

This teaching material is a copyrighted work protected by UCT Prague copyright.

Some parts of this lecture are based on third party copyrighted works that UCT Prague uses for the purpose of instruction of its students based on a statutory licence.

The content of this lecture is intended exclusively for the instruction of students at UCT Prague.

The content of this lecture cannot be reproduced, recorded, emulated, published or disseminated in any other way without written permission from the copyright owner.

When students at UCT Prague make a recording or emulation of the work exclusively for their use, or use the work in any other way that does not infringe copyright according to the law, this is not considered a breach of copyright.

© UCT Prague 2021



Head space (HS) (or Headspace or Head-space)

- Dominantly coupled to gas chromatography
- Based on the sampling of headspace, i.e. gas phase above the surface of a liquid sample or above the surface of a solid sample or above mixed (undefined) sample
- Realized using the special pressure vessel – vial, closed by cup equipped with elastic septum, necessary for sealing and sampling using the special gas tight syringe or autosampler
- HS-SPME connection is now very often applied, i.e. sampling using SPME fiber



Head space (HS) (or Headspace or Head-space)

Classic realization

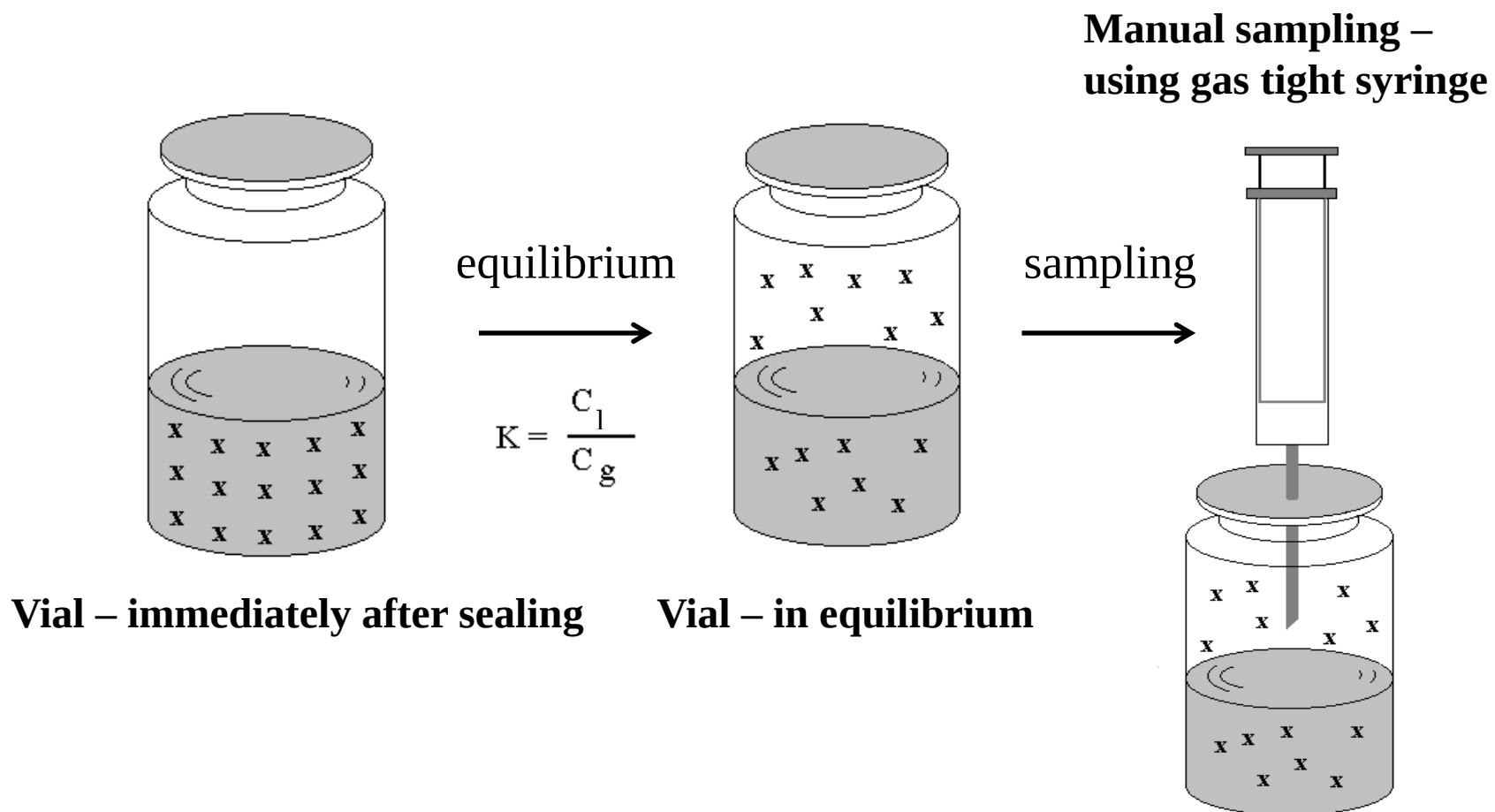
- manual sample preparation in a pressure vessel
- incubation - equilibration - tempering, mixing
- manual sampling with a gas-tight syringe
- alternatively manual sampling by SPME fiber

