" worth of computing power.

- Limitations for selected peaks:
  1. RF/DC settling time. If you are jumping from one mass to another how quickly your rf/dc voltages can stabilize to the proper target valves will determine how soon you can start your measurement. The sooner you can start the longer the dwell for a fixed measurement time and the better the S/N.

Pfeiffer Ion Sources for Prisma+ and QMG

More Ions (Higher Sensitivity)

Less Outgassing & ESD Ions (better for XHV)