Metrology for Climate Relevant VOCs

Dynamic reference gas mixture preparation and uncertainty: permeation and diffusion methods

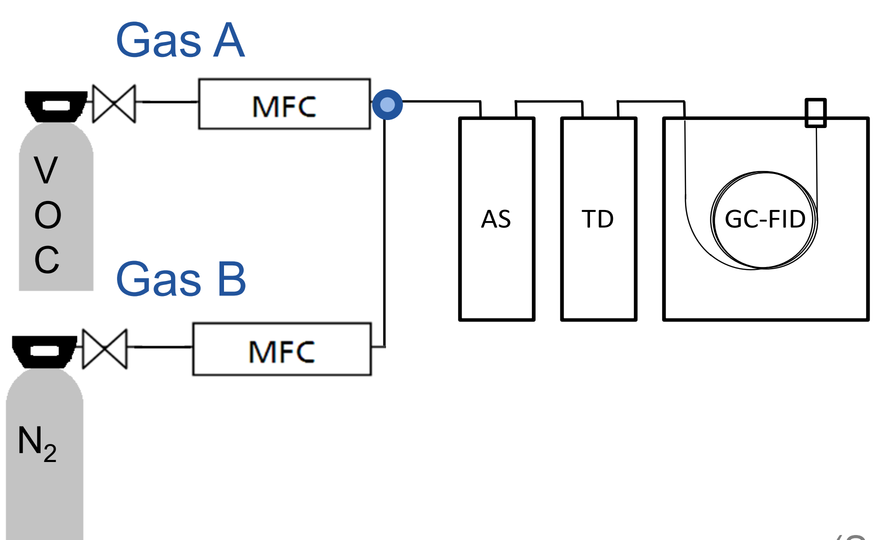
Maitane Iturrate-Garcia
Maricarmen Lecuna

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

ISO 6145 – dynamic methods

Preparation of calibration gas mixtures using dynamic methods, which relay in flow rates (gas A introduced at a known constant volume or mass flow rate into a known constant flow rate of gas B).

Dynamic dilution of a high fraction reference gas mixture with mass-flow controllers (MFCs)



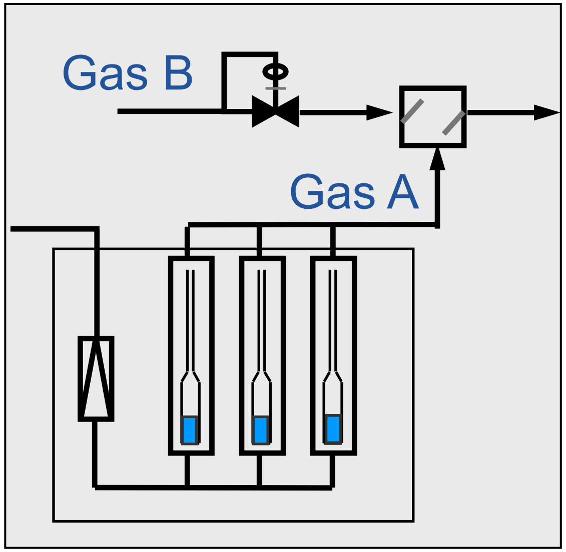
(Source: courtesy of VSL)

ISO 6145 – dynamic methods

Main dynamic methods

- Piston pumps
- Continuous injection
- Capillary
- Critical orifices
- Thermal mass-flow controllers
- **Diffusion**
- Saturation
- **Permeation**
- Electrochemical generation

Diffusion



(Source: courtesy of VSL)

Advantages and disadvantages

STATIC METHODS VS. DYNAMIC METHODS

- Wide range of concentrations.
- Un-tunability
- Suboptimal for unstable compounds
- Size and cost of cylinders
- Safety issues
- High minimal concentration
- Portability
- Limited long term stability

Advantages and disadvantages

STATIC METHODS VS. DYNAMIC METHODS

STATIC METHODS	DYNAMIC METHODS
Wide range of concentrations	Wide range of concentrations
Un-tunability	Tunability
Suboptimal for unstable compounds	Unstable compounds
Size and cost of cylinders	Long life low cost
Safety issues	Safety issues
High minimal concentration	Lower minimal concentration
Portability	Low portability
Limited long term stability	Long term stable

Permeation method

Permeation dynamic method: MSB

- TA Instruments (former Rubotherm)
- Glass/metal (SilcoNert 2000 coated SS)