Automated realization

- manual sample preparation in a pressure vessel
- incubation in autosampler - equilibration - tempering, mixing
- sampling by gas-tight autosampler system
- alternatively automated incubation and sampling by SPME fiber

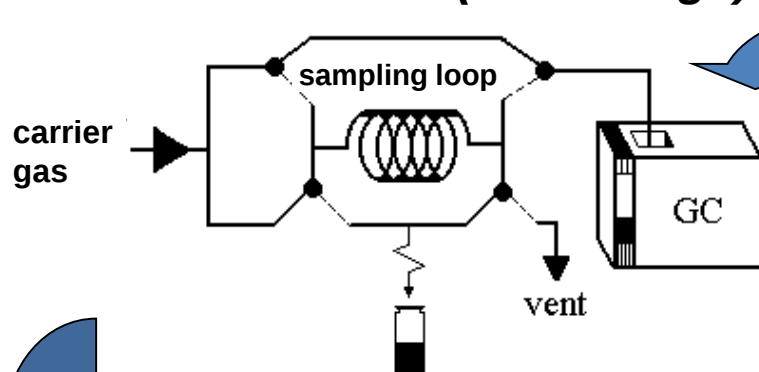


Head Space (HS): Classic realization

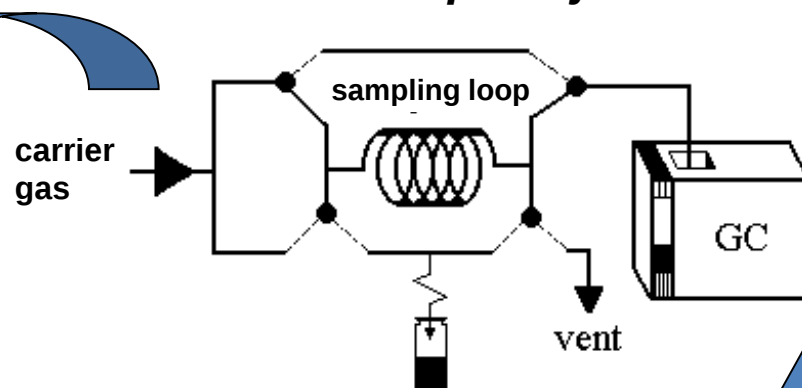


Head Space (HS): Automated realization

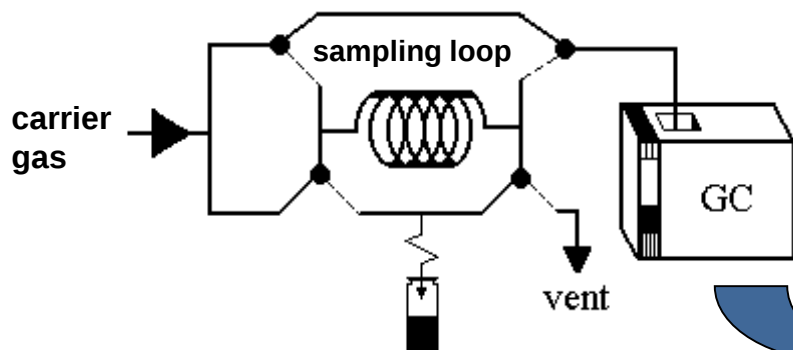
Phase 1 - idle (vial change)



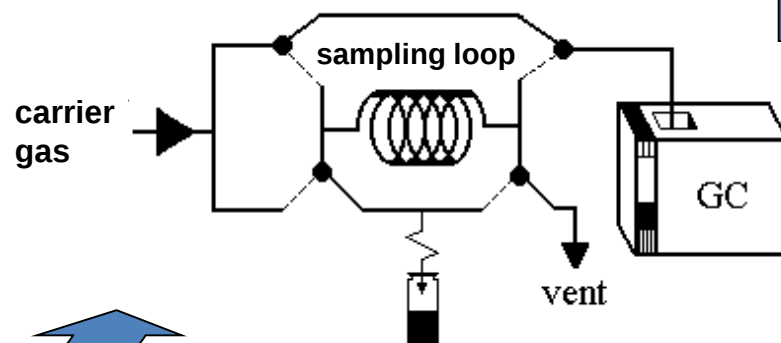
Phase 4 – sample injection



*Phase 2 – pressurisation
by carrier gas*



Phase 3 – sampling to loop



Head Space (HS): Parameters of realization

Parameters given by analyte and/or sample properties	Parameters that can be influenced experimentally
1. analyte volatility 2. thermal stability of the analyte 3. nature of the sample - solids content - homogeneity, etc.	1. V_g, V_l - pouring the sample with liquid (H_2O) 2. temperature - with higher temperature higher concentration of the analyte in the gas phase 3. mixing the sample - even analyte distribution in both phases 4. speed of equilibrium 5. chemical and physical properties - liquid modification, sorbent, pH adjustment



Head Space (HS): Parameters of realization

Injection volume comparison

solvent: usually 1 - 5 μl

gas: usually 1 - 5 ml

