

Trace Gas Analysis by GC

This is certainly one of the most challenging analyses in GC and some practical guidelines on improving the precision and accuracy of measurement will be discussed

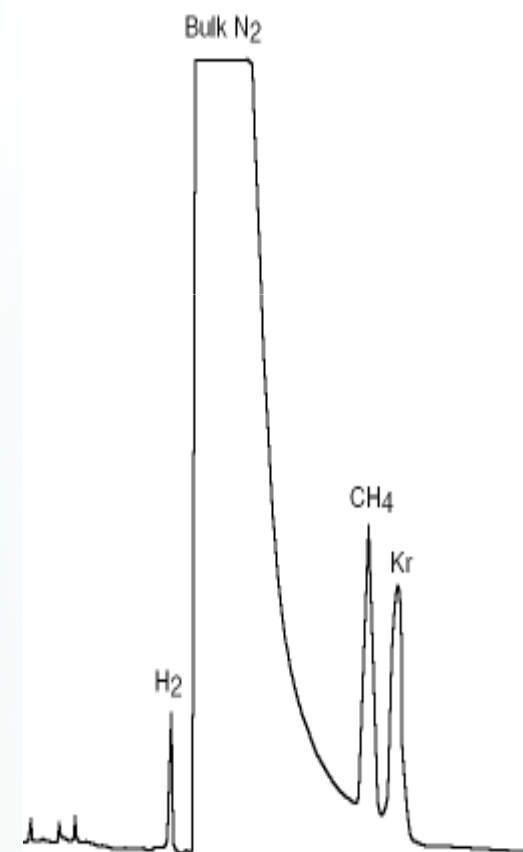
*John Swinley
Chromatography Consultants cc*

15th September 2009



What do we perceive as "Trace"

- ◆ Determination of materials which are present in extremely low concentrations in pure substances or mixtures of substances.
- ◆ The impurities that we are trying to measure are much lower in concentration than the same components in the carrier gas and fuel gases.
- ◆ Very often this is characterised by working very close to the detection limits of the system.
- ◆ Lowering of the detection limits is not always possible which infers that some form of sample pre-concentration step may also be required.



So who is interested in this?

◆ **Food and Beverage Industry**

- ◆ Residual vapours such as benzene on pharmaceutical capsules
- ◆ Beverage grade CO₂.
- ◆ Sulphur compounds in beer and wine.

◆ **Semiconductor Industry**

- ◆ Impurities in corrosive gases.
- ◆ Hydrocarbon contaminants spoil microchips in production.

◆ **Energy Industry**

- ◆ Hydrogen for cars and fuel cells.
- ◆ Dissolved gases in transformer oil
- ◆ Gas producers.
- ◆ Pebble bed reactors

◆ **Environmental**

- ◆ Air quality

◆ **Chemical Industry**

- ◆ Catalyst damage due to low levels of reactive gases.

Practical Considerations

- ◆ Thanks to gravity we have a world full of air which contains
 - ◆ 79% Dinitrogen and
 - ◆ 20% Dioxygen.
 - ◆ The next most abundant gases are:
 - ◆ Argon 0.9%
 - ◆ Carbon Dioxide 0.03%
 - ◆ Carbon Monoxide 0.0002%
 - ◆ Hydrogen 0.00005%(0.5ppm vol/vol)
- ◆ Therefore there is no way we will measure low O_2 or N_2 in a factory stack due to back diffusion of air.
- ◆ Also it is clear that the three most common problems with trace gas analytical systems are **LEAKS, LEAKS** and more **LEAKS**



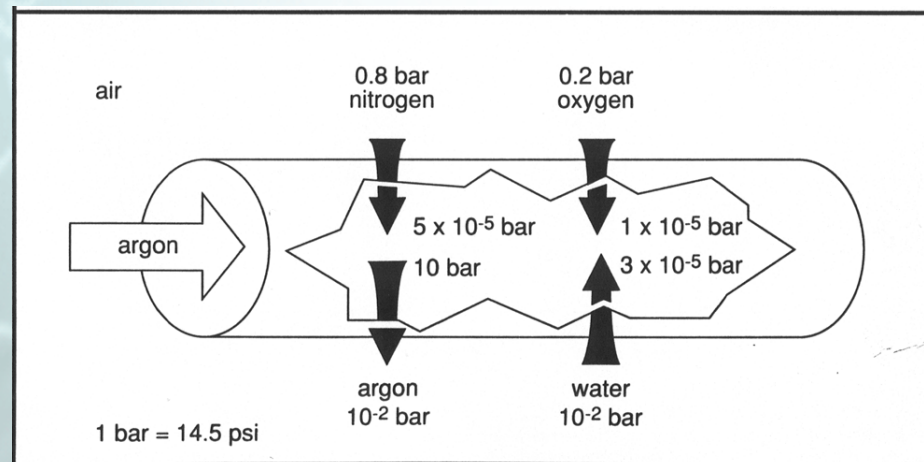
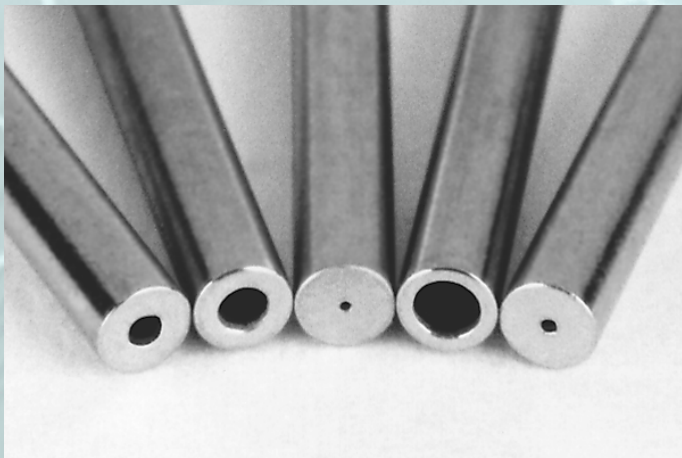
Contamination

