Training event “Atmospheric standardized observations: Methods and maintenance in observatories – In-Situ.”

Gas chromatography analyses for VOC measurements

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Ministero dell'Università e della Ricerca

Italiadomani

VOCs

Chemical compounds containing carbon that vaporize easily and enter into the atmosphere; refer to several groups of hydrocarbons, including non-methane oxygenated hydrocarbons (OVOC e.g. acetone) and halogenated hydrocarbons (e.g. methylchloride)

VOCs can participate in atmospheric photochemical reactions

VOC molecules occur in many forms and have both natural and anthropogenic sources

Classification of Inorganic Organic Pollutants (adapted from WHO[8])

Description	Abbreviation	Boiling Point Range (°C)	Example Compounds
Very volatile (gaseous) organic compounds	VVOC	<0 to 50-100	Propane, butane, methyl chloride
Volatile organic compounds	VOC	50-100 to 240-260	Formaldehyde, d-Limonene, toluene, acetone, ethanol (ethyl alcohol) 2-propanol (isopropyl alcohol), hexanal
Semi volatile organic compounds	SVOC	240-260 to 380-400	Pesticides (DDT, chlordane, plasticizers (phthalates), fire retardants (PCBs, PBB))

VOCs

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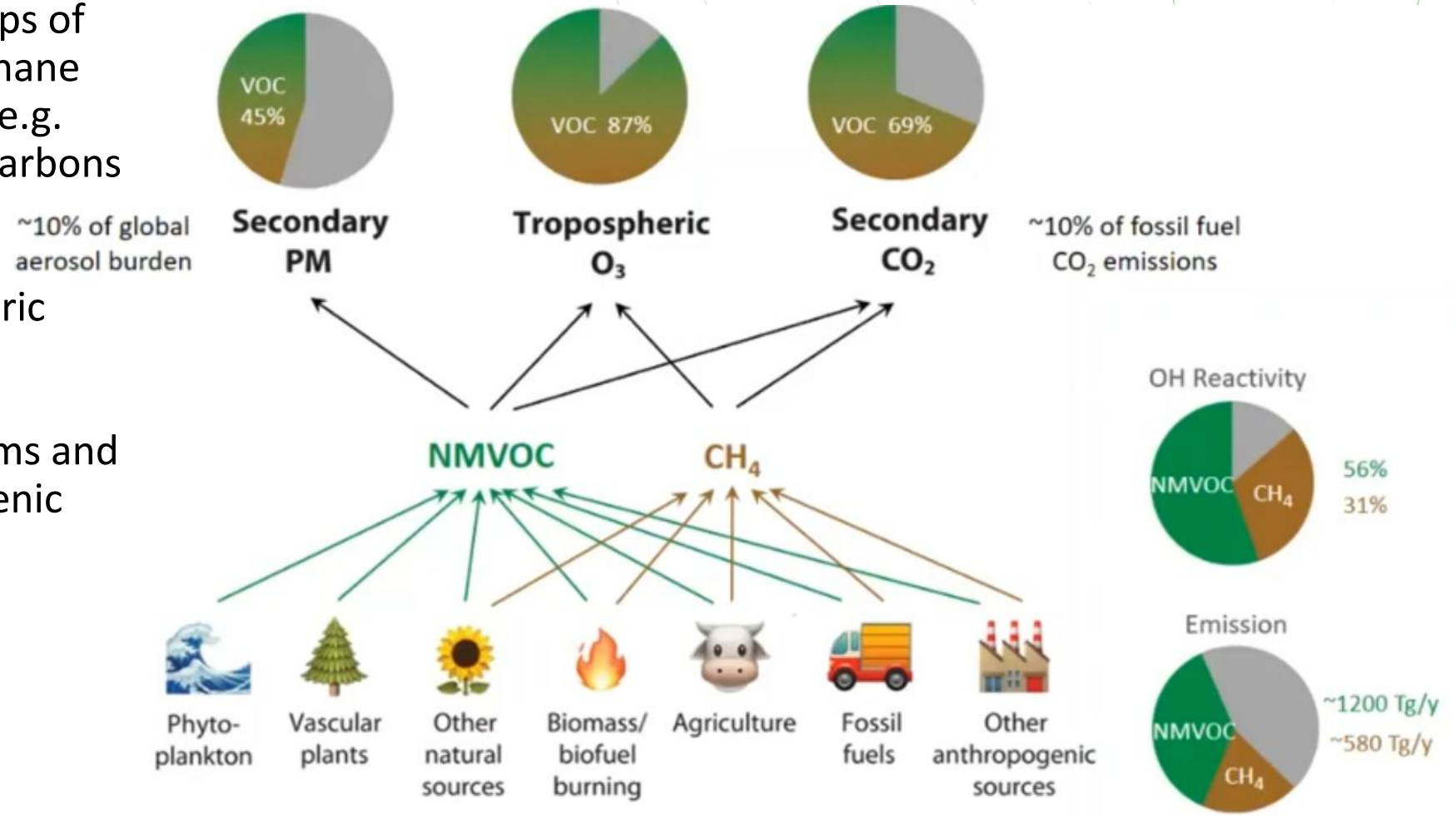


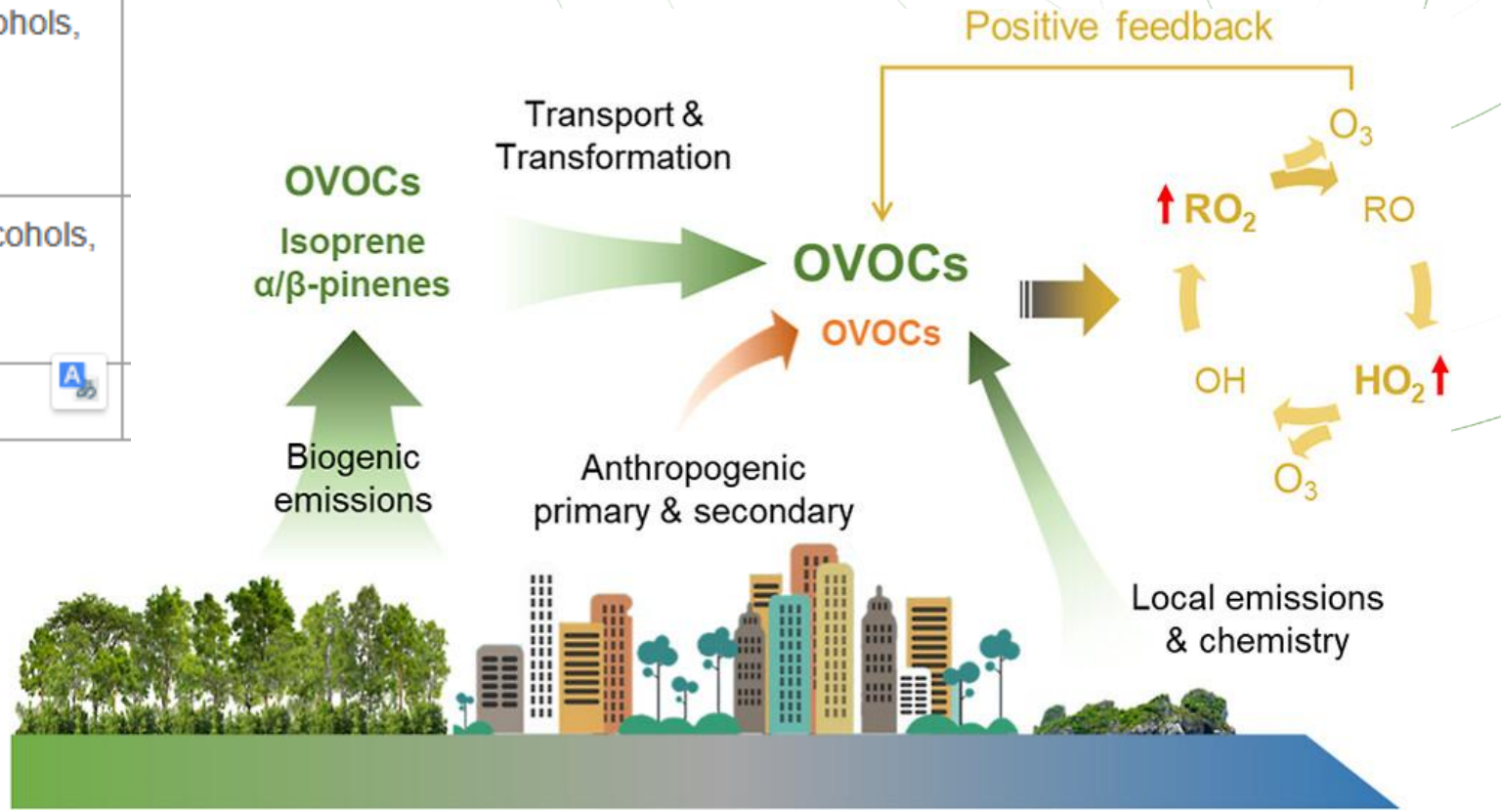
VOCs

Table 4-1. PAMS Priority and Optional VOCs Measured by Auto-GC

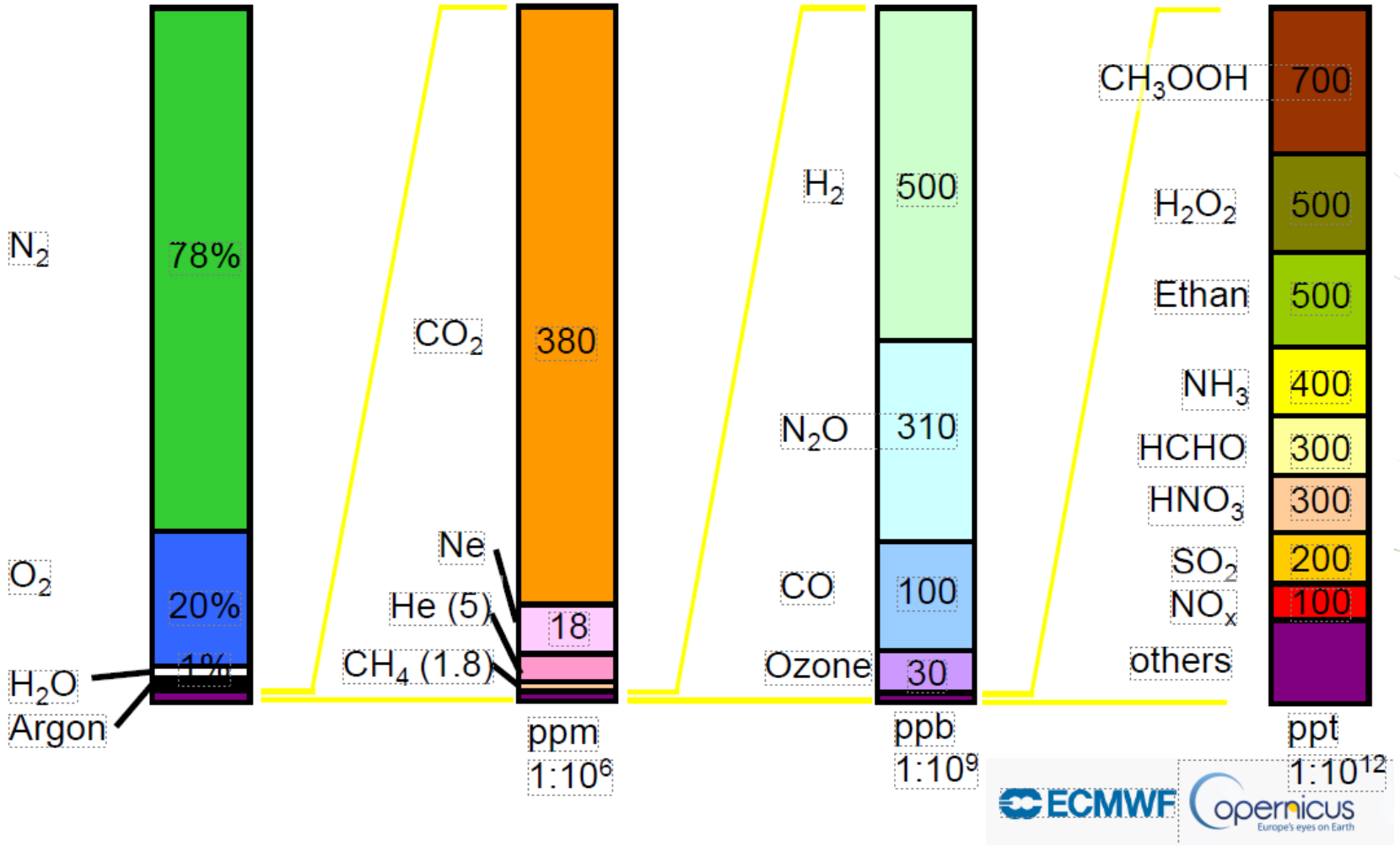
Priority Compounds		Optional Compounds	
1,2,3-trimethylbenzene	m-ethyltoluene	1,3,5-trimethylbenzene	isopropylbenzene
1,2,4-trimethylbenzene	n-butane	1-pentene	m-diethlybenzene
1-butene	n-hexane	2,2-dimethylbutane	methylcyclohexane
2,2,4-trimethylpentane	n-pentane	2,3,4-trimethylpentane	methylcyclopentane
benzene	o-ethyltoluene	2,3-dimethylbutane	n-decane
cis-2-butene	o-xylene	2,3-dimethylpentane	n-heptane
ethane	p-ethyltoluene	2,4-dimethylpentane	n-nonane
ethylbenzene	propane	2-methylheptane	n-octane
ethylene	propylene	2-methylhexane	n-propylbenzene
isobutane	styrene	2-methylpentane	n-undecane
isopentane	toluene	3-methylheptane	p-diethylbenzene
isoprene	trans-2-butene	3-methylhexane	trans-2-pentene
m&p-xylenes	total non-methane organic carbon (TNMOC)	3-methylpentane	α/β-pinene
		acetylene	1,3 butadiene
		cis-2-pentene	carbon tetrachloride
		cyclohexane	ethanol
		cyclopentane	tetrachloroethylene