The headspace may have 2-3 orders of magnitude
lower LOD at $C_g = C_l$



Head Space (HS): Content / concentration measurement

Balance of gas / liquid equilibrium system

m – mass (weight) of analyte $\Rightarrow m, m_l, m_g$

$$m = m_l + m_g$$

c - mass concentration of analyte (m/V) $\Rightarrow c, c_l, c_g$

$$K = c_l / c_g = m_l / (c_g V_l)$$

$$m = m_g + K c_g V_l \quad // : c_g$$

$m = c_g (V_g + K V_l)$ - operating factor

V_g, V_l - given by experimental setup

K - determined using calibration for given system at defined thermodynamic conditions (temperature, agitation, analyte concentration, solution composition, V_g, V_l)

c_g - measured at defined volume of gas phase



Head Space (HS): Content / concentration measurement

Practical methods

1. $m_l = 0$ - ideal state, occurring for extremely volatile analyte at given temp.

$$K = 0 \Rightarrow \underline{\mathbf{m = m_g = c_g V_g}}$$

2. Calibration using model system

- model close to real conditions:

- a) validity of model based K for real samples
(e.g. model system water / chloroform X blood plasma / chloroform etc.)
- b) validity of model based K for different concentration levels
(marginal concentrations - $c_g \rightarrow 0$ or $c_g \rightarrow c_{sat.}$)
 - the need of verification for the required concentration range