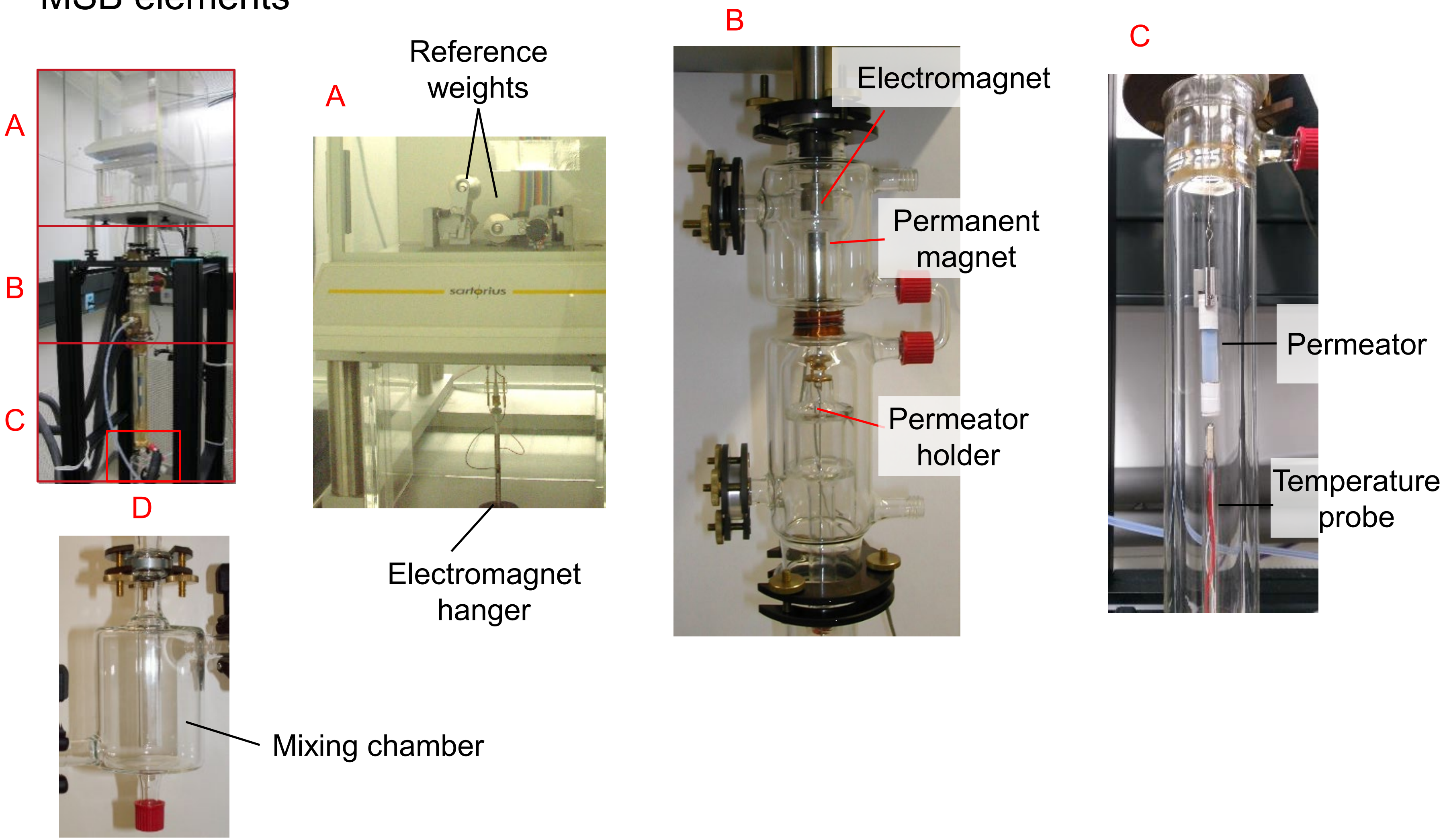
Magnetic suspension balance (MSB):

glass (left), metal (right)

https://www.metclimvoc.eu/training.html (March 2021)