VOCs

VOC	Sources	VOC groups
anthropogenic	Fossil fuel (transport) solvents biomass burning	alkanes, alkenes, alkynes, aldehydes, ketones, alcohols, aromatics
biogenic	plants (trees)	isoprene, terpenoids, alcohols, ketones (esp. acetone), aldehydes
total		



Atmospheric composition – gas&VOCs



Atmospheric composition – gas&VOCs

Gas	Atmospheric Composition in %	Atmospheric Composition in mixing ratio	Molecules in one Breath
Nitrogen	78%		100,000,000,000,000,000,000,000
Oxygen	21%		28,000,000,000,000,000,000,000
Carbon Dioxide (CO_2)	0.0410%	410 ppm	51,000,000,000,000,000,000
Methane (CH_4)	0.0019%	1.9 ppm	2,400,000,000,000,000,000
Nitrous Oxide (N_2O)	0.00032%	320 ppb	430,000,000,000,000,000
Surface Ozone (O_3)	0.00005%	50 ppb	67,000,000,000,000,000 (67 quadrillion)
VOC	0.00000001%	0.1 ppb	

Atmospheric composition – gas&VOCs

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Nitrogen	78%		100,000,000,000,000,000,000,000
			28,000,000,000,000,000,000,000
		410 ppm	51,000,000,000,000,000,000
		1.9 ppm	2,400,000,000,000,000,000
		320 ppb	430,000,000,000,000,000
		50 ppb	67,000,000,000,000,000 (67 quadrillion)
VOC	0.00000001%	0.1 ppb	

400,000 x

500 x

40,000,000 x

Atmospheric composition – gas&VOCs

Gas	Atmospheric Composition		Molecules in one Breath
	in %	in mixing ratio	
			100,000,000,000,000,000,000

40,000,000 x

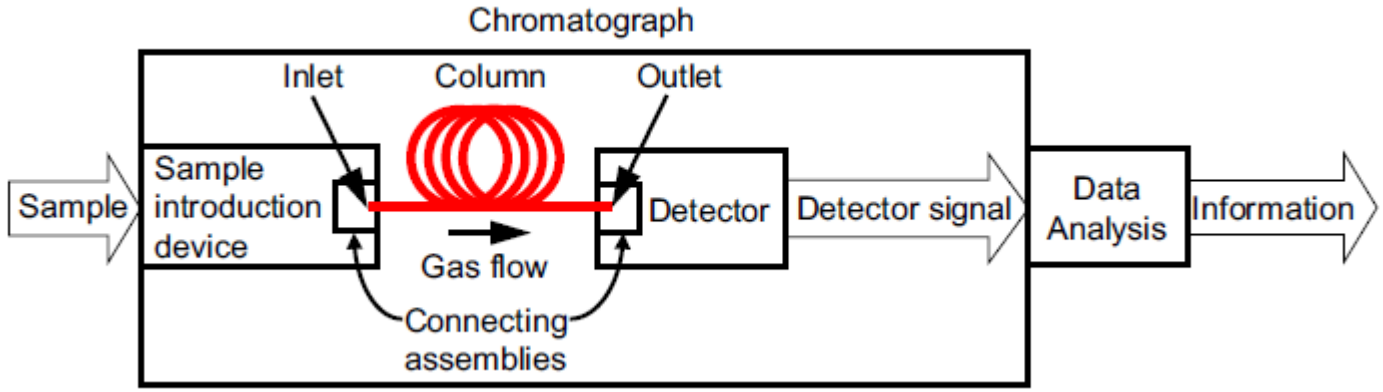
VOC	0.00000001%	0.1 ppb

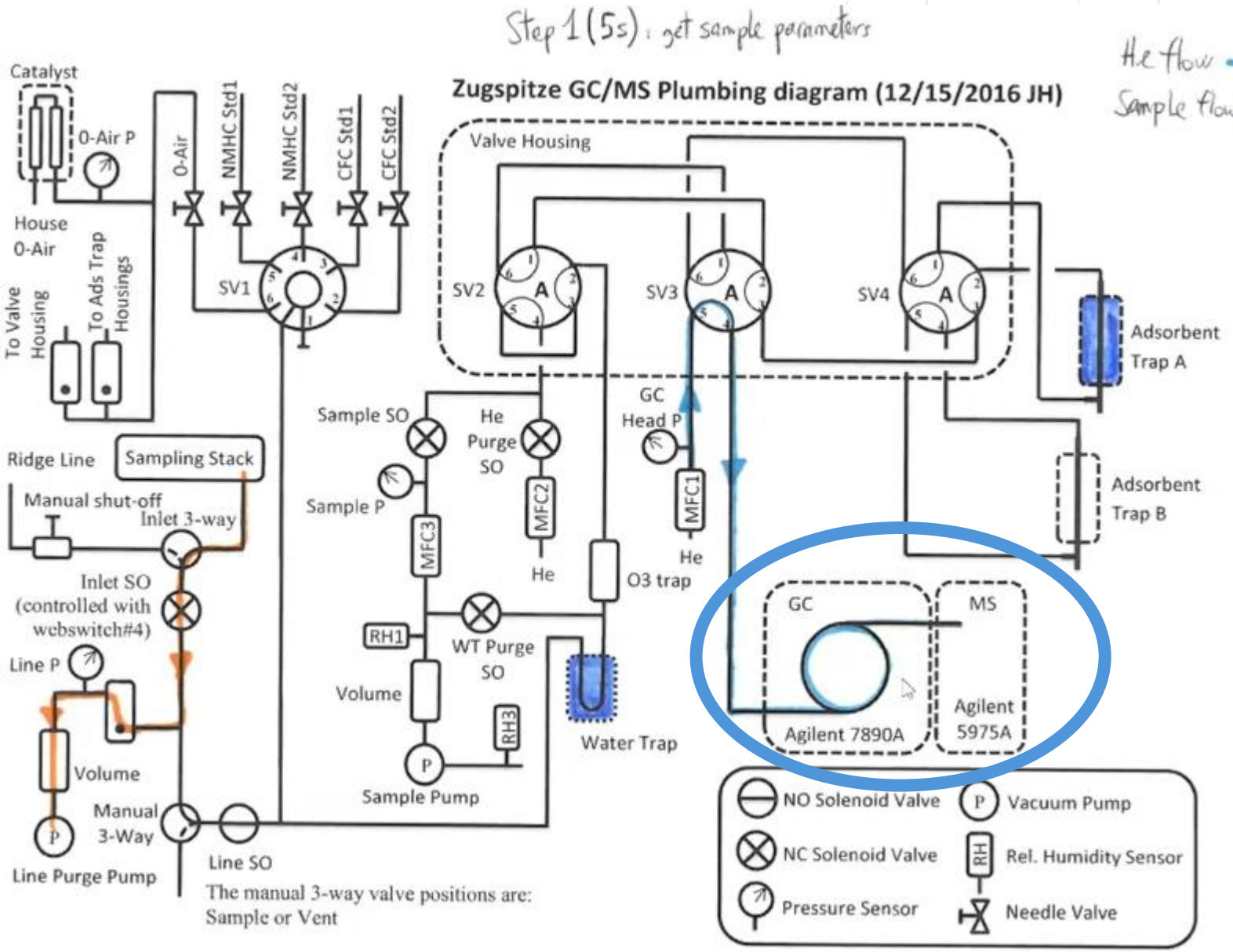
Overview of VOC Analysis Principles

- Look from the distance (satellites)
- Look through the air (FTIR column)
- Go to where the air is and measure it there with an instrument (GC, PTR-MS, PTR-TOF, FTIR)
- Collect some air and measure it at home with an instrument (whole air sampling – flasks, canisters)
- Catch the VOCs and bring them back home
- Make the VOCs into something different to bring back
- ……

VOC analysis **Gas Chromatography** principles

- VOC preconcentration
- VOC separation by GC
- VOC detection – Identification and quantification; most commonly flame ionization detection (FID) or mass spectrometry (MS) – (electron capture detection; photoionization detection ….)

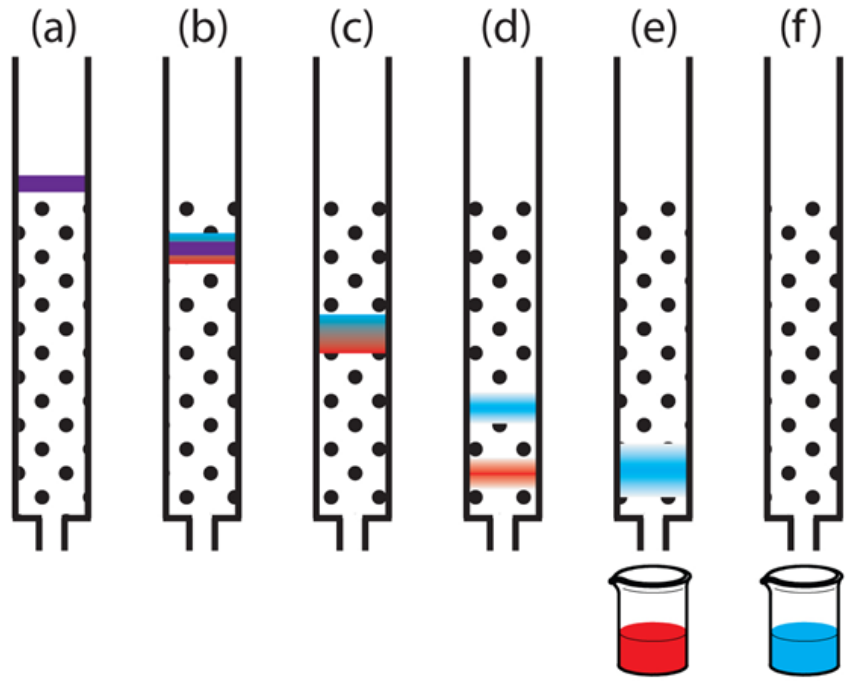



Step 1 (5s): get sample parameters
He flow
Sample flow
Zugspitze GC/MS Plumbing diagram (12/15/2016 JH)
Catalyst
0-Air P
House 0-Air
To Valve Housing
To Ads Trap Housings
0-Air
NMHC Std1
NMHC Std2
CFC Std1
CFC Std2
SV1
Valve Housing
SV2
SV3
SV4
Adsorbent Trap A
Adsorbent Trap B
Ridge Line
Sampling Stack
Manual shut-off
Inlet 3-way
Inlet SO (controlled with webswitch#4)
Line P
Volume
Manual 3-Way
Line Purge Pump
Line SO
Sample SO
He Purge SO
Sample P
MFC3
MFC2
He
RH1
WT Purge SO
Volume
RH3
Sample Pump
Water Trap
O3 trap
GC Head P
MFC1
He
GC
MS
Agilent 7890A
Agilent 5975A
NO Solenoid Valve
NC Solenoid Valve
Pressure Sensor
Vacuum Pump
Rel. Humidity Sensor
Needle Valve
The manual 3-way valve positions are:
Sample or Vent

“Chromatography is a physical method of separation in which the components to be separated are distributed between two phases, one of which is stationary (stationary phase), while the other (the mobile phase) moves in a definite direction”. [L.S. Ettre, “Nomenclature for Chromatography”, Pure & Appl. Chem., 65 (1993), 819-872].