Head Space (HS): Content / concentration measurement

3. Standard addition method

- assumption that small analyte addition does not have significant effect to K
- m_s – mass of addition, A_s – peak area for sample with analyte addition

$$\boxed{\frac{m}{m + m_s} = \frac{A}{A_s}} \longleftrightarrow \boxed{\frac{m}{A} = \frac{m + m_s}{A_s}}$$

$$\Rightarrow mA_s = mA + m_s A \quad \Rightarrow \quad mA_s - mA = m_s A$$

$$\Rightarrow \boxed{m = \frac{m_s A}{A_s - A}} \longleftrightarrow \boxed{m = \frac{m_s}{A_s/A - 1}}$$

- verification of the calibration line trend → 2 or more additions at different levels



Head Space (HS): Content / concentration measurement

4. Double sampling method

m - mass of analyte before 1. sampling

$m - m_1$ = mass of analyte before 2. sampling

m_1 – mass decrease caused by 1. sampling

m_1 – *determined by the absolute calibration*

$$\frac{m}{m - m_1} = \frac{A_1}{A_2} \Rightarrow \frac{m}{A_1} = \frac{m - m_1}{A_2} \Rightarrow m = \frac{m_1}{1 - A_2/A_1}$$

$A_2 / A_1 = q$ *q is defined as the quotient of an infinite geometric series*



Head Space (HS): Content / concentration measurement

5. Multiple sampling method- I

$$\frac{A_2}{A_1} = q \quad \Rightarrow \quad m = \frac{m_1}{1 - q}$$

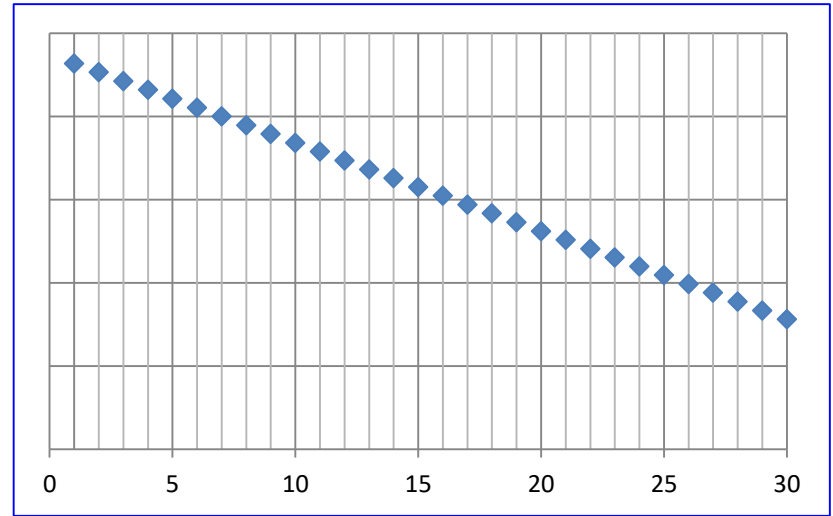
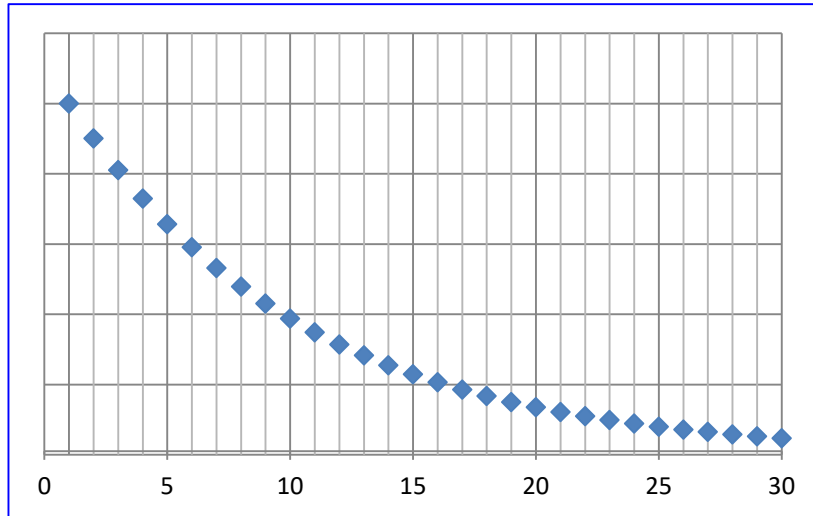
For automatic multiple sampling $\rightarrow$ graphic form: $y = \ln m_n$; $x = n-1$