- ◆ The small volume of air in the neck of the regulator at ambient pressure will contaminate a large cylinder at 20 MPa if allowed to mix. Must purge several times when initially fitting the regulator.
- ◆ A cheap and nasty cylinder regulator will add more than 10 ppm air to the gas.
- ◆ Each leak tight fitting adds about 0.2 ppm oxygen to the gas.
- ◆ One piece of Teflon tape represents a considerable oxygen leak.



Gas Purity

- ◆ We buy Instrument grade gases that are 5.0 purity i.e.99.999% or a maximum of 10 ppm total impurities-*this may soon change to 5.5.*
- ◆ If we do not use an electronic grade regulator the gas will be badly contaminated before the first connection.
- ◆ Even metals are permeable so we use stainless steel tubing and fittings with a good wall thickness.
- ◆ The quality of gas worsens after each component or fitting as we move toward the GC system.



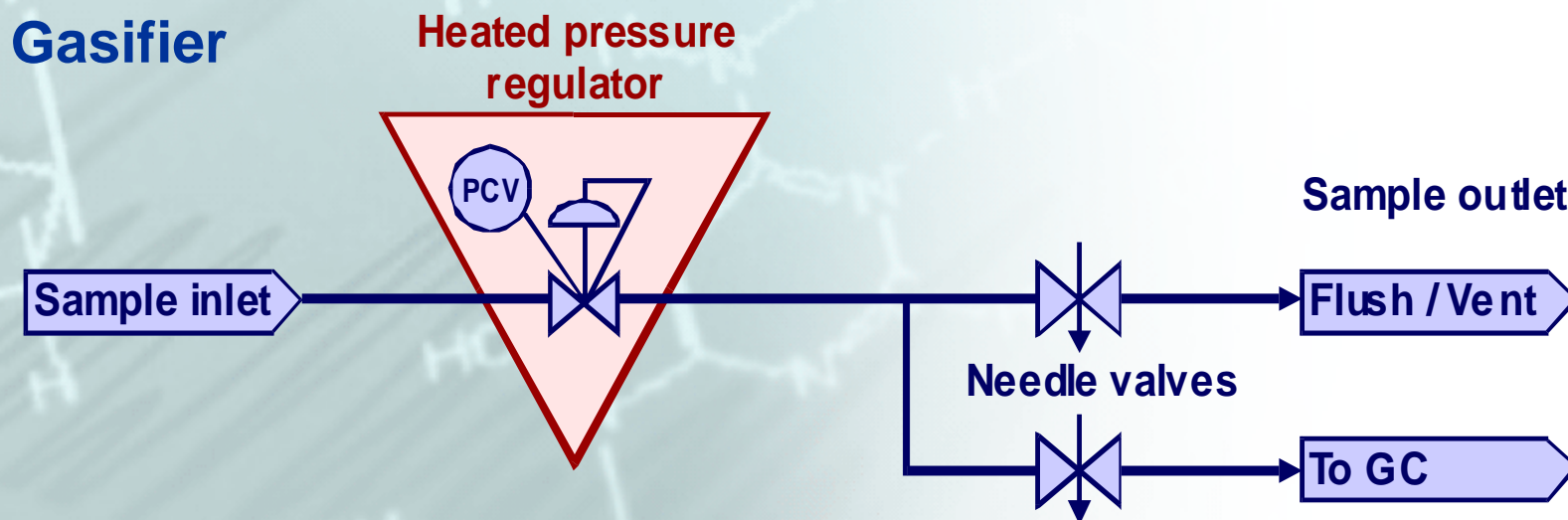
Gas Purity

- ◆ To restore the gas to the quality within the cylinder or better, in-line filters are needed to clean the gas but have limited lifetime.
- ◆ The Zirconium getter system eliminates most impurities and can produce 6.0 purity or better from 5.0 supply. In series, 7.0 can be obtained.
 - ◆ Can handle at least 10 large cylinders
 - ◆ The gas is absolutely **DRY**.
- ◆ It takes about one week for the rest of the plumbing to dry out unless we heat the lines and components.
- ◆ Modern Electronic Flow Controllers are not necessarily leak free.
 - ◆ After an EPC module a mini purifier is used
- ◆ Tubing crimps are the only flow controllers that can be used for low level O₂ and N₂ analysis