There are two types: Gas Chromatography (GC) & Liquid Chromatography (LC)

Gas chromatography separates gaseous substances based on partitioning in a stationary phase from a gas phase.
While the mechanisms of retention for various types of chromatography differ, they are all based on the dynamic distribution of an analyte between a fixed stationary phase and a flowing mobile phase.



Each analyte will have a certain affinity for each phase:

- partition constant Ki= cs/cm

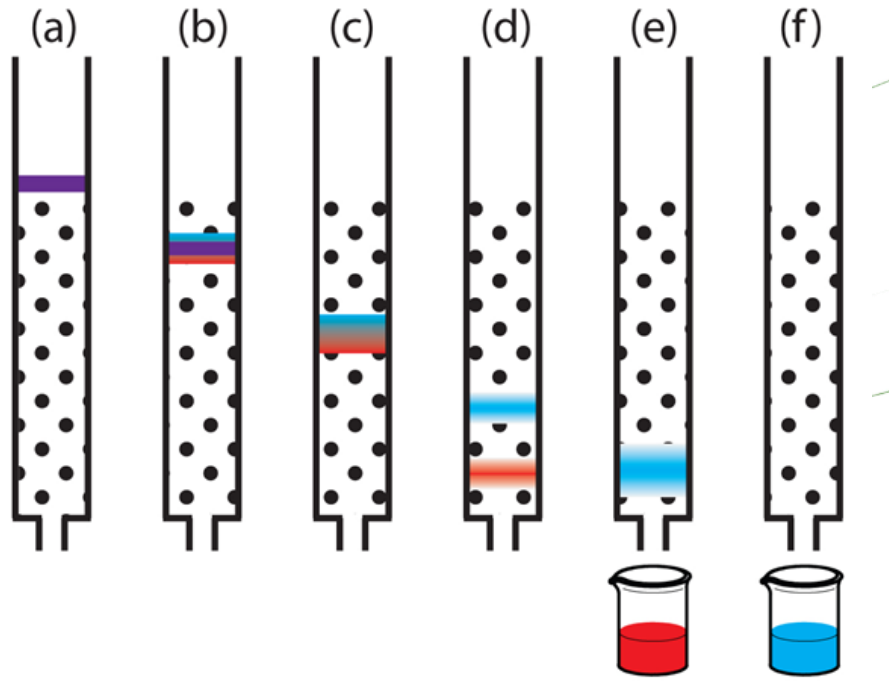
where cs and cm are the stationary and the mobile phases concentrations.

The partition ratio is simply the ratio of the time a solute spends in the stationary phase to that it spends in the mobile phase.

The distribution of the analyte between two phases is governed by:

- Temperature
- the physico-chemical properties of compound
- the physico-chemical properties of the stationary and mobile phases.

Analytes with a large K value will be retained more strongly by the stationary phase than those with a small K value. The result is that the latter will move along the column (be ELUTED) more rapidly.



Chromatographic processes can be classified according to the type of equilibration chemistry involved, which is determined by the type of the stationary and mobile phases.

There are various bases of equilibration:
- Adsorption
- Partition
- Ion exchange
- Size dependent pore penetration

More often that not, analyte stationary-phase-mobile-phase interactions are governed by a combination of such processes.

The stationary phase is a solid or a liquid supported on which the sample components are adsorbed or partitioned. The components distribute differently between two phases through a combination of adsorption/sorption and desorption processes (thermodynamic equilibrium) while transported by the mobile phase during the elution (dynamic process).

Plenty of theoretic descriptions of the chemical-physical processes involved

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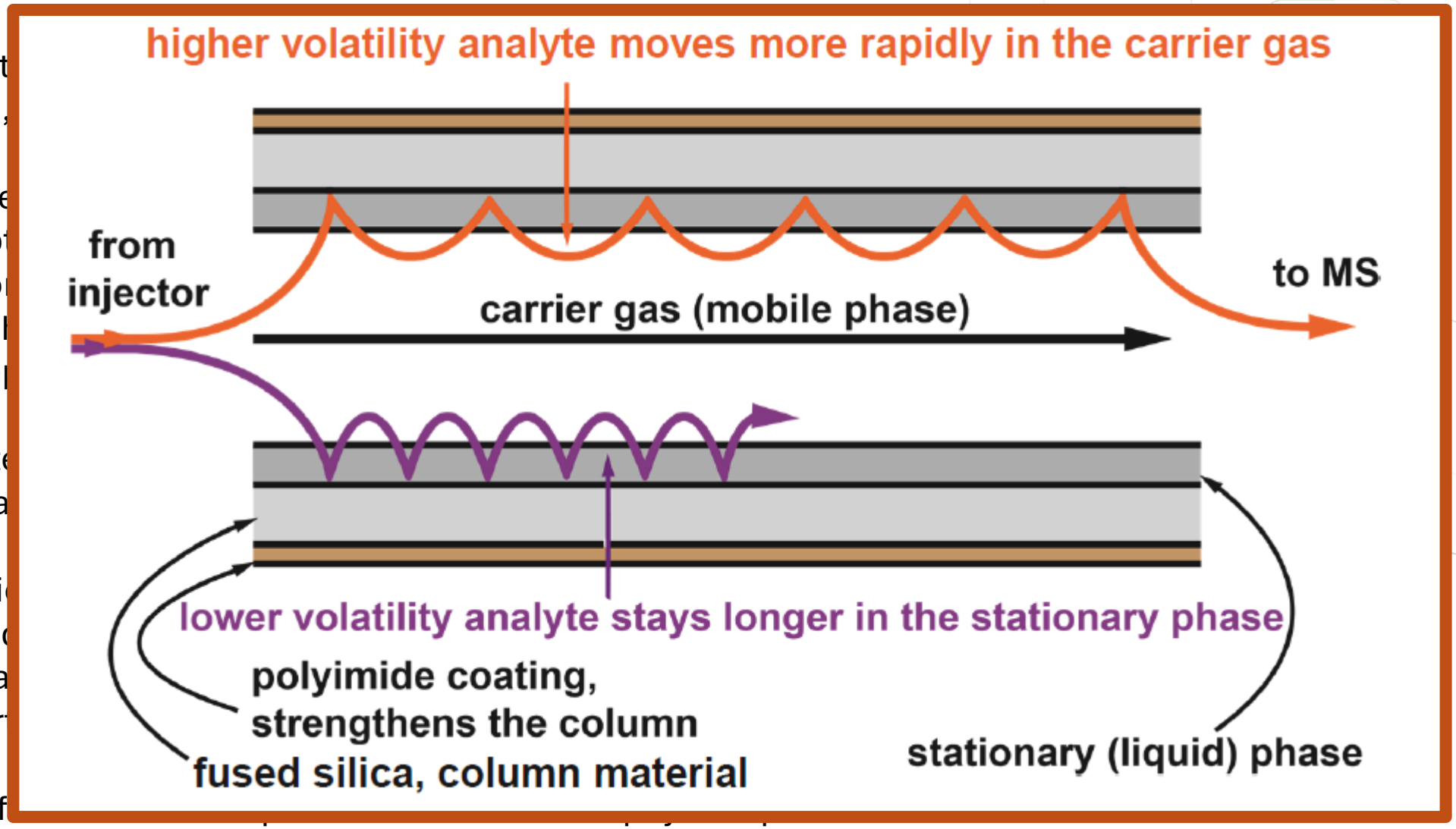

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higher volatility analyte moves more rapidly in the carrier gas

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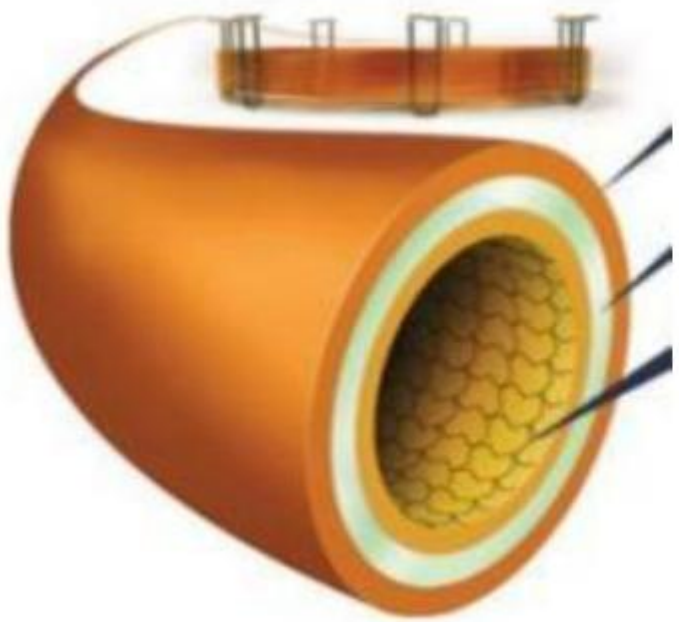

Special high temperature polyimide coating

Fused silica

Stationary phase with Engineered Self Cross-linking (ESC) technology

low

polyimide coating, strengthens the column

fused silica, column material

stationary (liquid) phase

Plate height	$H = \frac{L}{N}$
Plate number	$N = 5.545 \left(\frac{t_R}{w_{½}}\right)^2$
Adjustment retention time	$t'_R = t_R - t_M$
Retention factor	$k = \frac{t'_R}{t_M}$
Van Deemter Equation Capillary (open tubular) GC Column	$H = A + \frac{B}{\bar{u}} + C\bar{u}$
Golay equation Packed GC column	$H = A + \frac{B}{\bar{u}} + C_s\bar{u} + C_m\bar{u}$
Resolution	$R = \frac{t_{R2} - tR_1}{(W_{b1_+} W_{b2})^2}$
Separation factor	$\alpha = \frac{t'_{R2}}{t_{R1}} = \frac{k_2}{k_1}$
Resolution	$R_s = \frac{1}{4}\sqrt{N}\left(\frac{a-1}{a}\right)\left(\frac{k_2}{k_{ave}+1}\right)$

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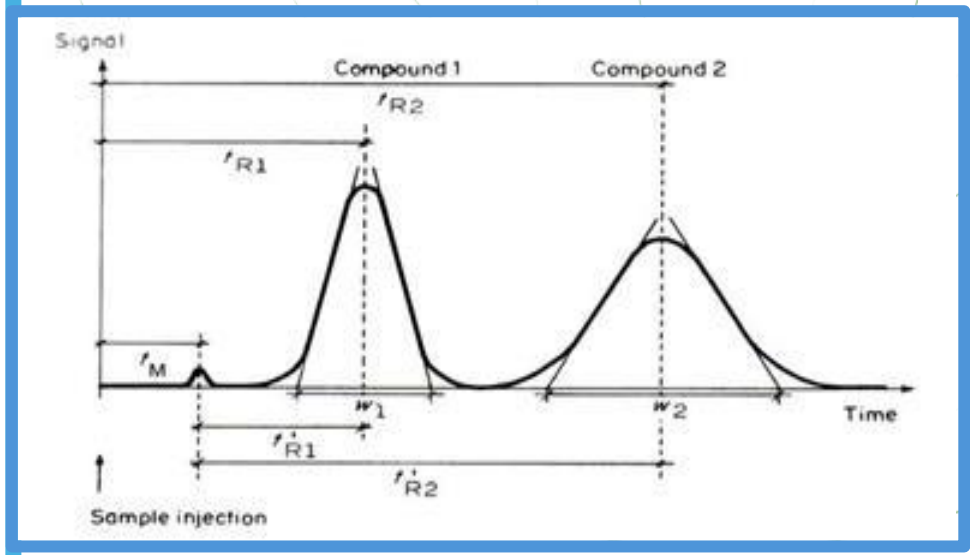

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The resolution of two chromatographic peaks:-

$R_s = (t_{R2} - tR_1)/[(wb_1 + wb_2)/2]$

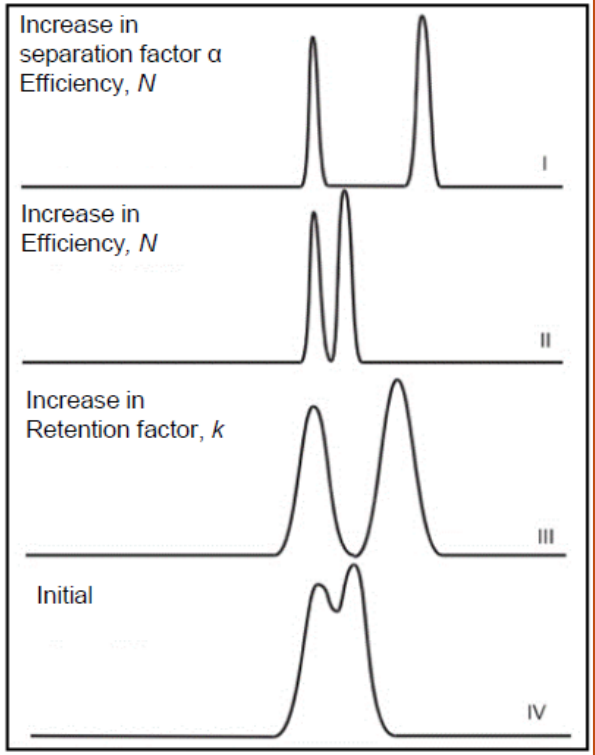
t_{R1} and t_{R2} are the retention times of the two peaks (peak 1 elutes first)

w_{b1} is the baseline width of the peaks.