$$m = \frac{m_1}{1 - e^{\frac{d \ln m_n}{dn}}}$$



Head Space (HS): Content / concentration measurement

5. Multiple sampling method- II



$$m = \frac{m_1}{1 - A_2/A_1}$$

$$m = \frac{m_1}{1 - e^{\frac{d \ln m_n}{dn}}}$$



Head Space (HS): Content / concentration measurement

5. Multiple sampling method- III

Multiple Headspace Extraction for the Quantitative Determination of Residual Monomer and Solvents in Polystyrene Pellets Using the Agilent 7697A Headspace Sampler

$$\ln A_i = -q(i-1) + \ln A_1$$

$$Q = \frac{A_2}{A_1} = \frac{A_3}{A_2} = \frac{A_{i+1}}{A_i} = e^{-q}$$

$$\sum_{i=1}^{i \rightarrow \infty} A_i = \frac{A_1}{1 - e^{-q}} = \frac{A_1}{1 - Q}$$

$$\ln A_1 = B - q$$

q: The slope of the logarithmic peak area-versus-extraction number plot

B: The intercept of the logarithmic peak area-versus-extraction number plot

A: Peak area of the headspace analyte

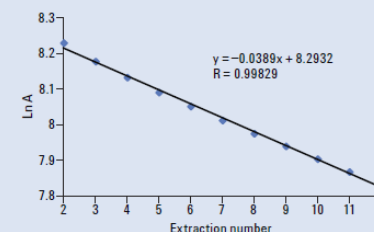
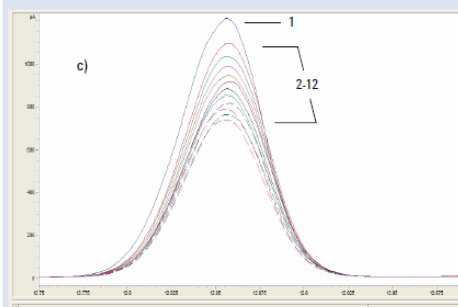
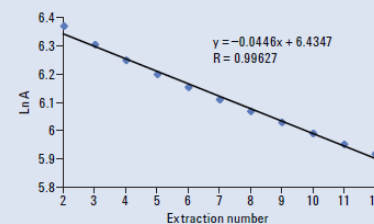
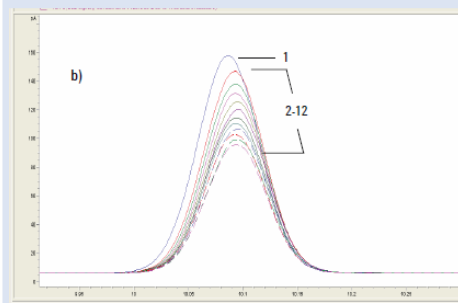
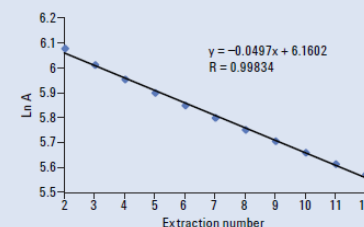
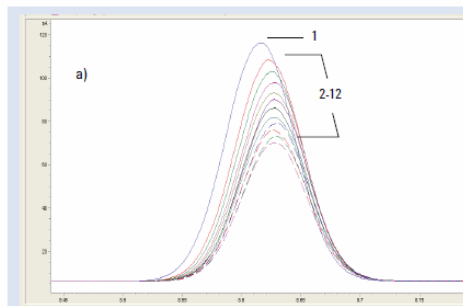
i: The i^{th} extraction