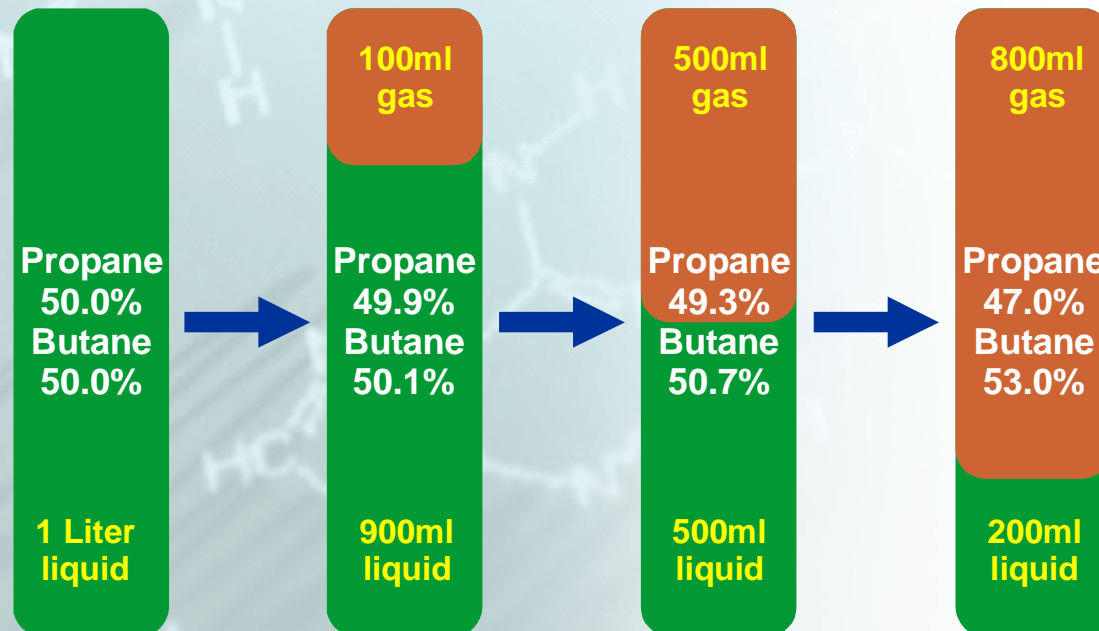
Sampling- Controlled pressure reduction

- ◆ Very high pressure samples require pressure reduction as part of sampling
 - ◆ However, pressure reduction cools down the sample
 - ◆ This may create cold spots in the sampling system
 - ◆ Sample discrimination by retention outside the GC, prior to injection will occur
- ◆ Sample pressures are not always the same and therefore
 - ◆ Flush flow through the sampling system is not constant

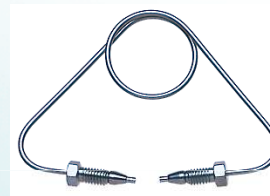
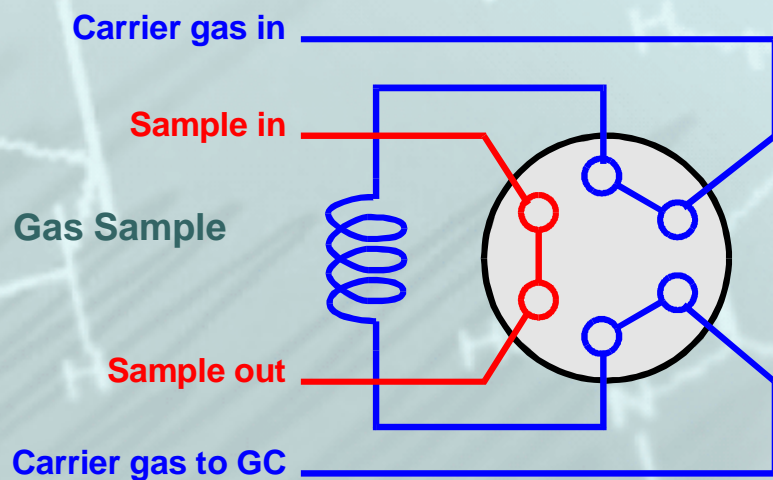
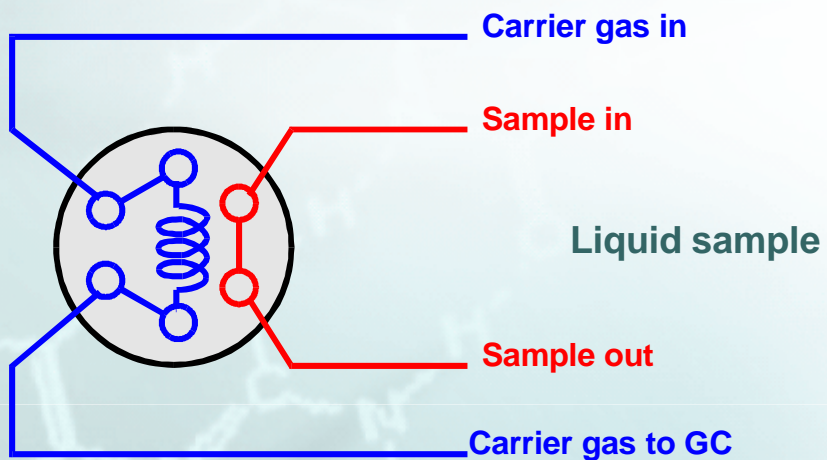


Sampling- High pressure gas sample containers

- ◆ Propane and Butane mixture in a 1 litre sample container
 - ◆ Use fully filled containers otherwise sample discrimination will occur
 - ◆ Repeated analysis of a relatively small sample may result in changes of relative amounts
 - ◆ This is especially problematic in sampling gases that condense under their own vapour pressure