The separation factor, α, also the selectivity and is a thermodynamic quantity that is a measure of the relative retention of analytes.

$$\alpha = \frac{t'_{R2}}{t'_{R1}} = \frac{k_2}{k_1}$$

k_2 and k_1 are the retention factors of the adjusted retention times. This describes how well the chromatographic conditions discriminate between the two analytes.



$$R_s = \frac{1}{4}\sqrt{N}\left(\frac{a-1}{a}\right)\left(\frac{k_2}{k_{ave}+1}\right)$$

k_{ave} is the mean of the two capacity factors.

N is proportional to L, the R_s is proportional to $\sqrt{L}$. So doubling the column increases the R_s by $\sqrt{2}$ or 1.4. The retention times would be increased in direct proportion to the length of the column.

Rate theory of chromatography is the best known and most used to explain and determine conditions for efficient separations.

The retention factor, *k* is the ratio of the time the analyte spends in the stationary phase to the time it spends in the mobile phase.

$$k = \frac{t'_R}{t_M}$$

$$H = A + \frac{B}{\bar{u}} + C\,\bar{u}$$ *the plate height for a packed GC column the van Deemter equation*

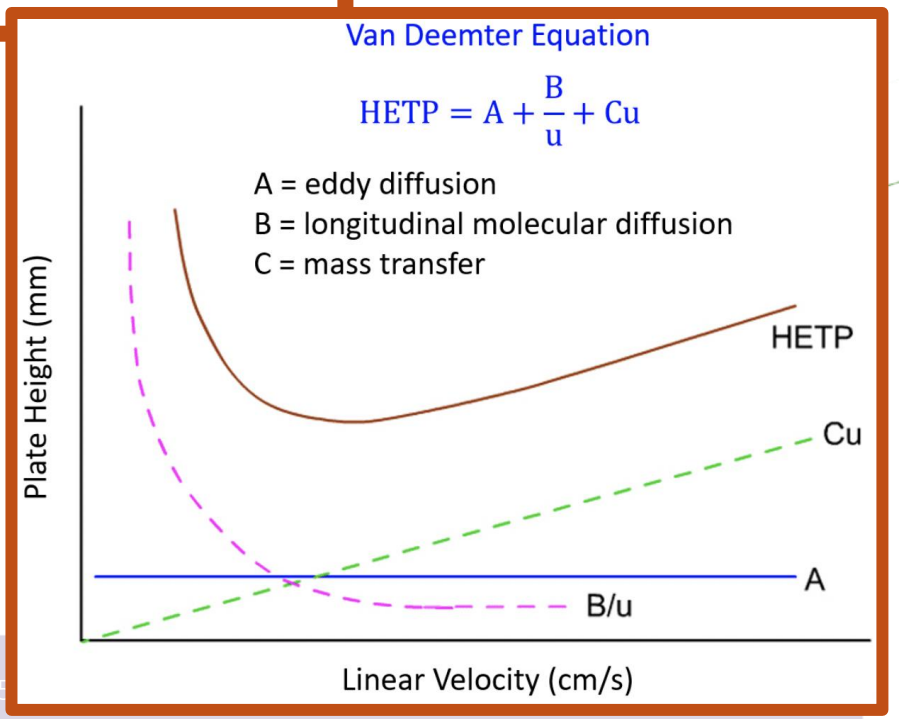
A, *B* and *C* are constants for a given system and related to the three major factors affecting H, and $\bar{u}$ is the average linear velocity of the carrier gas in cm/s.

The Van Deemter equation highlights the key factors influencing HETP:

Particle Size: Smaller stationary phase particles generally lead to lower HETP (better efficiency).

Diffusion Coefficients: Diffusion coefficients in the mobile and stationary phases affect the B and C terms.

Flow Rate: As mentioned above, the optimal flow rate balances the effects of the different terms.



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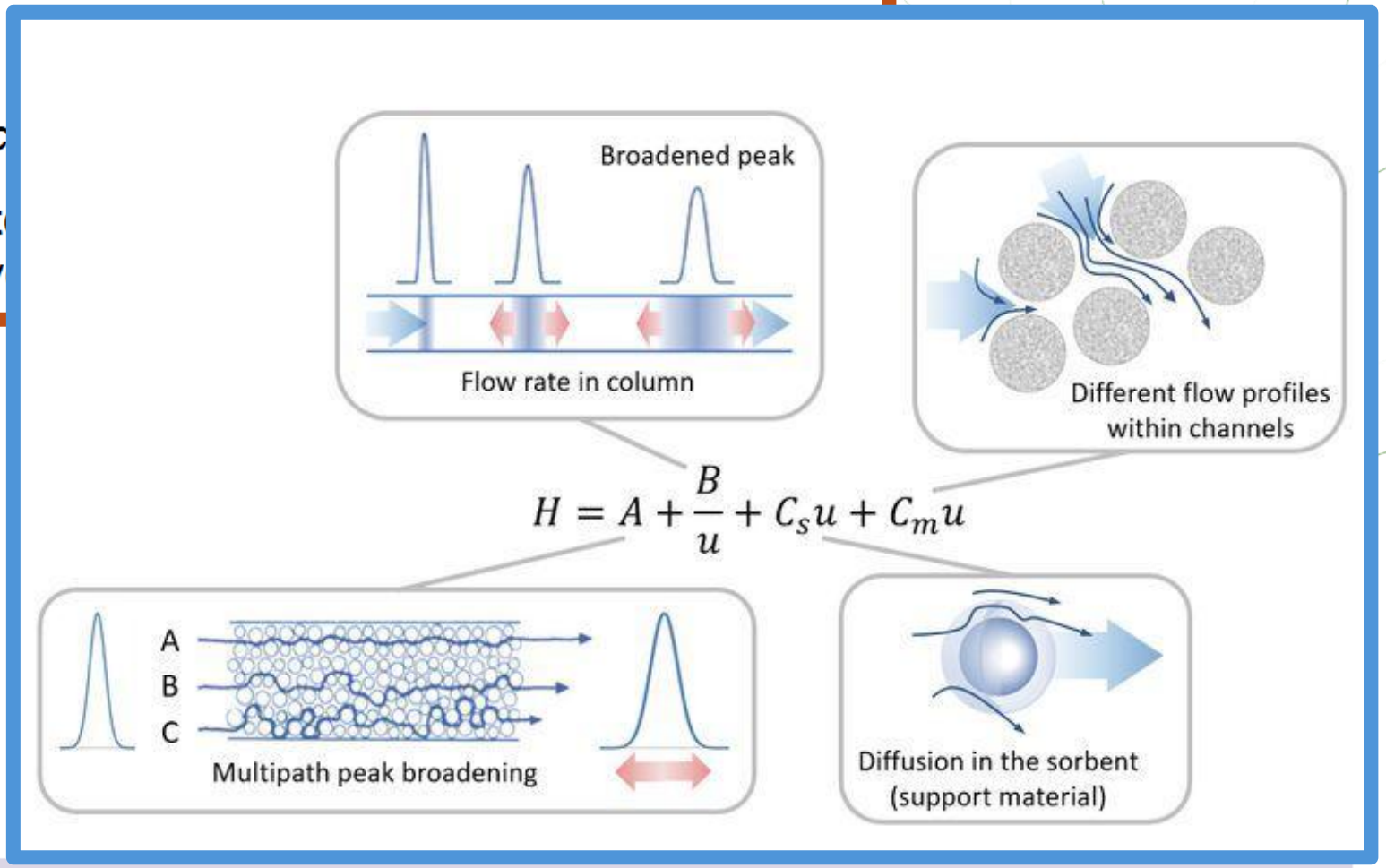
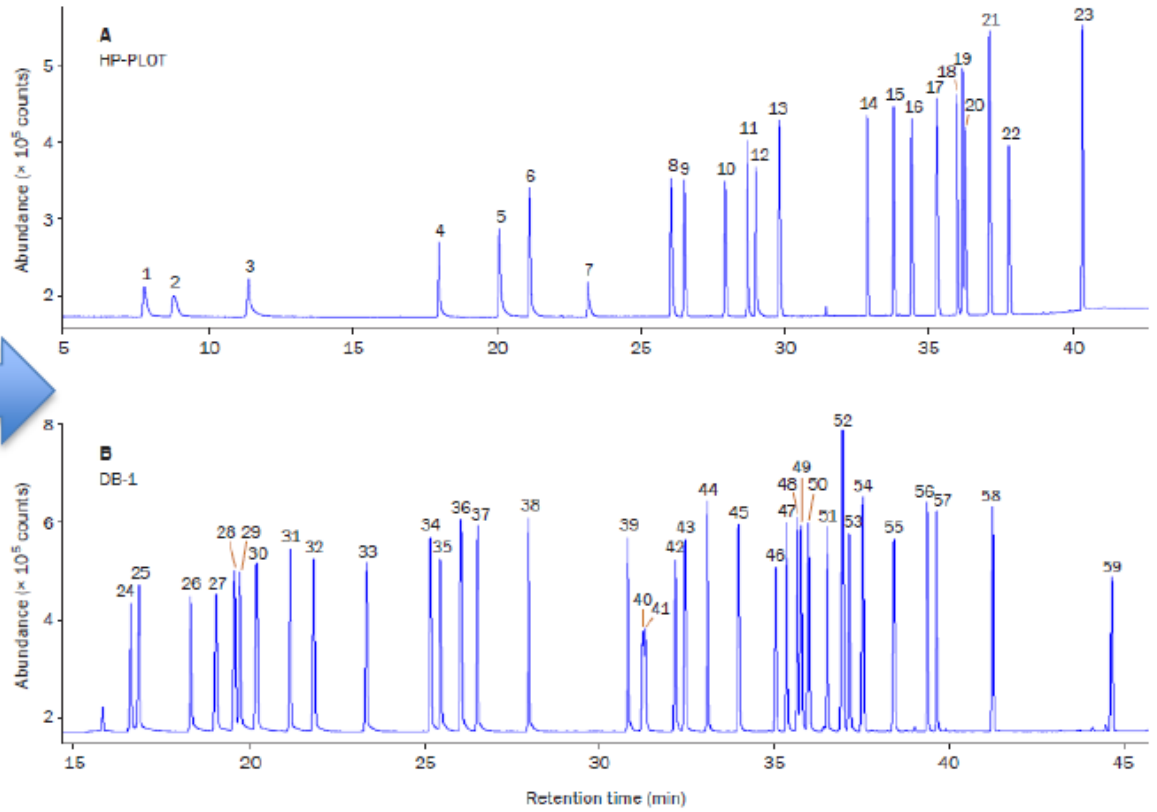


GC:

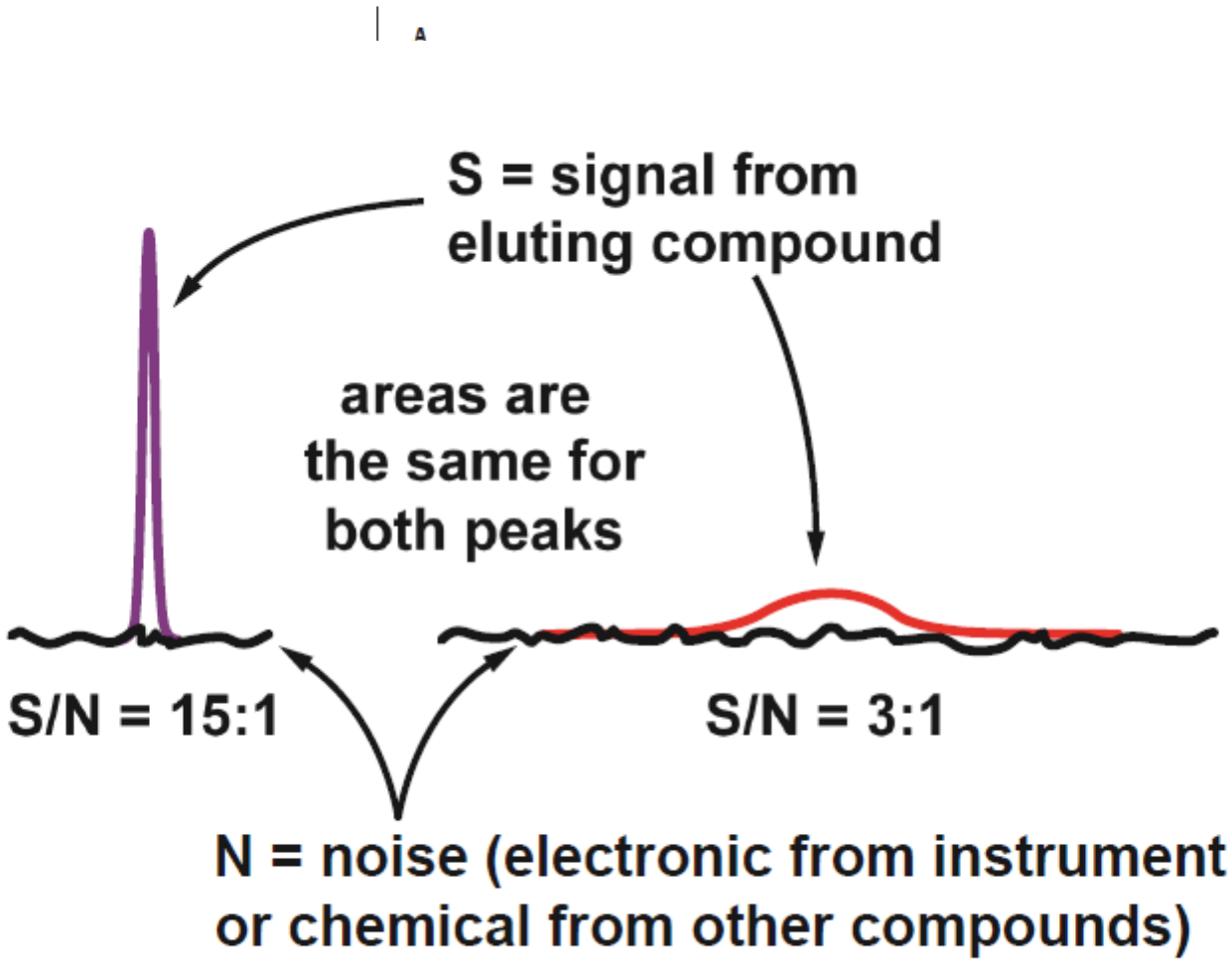
Column 1:	DB-1™ (polydimethylsiloxane), 60 m × 0.25 mm × 1 µm
Column flow:	2.4 mL/min (helium)
Pressure:	45.6 psi (constant)
Column 2:	HP-PLOT™ (Al_2O_3 S), 50 m × 0.32 mm × 8 µm
Column flow:	3.2 mL/min (helium)
Pressure:	22.4 psi (constant)
Oven ramp:	35°C (12 min), then 5°C/min to 170°C (10 min), then 15°C/min to 200°C (5 min)
GC run time:	46 min
Deans switch:	On for 15.5 min, then off (see Figure 3 for the column/detector setup)

FID (1 and 2):

Heater:	250°C
H_2 flow:	40 mL/min
Air flow:	400 mL/min

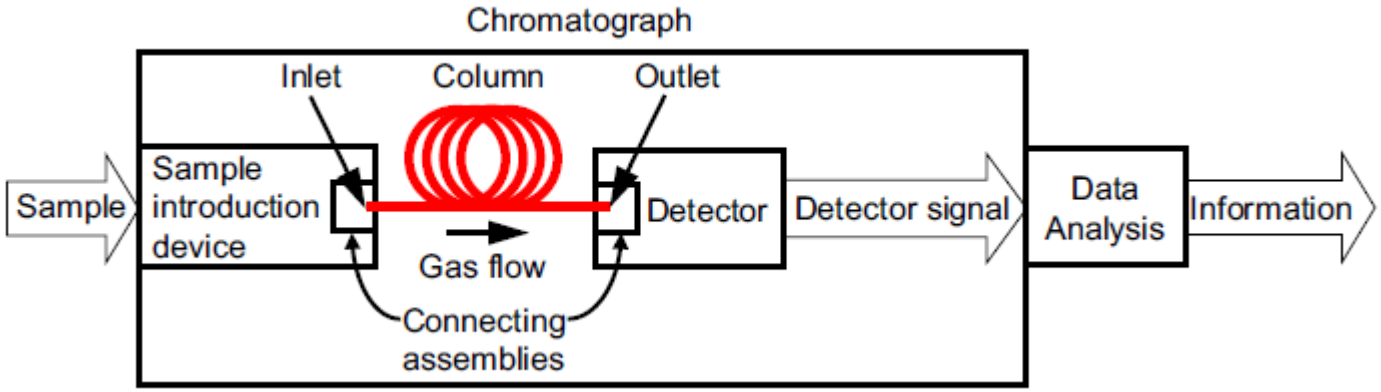


1 Ethane	11 Cyclopentane	21 Acetone	31 3-Methylhexane	41 *m*-/*p*-Xylene	51 1-Methyl-2-ethylbenzene
2 Ethylene	12 2-Methylbutane	22 Isoprene	32 2,2,4-Trimethylpentane	42 Styrene	52 β-Pinene
3 Propane	13 n-Pentane	23 2-Methylpent-1-ene	33 n-Heptane	43 *o*-Xylene	53 1,2,4-Trimethylbenzene
4 Propylene	14 *trans*-Pent-2-ene	24 n-Hexane	34 Methylcyclohexane	44 n-Nonane	54 Decane
5 2-Methylpropane	15 Pent-1-ene	25 Methylcyclopentane	35 2,3,4-Trimethylpentane	45 Isopropylbenzene	55 1,2,3-Trimethylbenzene
6 n-Butane	16 *cis*-Pent-2-ene	26 2,4-Dimethylpentane	36 Toluene	46 α-Pinene	56 1,3-Diethylbenzene
7 Acetylene	18 2,2-Dimethylbutane	27 Benzene	37 2-Methylheptane	47 n-Propylbenzene	57 1,4-Diethylbenzene
8 *trans*-But-2-ene	19 2,3-Dimethylbutane	28 Cyclohexane	38 3-Methylheptane	48 1-Methyl-3-ethylbenzene	58 n-Undecane
9 But-1-ene	17 2-Methylpentane	29 2-Methylhexane	39 n-Octane	49 1-Methyl-4-ethylbenzene	59 n-Dodecane
10 *cis*-But-2-ene	20 3-Methylpentane	30 2,3-Dimethylpentane	40 Ethylbenzene	50 1,3,5-Trimethylbenzene	


S = signal from
eluting compound
areas are
the same for
both peaks
S/N = 15:1
S/N = 3:1
N = noise (electronic from instrument
or chemical from other compounds)

VOC analysis **Gas Chromatography** principles

- VOC preconcentration
- VOC separation by GC
- VOC detection – Identification and quantification; most commonly flame ionization detection (FID) or mass spectrometry (MS) – (electron capture detection; photoionization detection ….)



GC detection options

- Mass Spetrometry (MS):

good for compound identification

can use mass spectrum and retention time

identify co-elution problems

need standard gas of compounds to be quantified

drifts over time, need to do frequent calibrations

- Flame Ionization Detection:

very sensitive

simple, cheap

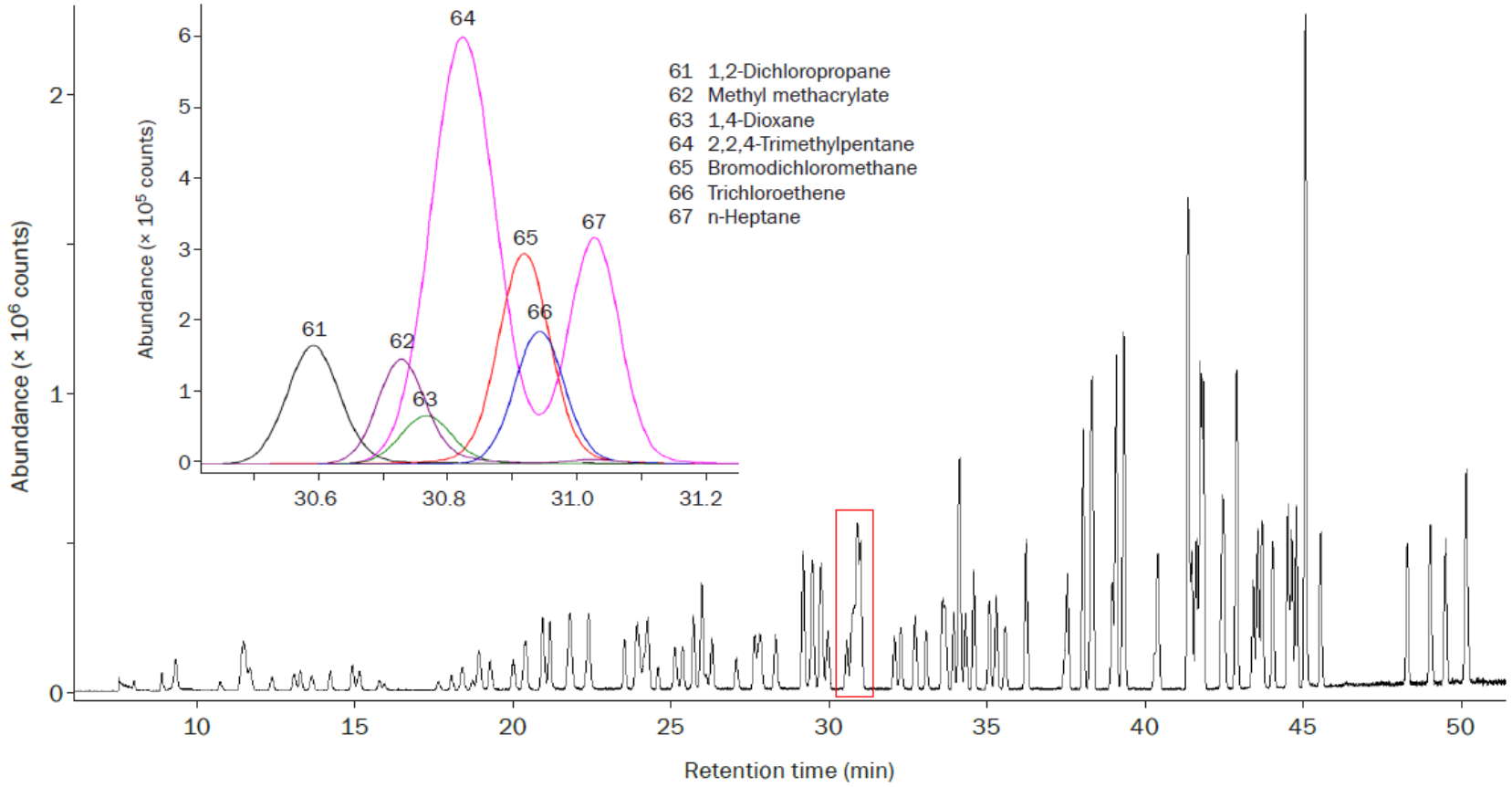
can quantify many compounds, don't necessarily need standard of compound to be quantified

needs hydrogen and compressed air supply

stable response over long periods of time

	FID	MS
Advantages	+ sensitive, robust, simple in design and easy to use + very stable performance with typically less than 2% sensitivity drift over one month + response of NMHC is proportional to the mass or carbon number and allows easy quantification + quantification other VOCs with effective carbon number (ECN) concept + not sensitive to traces of water, N_2, O_2, and noble gases + relatively low costs	+ compound identifying capabilities + second dimension (mass tracks) for better resolution + substance-specific quantification (overlaying peaks can be separated by compound specific mass tracks)
Disadvantages	- not substance-specific, identification just by retention time -Co-eluting peaks cannot be quantified individually	- each substance needs individual calibration - variable sensitivity requires more frequent calibration measurements, generally, calibration of each sample run is recommended - instruments need regular tuning - expensive - may show non-linear behaviour

FID is the favourable detection system whenever identification can be achieved simply based on the retention times. If the resolution of the chromatographic system does not allow unambiguous identification of different compounds based on retention time alone, a mass spectrometer is recommended as detector for its compound identifying capabilities.