Note

1. sampling – air

2+. sampling - He, N₂

$$\sum_{i=1}^{i \rightarrow \infty} A_i = A_1 + \frac{A_2}{1 - Q}$$



Application Note 5991-0974EN

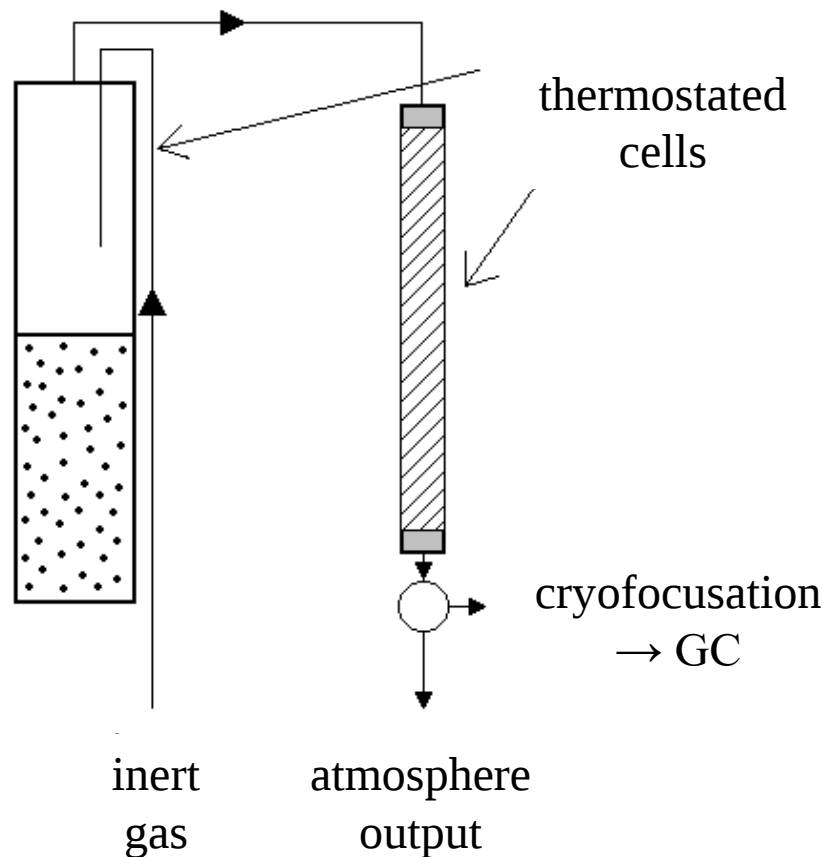
© Agilent Technologies, Inc., 2012
Printed in the USA
August 10, 2012
5991-0974EN