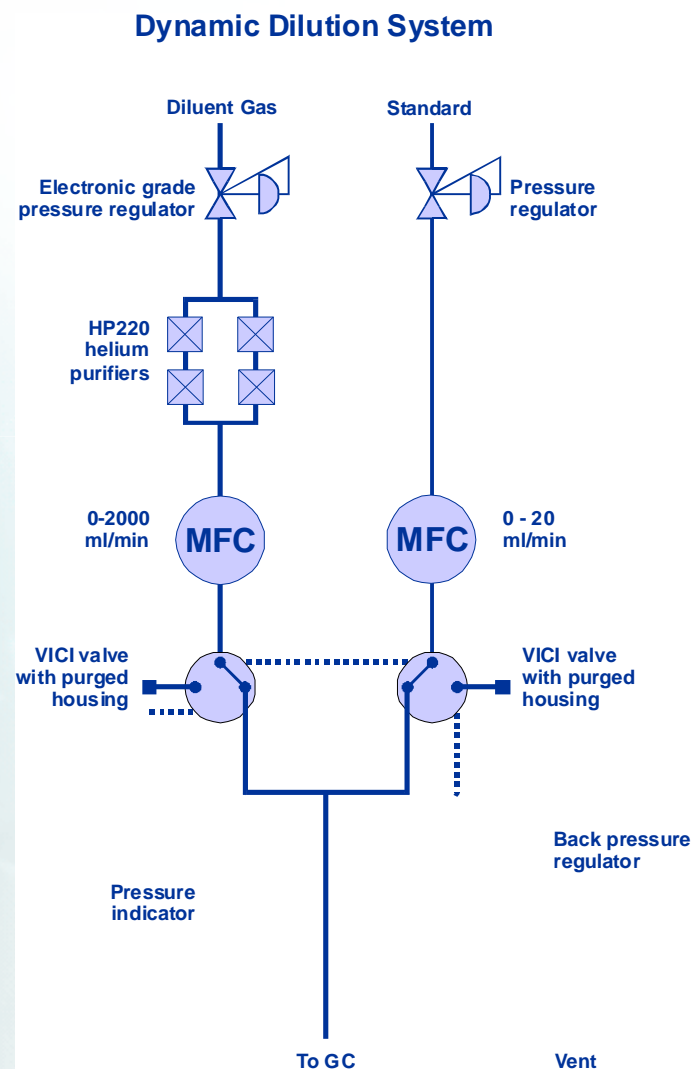


Sampling Valves & Purged Housings



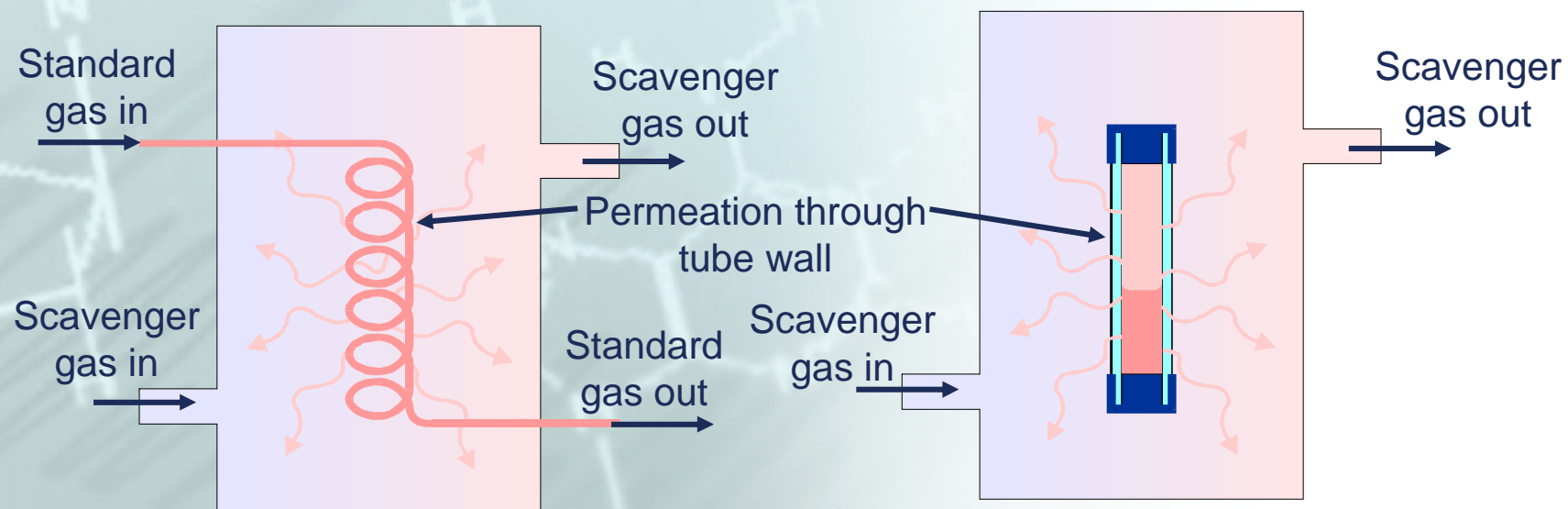
Calibration-Dynamic Dilution

- Accurate high level mixtures are made gravimetrically
- Dilution with very pure gas allows wide range of different concentrations
- Allows multipoint calibrations from a single standard
- Can be used for standard addition and for internal standard addition using a dual injection ten port valve
- Method of choice for generating relatively high concentration standards using 100% gases to start with