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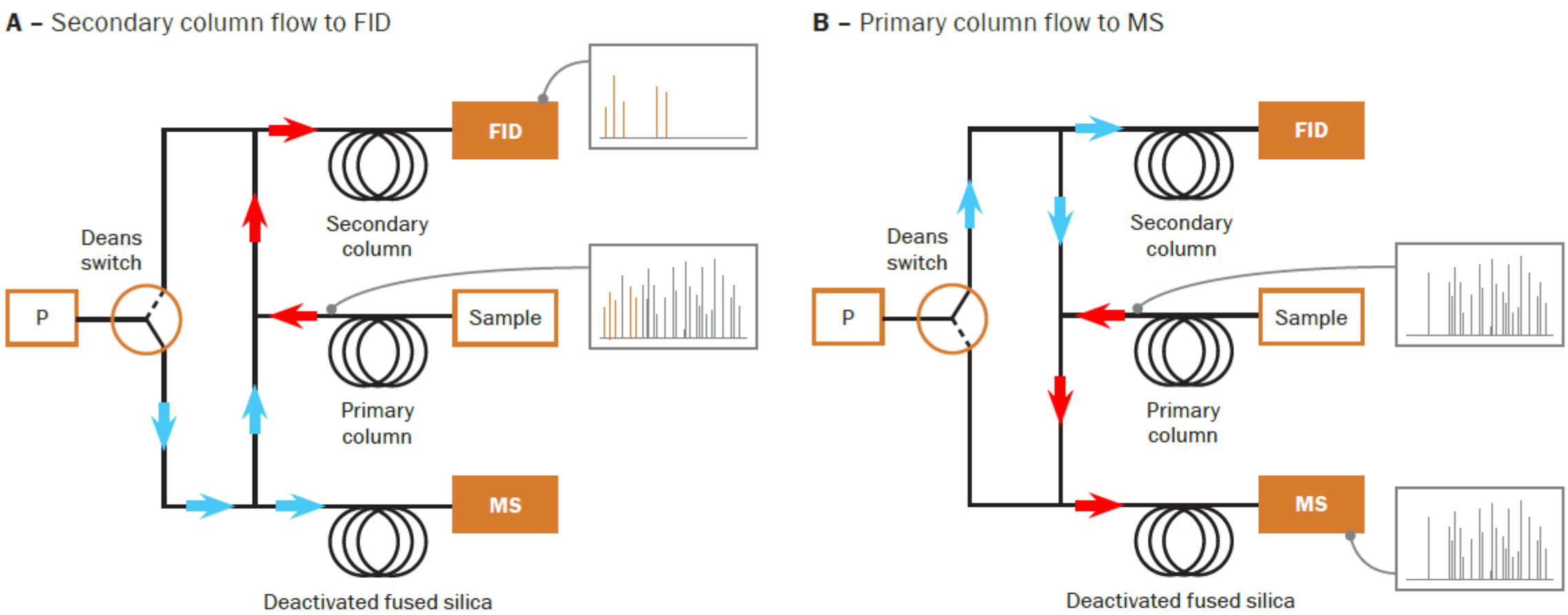

Figure 4: Dual-column GC–MS/FID instrument operation. = Analyte flow. = Gas flow. P = Carrier gas pressure supply.

VOC analysis **Gas Chromatography** principles

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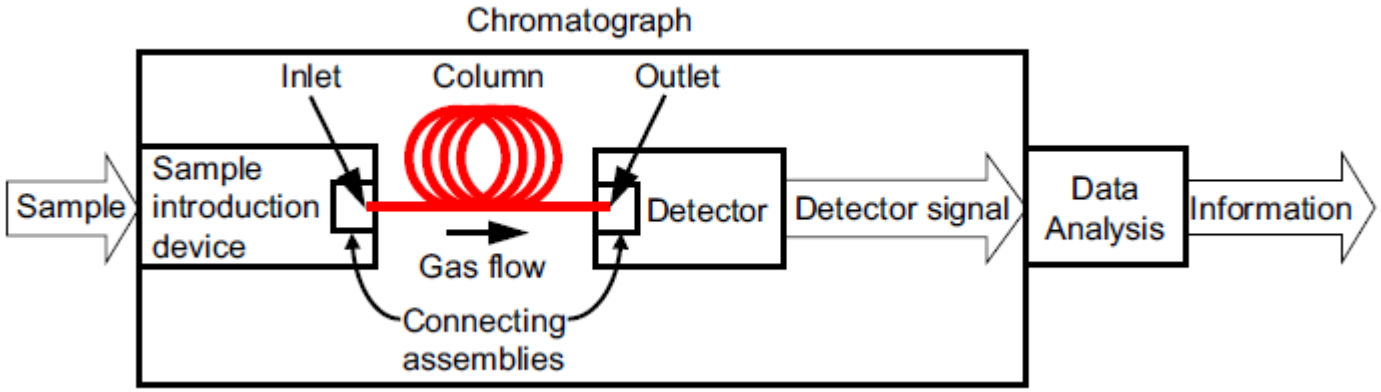


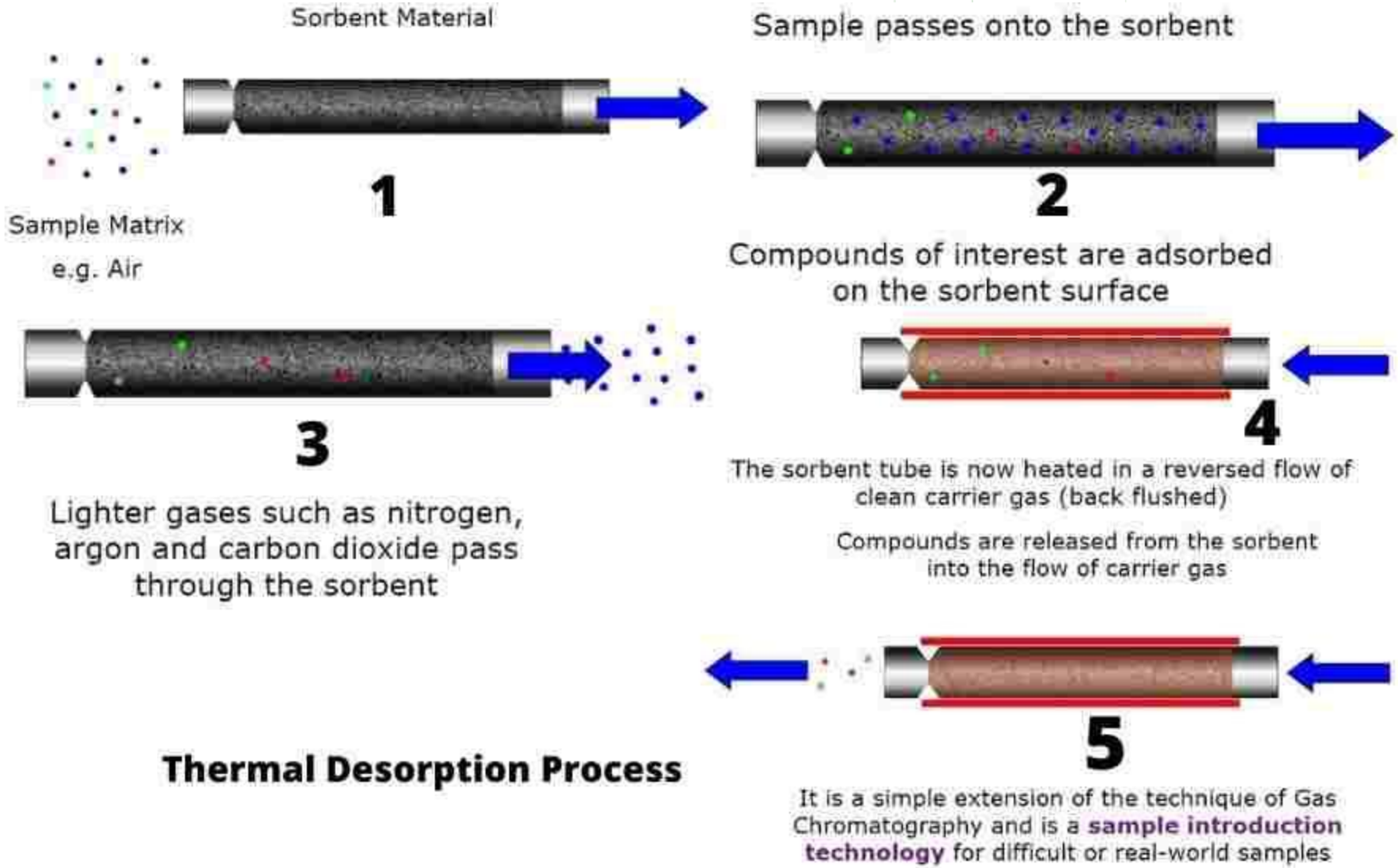
Sample preconcentration/focusing techniques

<u>Cryogenic techniques</u>

- Use liquid nitrogen (-196 deg C), argon (-186 deg C), CO_2
- Pros: wide range of analytes, low blanks, can use same trap for a long time
- Cons: need cryogen, expensive, uses a lot of energy to generate
- Will also retain water, CO_2

<u>Adsorbent techniques</u>

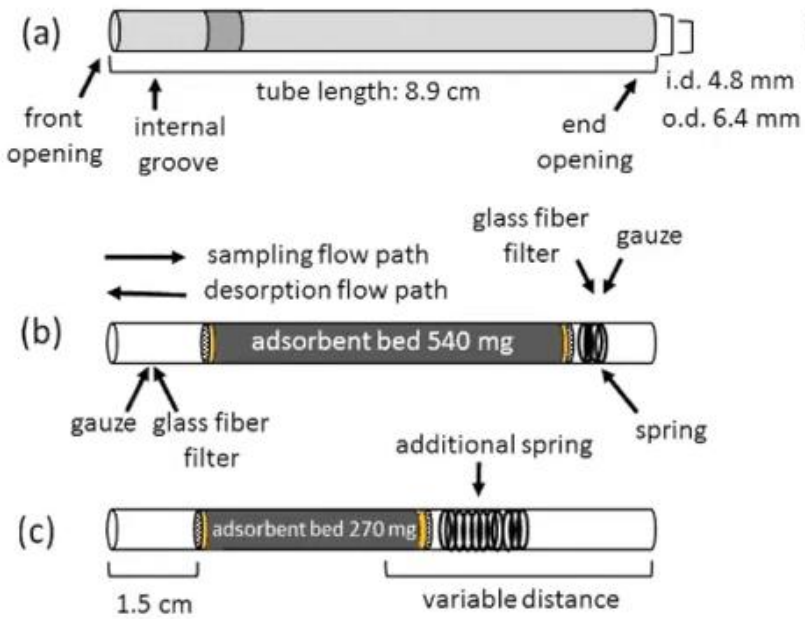
- Many choices: polymeric organic materials, activated carbon, molecular sieves
- Use multistage combinations to analyze for a wider range of volatilities
- No cryogen required
- Can be operated for a long time
- Allows some control over water, CO_2 co-trapping