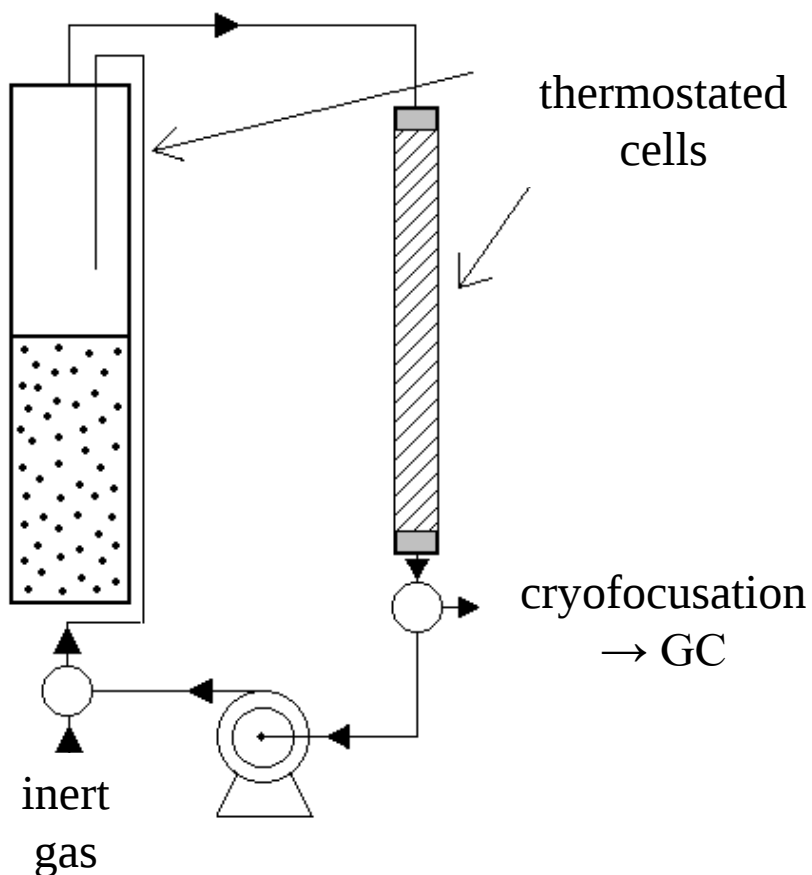
Dynamic headspace

Currently realized in combination with sorption column (trap) or cryofocustion and/or with both (trap is followed with cryofocustion)

A. Open system - dynamic HS



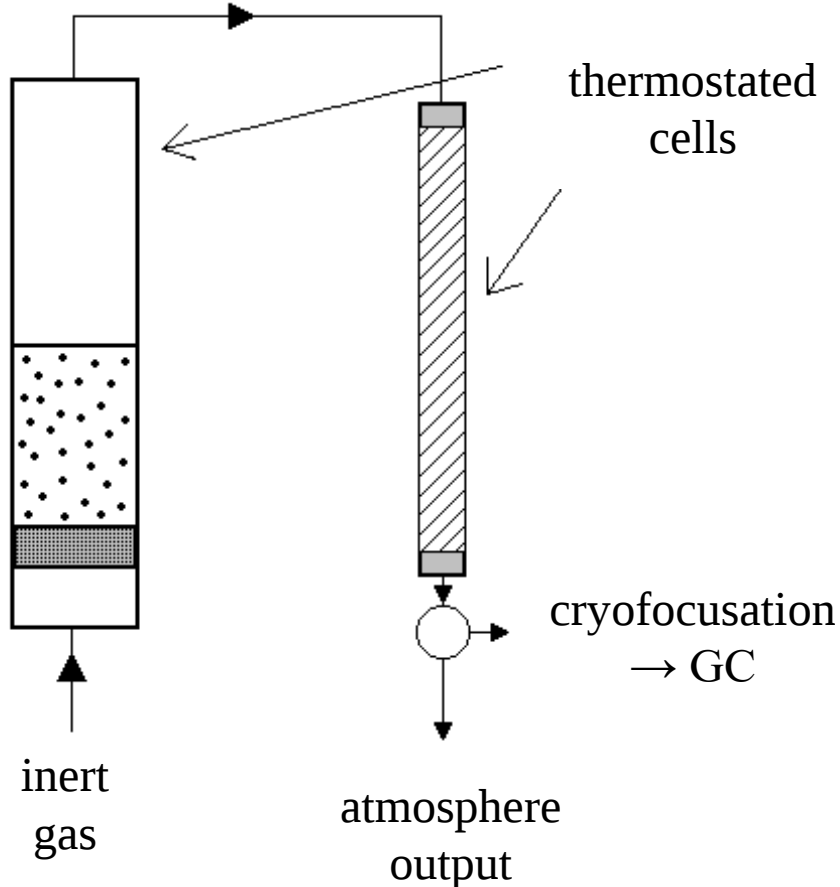
B. Closed system - dynamic HS



Purge & Trap

Currently realized in combination with sorption column (trap) or cryofocustion and/or with both (trap is followed with cryofocustion)

C. Open system - P&T



D. Closed system - P&T