Calibration-Gas or Liquid Permeation

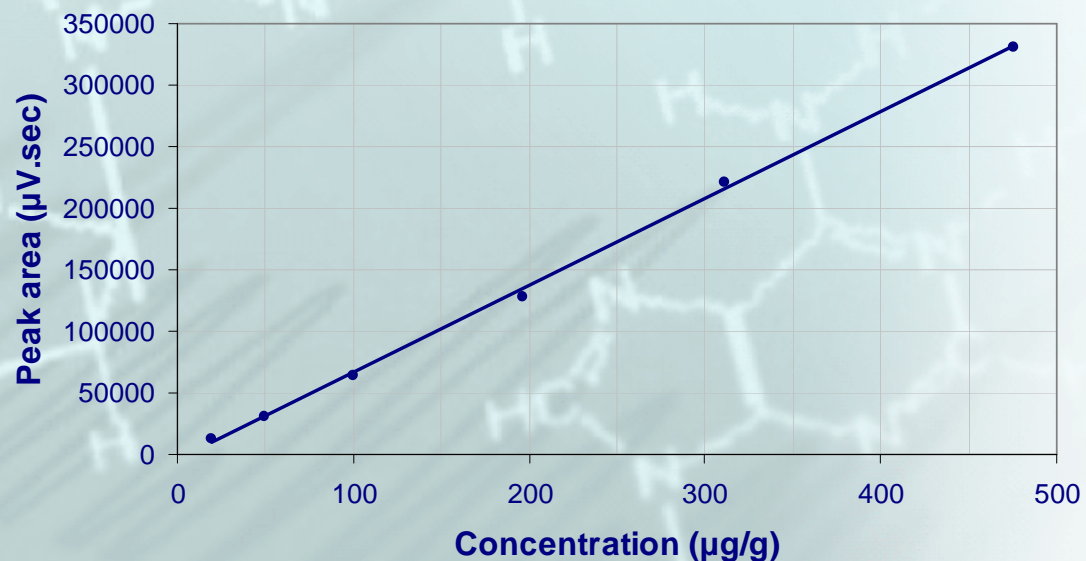
- ◆ A semi-permeable membrane (tube) is filled with the liquid to be added as a standard, or
- ◆ Pure gas of the compound to be added is passed through a semi-permeable tube at a constant pressure, flow and temperature
- ◆ A continuous regulated and precisely controlled flow of scavenger gas is passed over the permeation tube
- ◆ The constant "leakage" of the compound of interest across the porous membrane, wafer or tube effectively adds a fixed concentration of the compound to the scavenger gas, which is used as a standard- verified by loss of mass.



Calibration Curves

- Calibration curves should be constructed with at least 5 calibration points for every two orders of magnitude of range
- A minimum of 3 replicates should be run at each level

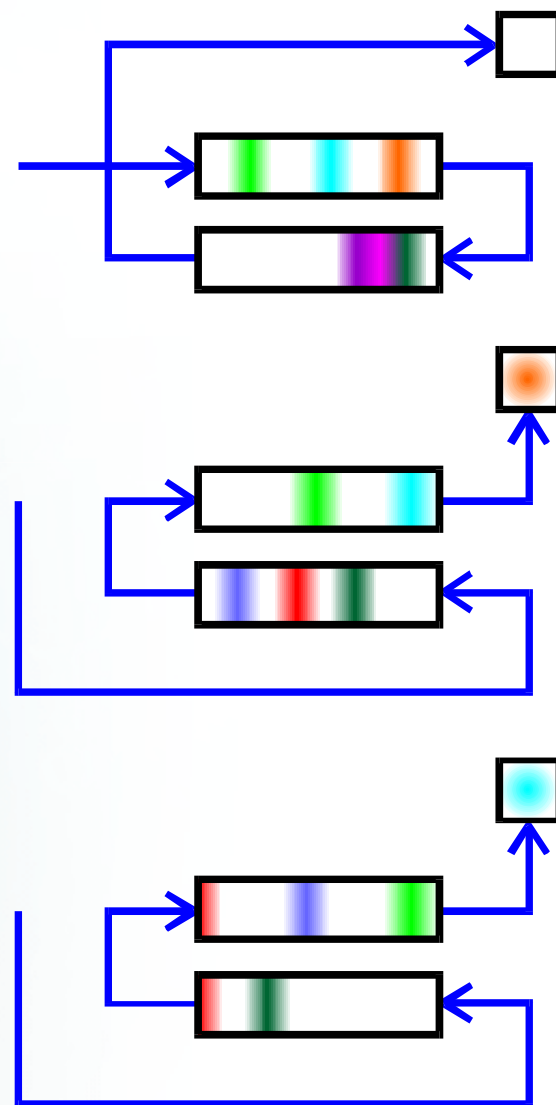
Calibration curve for butyl acetate in industrial solvents



Conc.	Area
19.55	12608
49.18	31087
100.1	63867
196.1	128397
310.8	220462
475.7	331200