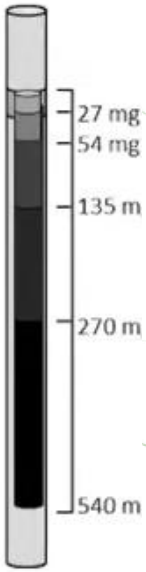


Thermal Desorption Process

Catch the VOCs and bring them back home

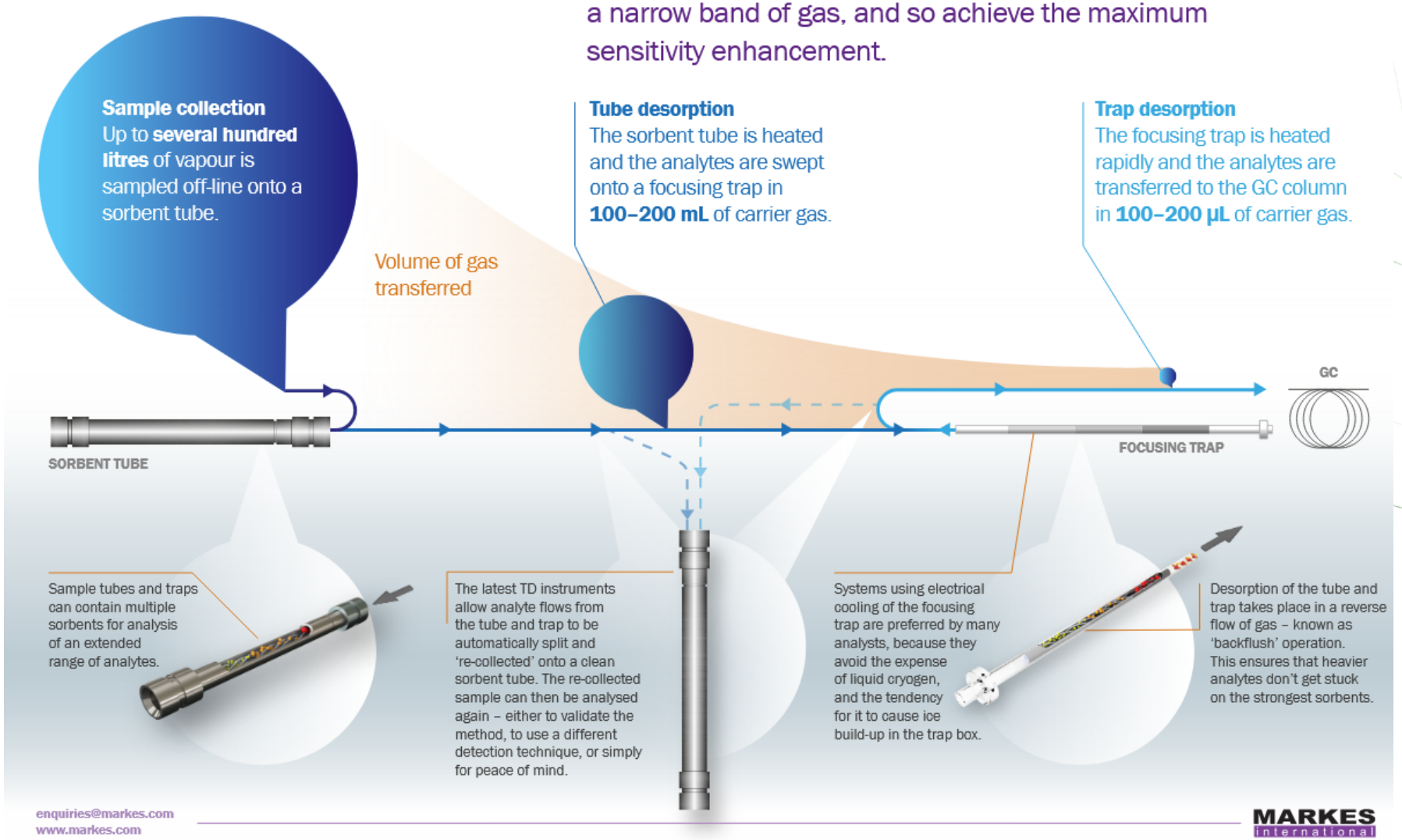
Solid Adsorbent Sampling

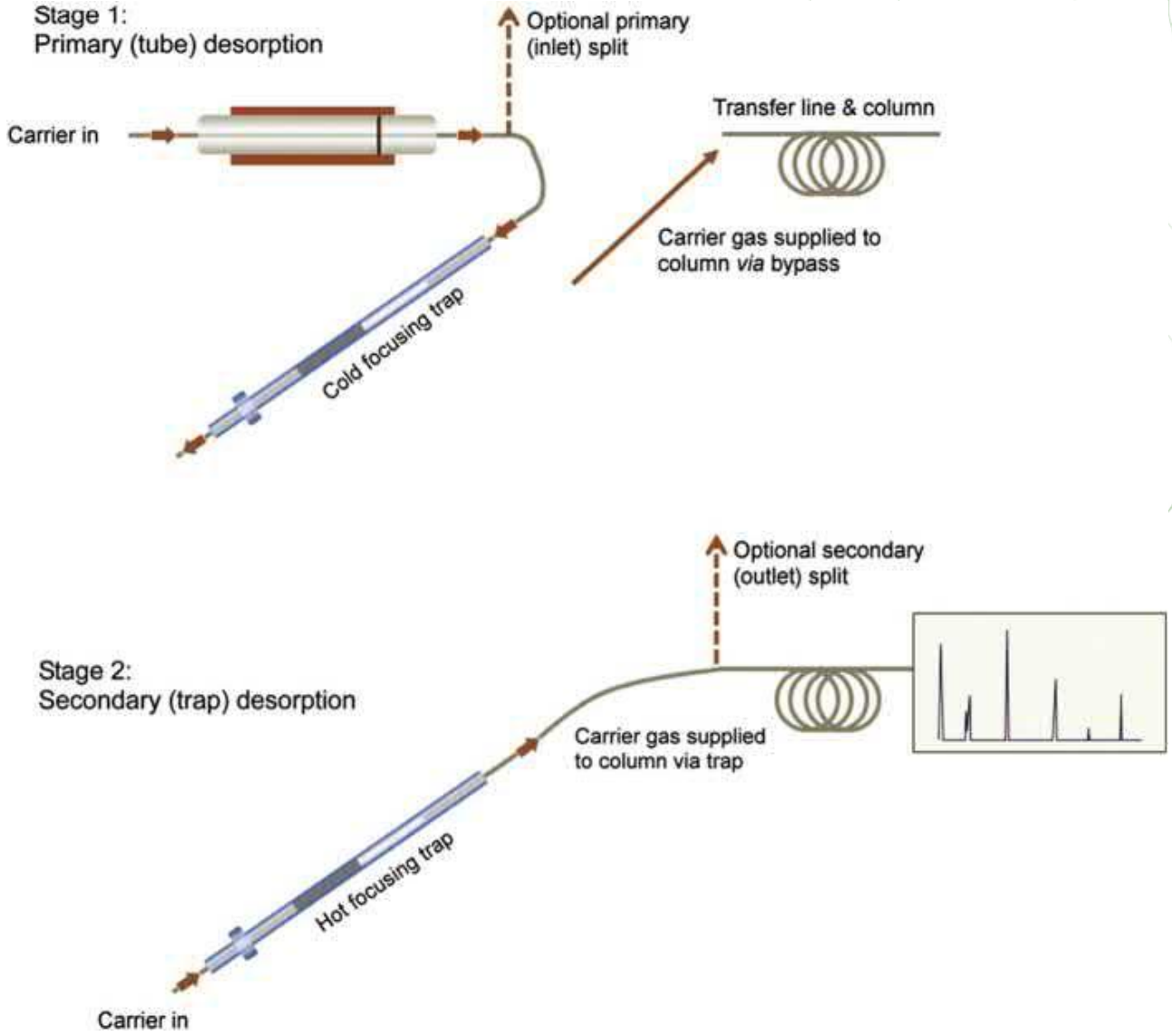


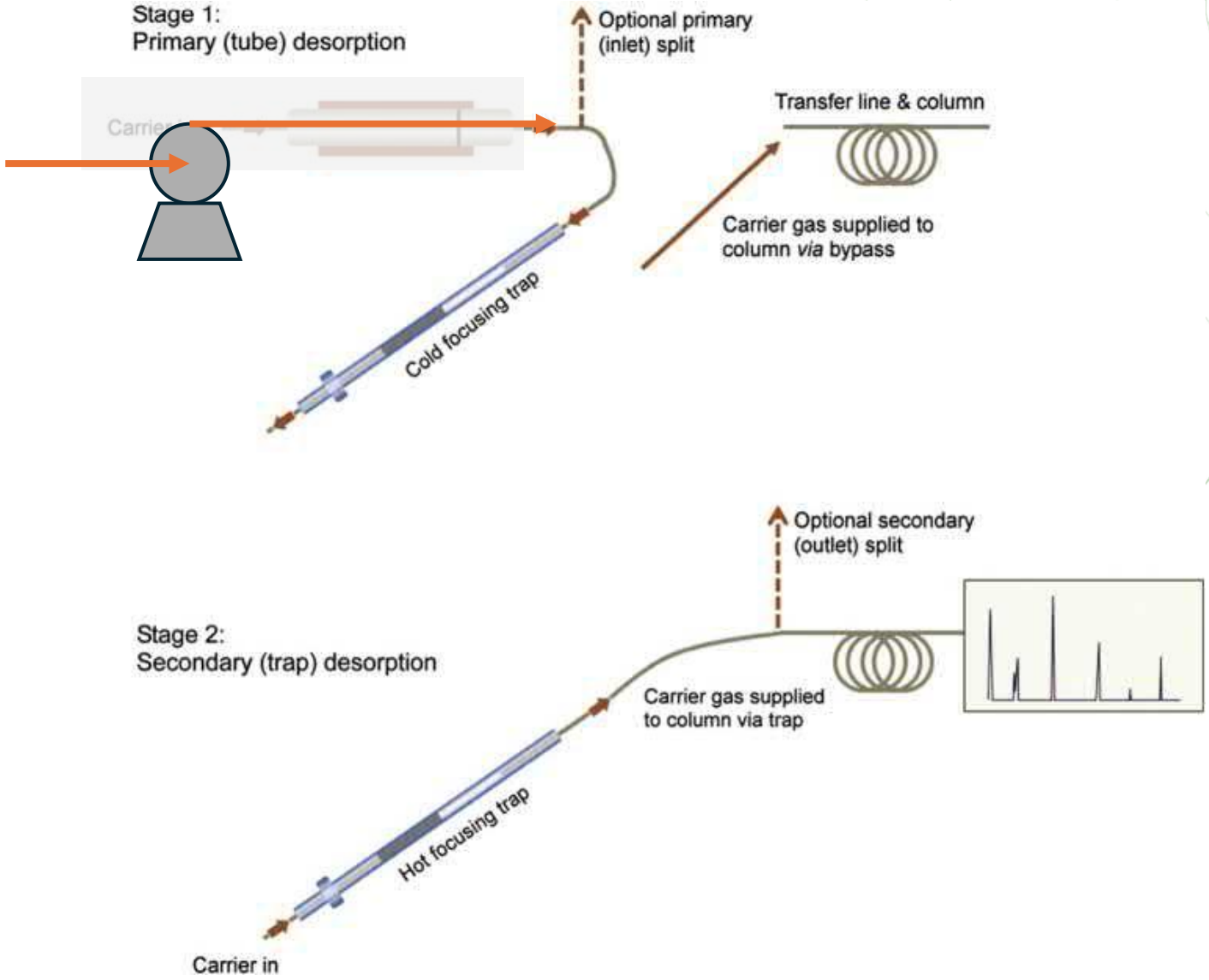


How does TD work?

The majority of TD applications use sorbent tubes and a two-stage desorption process to focus the analytes into a narrow band of gas, and so achieve the maximum sensitivity enhancement.