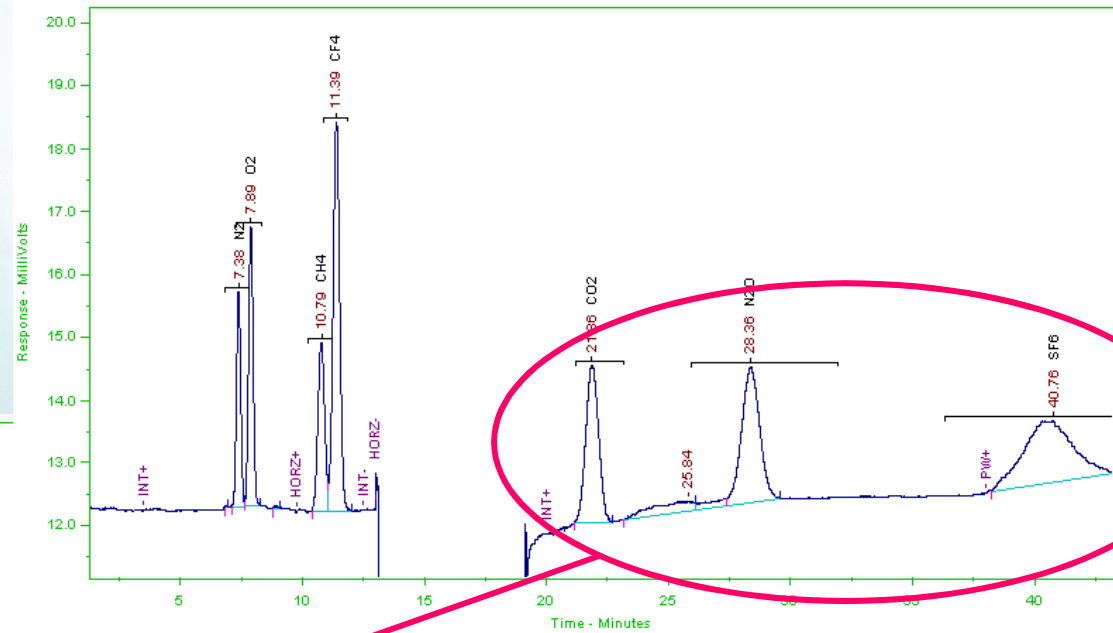
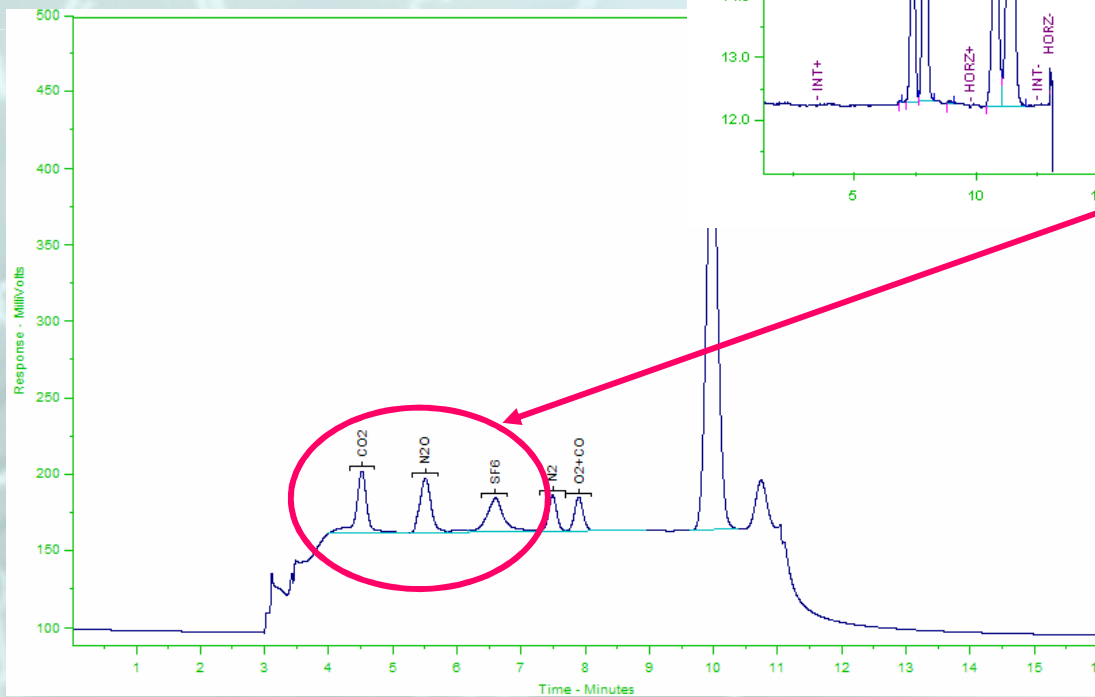
Column sequence reversal

- ◆ Sequence reversal is used to reduce analysis time by allowing late eluting compounds to elute earlier which significantly improves the peak shape of these compounds.
- ◆ The first eluting compounds may pass through the first column twice and are therefore slightly broader than normal.
- ◆ A much shorter first column can be used. After separation on the first column, the early eluting compounds are passed on to the second column for further separation
- ◆ The valve is switched and the compounds from the second column are passed on to the detector first
- ◆ With the valve in this position the effluent from the second column re-enters the first column, and elutes after the compounds that elute last in a single column configuration.

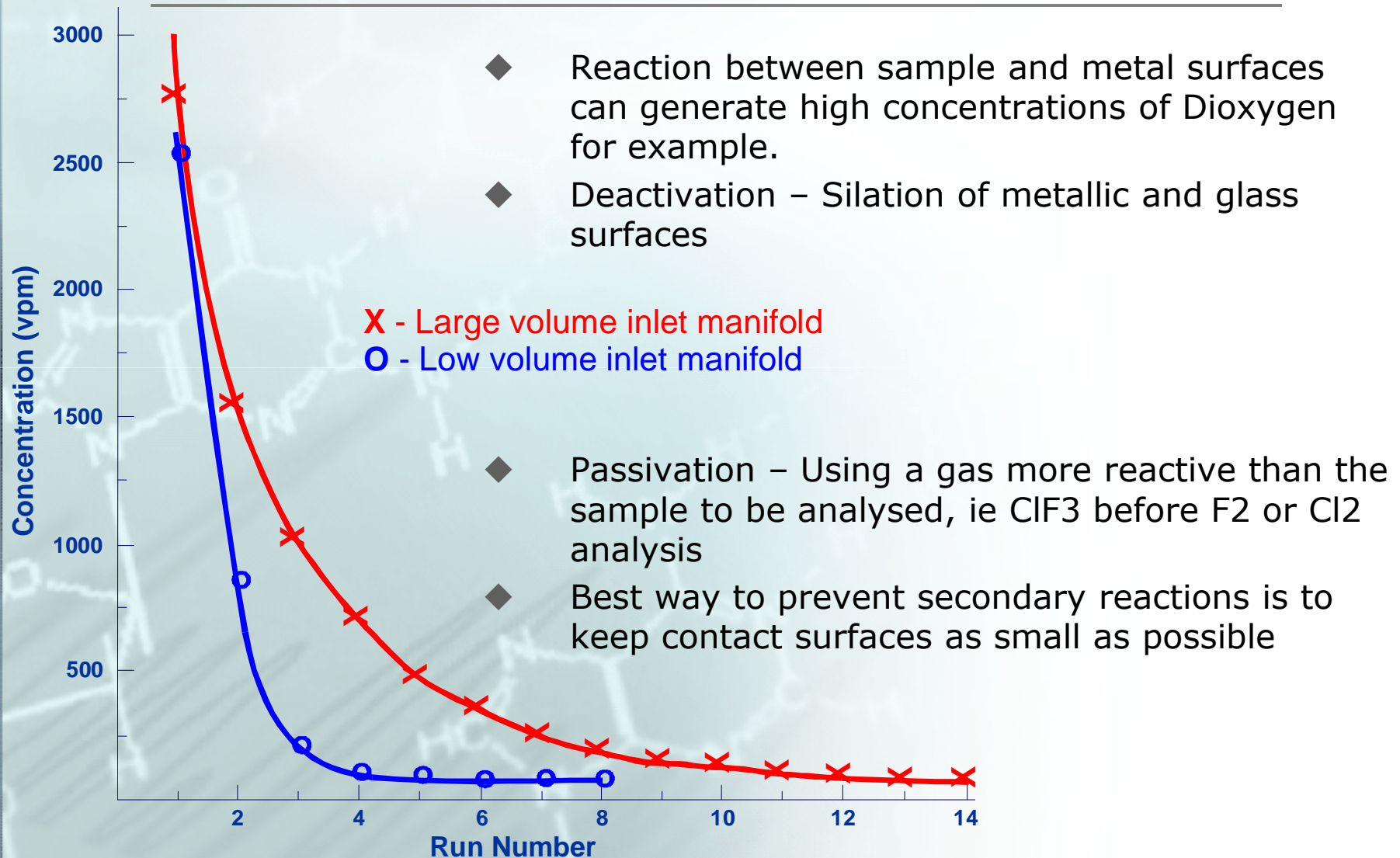


Column Sequence Reversal

- ◆ Can be used to artificially change elution order which gives improved peak shapes for better quantitation.