Stage 1:
Primary (tube) desorption
Optional primary
(inlet) split
Carrier in
Transfer line & column
Carrier gas supplied to
column *via* bypass
Cold focusing trap
Optional secondary
(outlet) split
Stage 2:
Secondary (trap) desorption
Carrier gas supplied
to column via trap
Hot focusing trap
Carrier in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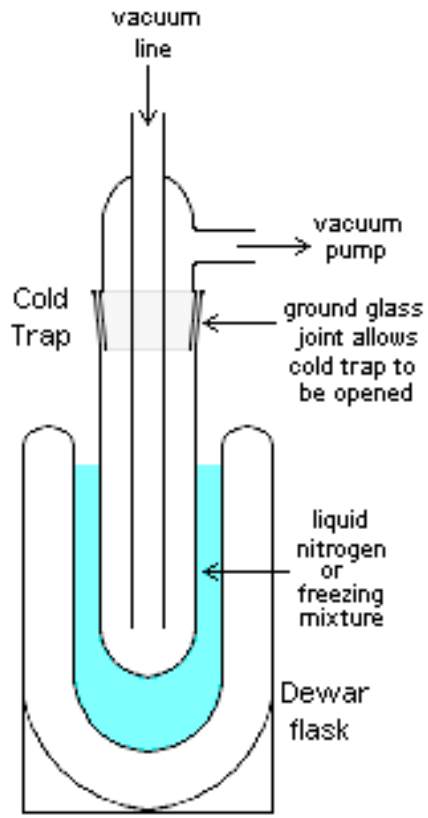
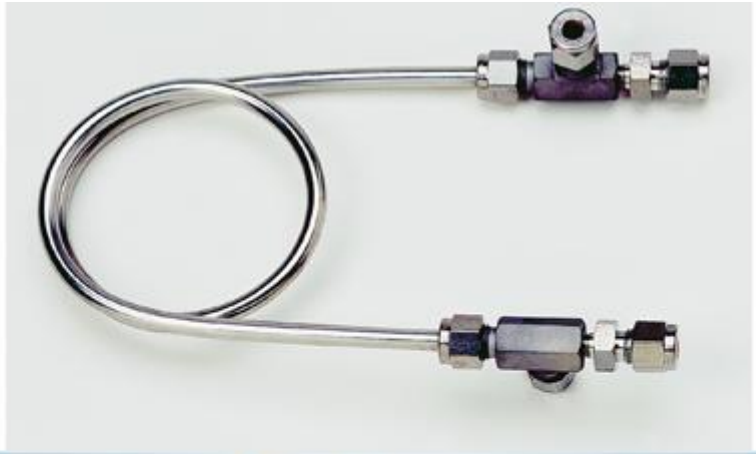
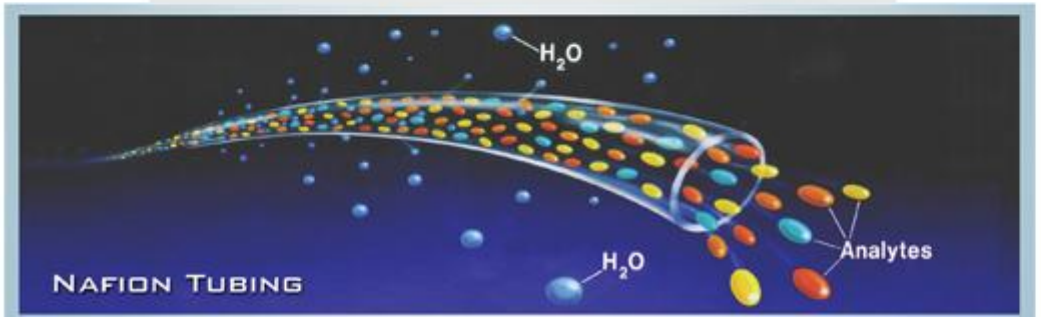
Transfer line & column
Carrier gas supplied to
column *via* bypass
Cold focusing trap
Optional secondary
(outlet) split
Stage 2:
Secondary (trap) desorption
Carrier gas supplied
to column via trap
Hot focusing trap
Carrier in

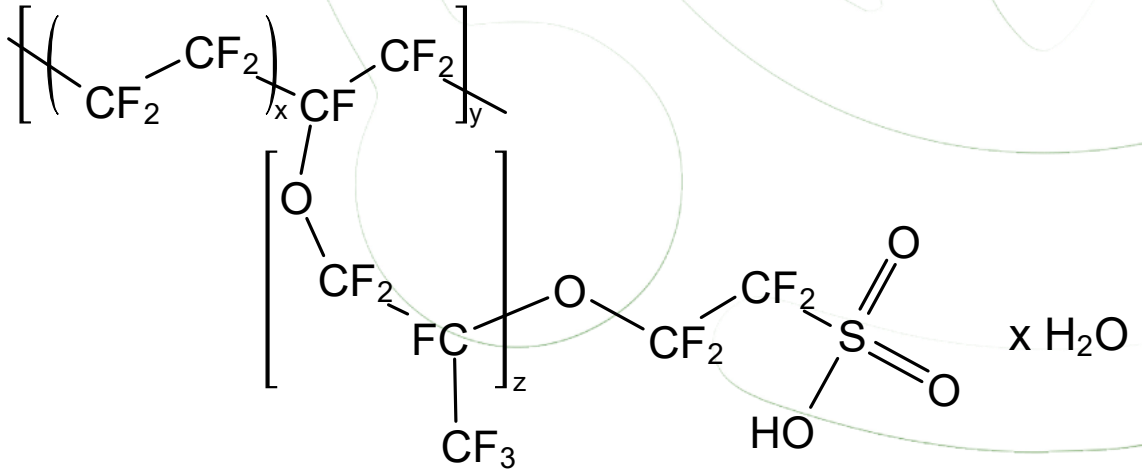
Two stage
water removal
with cold traps
(-30 °C; -40°C)






H_2O
H_2O
Analytes
NAFION TUBING

PERMA PURE


CF2
CF2
CF2
x
CF
y
O
CF2
FC
z
O
CF2
CF2
S
O
O
HO
CF3
x H2O

1 Air sampling and water removal

Canister or whole-air samples pass through the drying trap (where vapour-phase water is selectively deposited as ice), before being concentrated on the focusing trap.

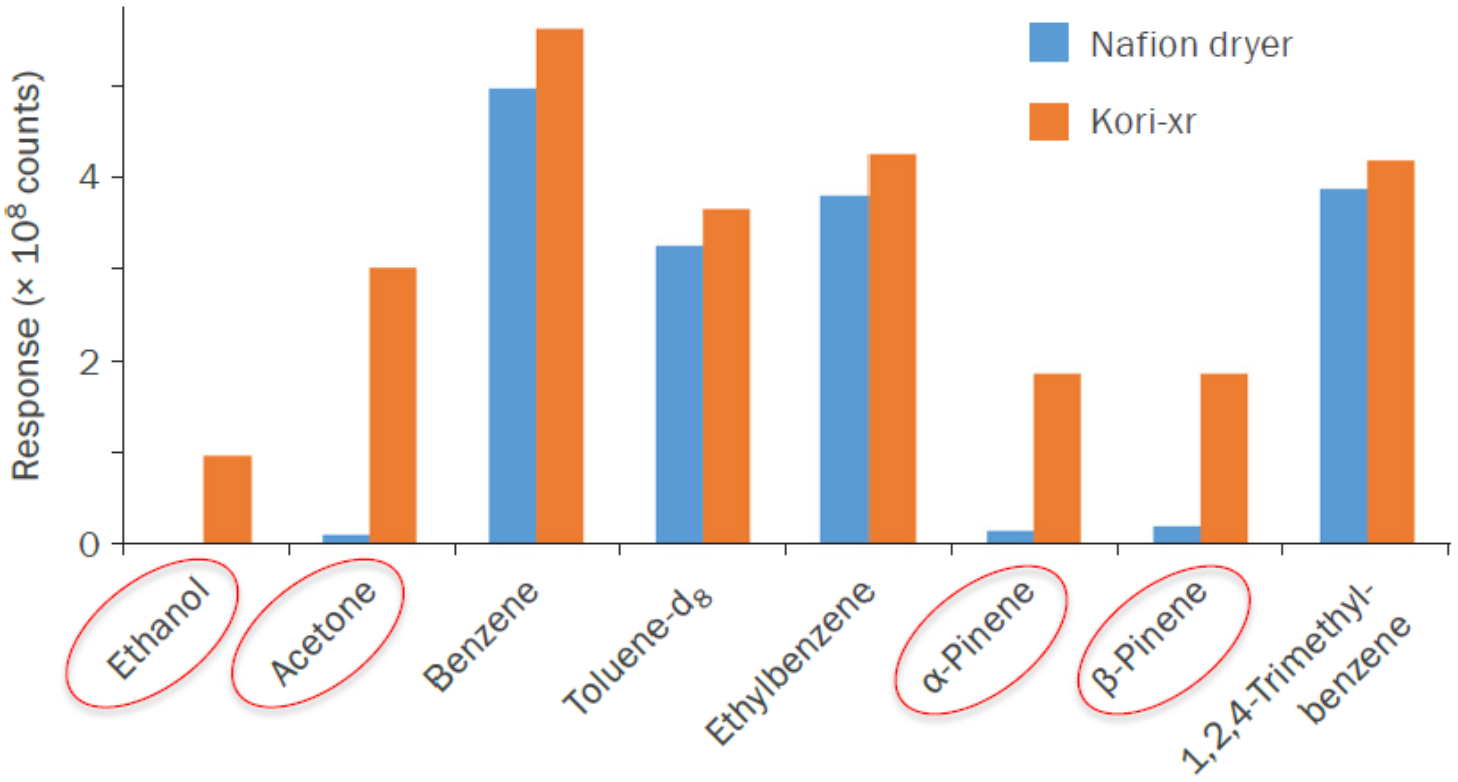
2 Purging of residual water

Optional temperature-programmed dry-purging of the focusing trap with carrier gas (between –30°C and 50°C) selectively eliminates any residual water while retaining 100% of target analytes.

3 Trap desorption

The focusing trap is rapidly heated in a reverse flow of carrier gas, to transfer analytes to the GC. Simultaneously, the drying trap is heated in a flow of gas to expel the trapped ice and regenerate it for the next sample.

Markes TD



Comparison of Kori-xr *vs.* nafion rryer running a 4 ppbC 80% RH standard

Markes TD

Other interference from the sample:

- Ozone
- Particles
- CO_2

Specific filters are available but need to be checked regularly for possible contaminations, loss of some analytes, artfefacts formations: regular maintenance is required

Samples could collected as whole air and transported back at the laboratory for subsequent analysis

Make the VOCs into something different to bring back

Derivatization Methods – DNPH for aldehydes, ketones

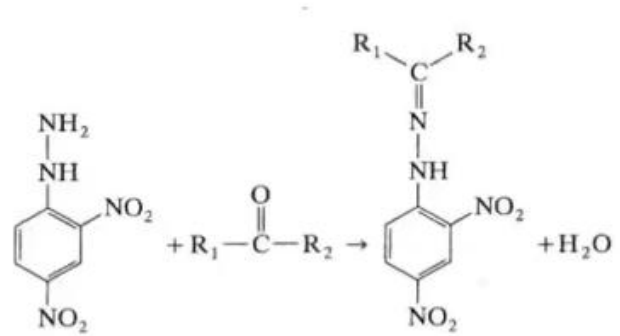
EPA/625/R-96/010b

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

Second Edition

Compendium Method TO-11A

Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology]



Data quality objectives

Table 3 Data quality objectives (DQOs) for the measurements of NMHCs in whole air compressed test gases (inter-laboratory compatibility) expressed as the expanded combined uncertainty (k=2) and the repeatability (k=1; standard deviation). The basic station performance requirements correspond to the former and weaker DQOs of GAW Report 171 (2006).

	GAW basic performance expanded combined uncertainty	GAW basic performance repeatability	GAW target performance expanded combined uncertainty	GAW target performance repeatability
Alkanes	10%	5%	5%	2%
alkenes incl. isoprene	20%	10%	5%	2%
Alkynes	15%	5%	5%	2%
Aromatics	15%	10%	5%	2%

Calibration

For many VOCs, lack of reference gas mixtures (RGMs) that are:
- stable
- traceable to the international system of units SI
- at atmospheric level (pmol/mol to nmol/mol)

NMHCs: National Physical Laboratory (NPL, UK)
Ozone precursor mixture, 31componds , alkanes, alkenes and aromatics); recently also Oxy-vocs

Monoterpenes (MTs) e.g. a-pinene, limonene: National Institute of Standards (NIST, USA)

Long chain to keep it consistent and traceable: need of a Central Calibration Laboratory to define a calibration scale through fully controlled preparation of Primary Calibration mixture;

Calibration

Minimum requirements for a station that need to be fulfilled:

1. **A (secondary) laboratory standard** which has to be a multi-component standard (synthetic mixture), produced and certified by the CCL (recommended), or at least traceable to the CCL, for ensuring traceability of the measurements to the WMO GAW calibration scale.
2. **One or more (tertiary) working standards** that cover most (ideally all) components measured and are used for regular calibration of the measurements, regular or high consumption applications like standard addition or dilution series, etc. These working standards can be either other certified or custom made synthetic mixtures and are calibrated versus the laboratory standard.
3. **A target gas** which is preferably compressed whole air but could also be a synthetic mixture calibrated by a reference laboratory (CCL or WCC) (recommended) but at least calibrated by the station against the laboratory standard: it is used to check the assigned values of the calibration mixtures and the calibration process itself and is treated as an air sample with unknown mole fraction.

Monitoring of the target gas results yields information about the performance of the instrument, drifts of the laboratory standard and potential instrumental problems.

Calibration

Role of ACTRIS: measurement guideline provides recommendations for good measurement practice for the analysis VOCs; update WMO guidelines; develop RI to support end users through the CCLs

https://www.actris.eu/sites/default/files/Documents/ACTRIS-2/Deliverables/WP3_D3.17_M42.pdf

THANKS!

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