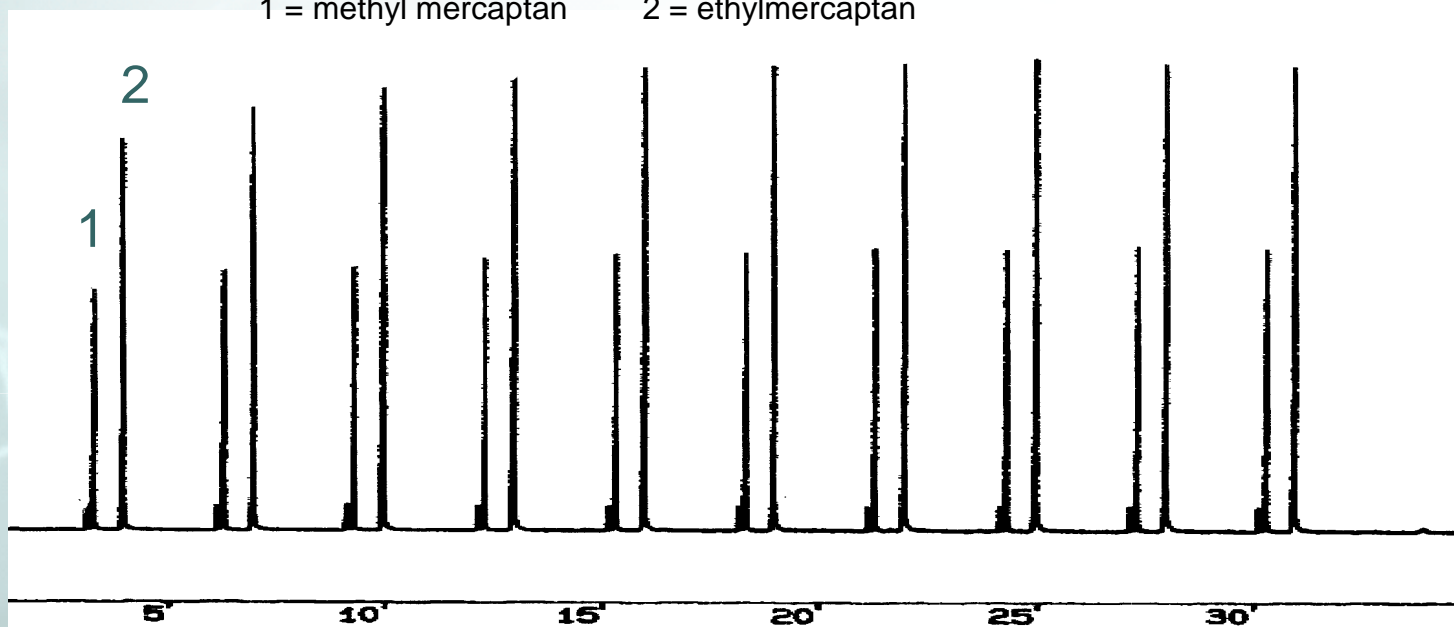
Deactivation and passivation



Repeat injection until equilibrium reached

10 injections after installation of column

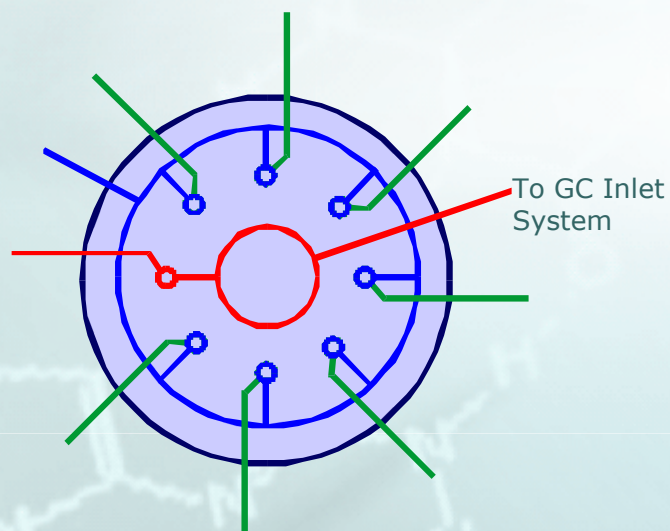
1 = methyl mercaptan 2 = ethylmercaptan



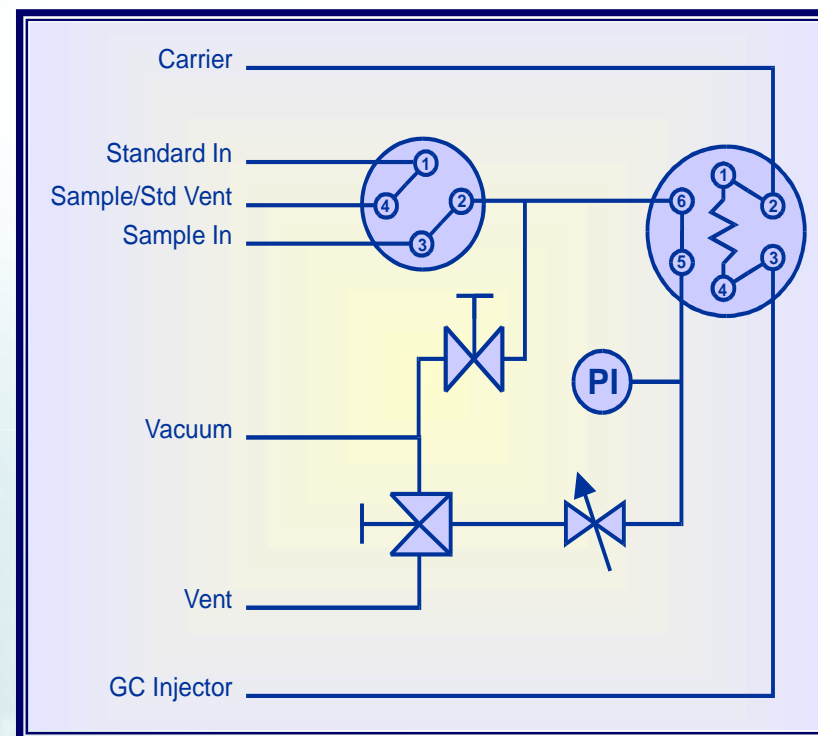
Priming effects visible in first injections

- ◆ Can occur anywhere in inlet system, column or detector
- ◆ High degree of automation essential- GSV as well as stream selectors

A typical gas sample inlet



- ◆ Installed in carrier gas line it allows:
 - ◆ Static sampling
 - ◆ Dynamic sampling
 - ◆ Sampling above atmospheric pressure
 - ◆ Sampling below atmospheric pressure
 - ◆ Can be rapidly evacuated
 - ◆ High precision = repeatability
 - ◆ Vent line and back diffusion



References

- ◆ Specialty gas analysis – Jeremiah D Hogan
- ◆ Gas chromatographic analysis of trace impurities in chlorine trifluoride. Laurens, Swinley and de Coning. *Journal of Chromatography A* (2000)
- ◆ Gas chromatographic analysis of trace gas impurities in tungsten hexafluoride. Laurens, de Coning and Swinley. *Journal of Chromatography A* (2001)
- ◆ Trace analysis of impurities in bulk gases by gas chromatography-pulsed discharge helium ionization detection with "heart-cutting" technique. Weijun. *Journal of Chromatography A* (2007)
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Thank you for your attention