Permeation dynamic method: MSB

MSB elements

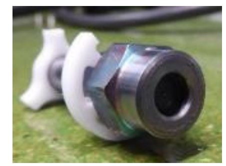


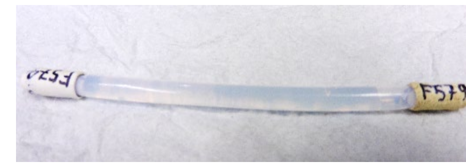
Permeation dynamic method: generation

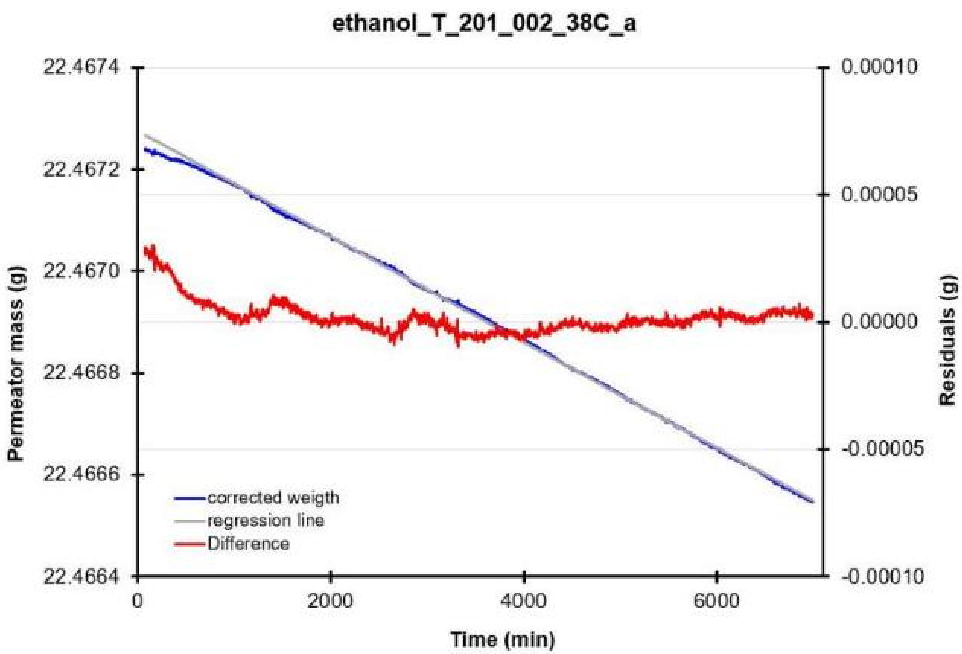
Primary reference gas mixtures using a MSB (magnetic suspension balance)

Step 1: Calibration of the permeation unit

Controlled conditions (T, P, flow)





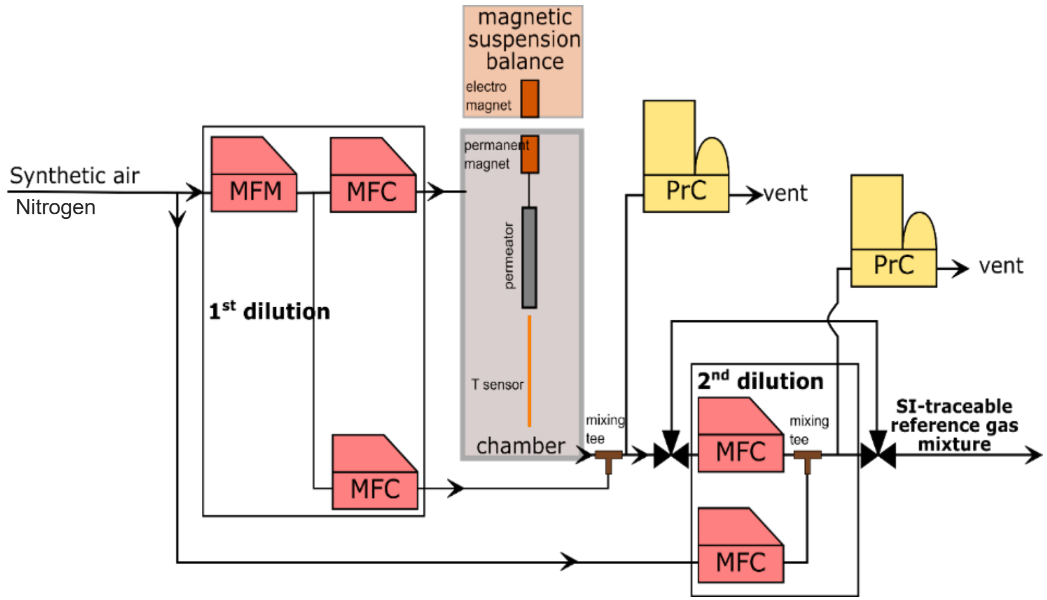


Permeation rate:

$$q_m = \frac{\Delta m}{\Delta t} = \frac{m_2 - m_1}{t_2 - t_1}$$

Permeation dynamic method: generation

Step 2: Dilution



1st dilution: $X_{RGM} = q_m \cdot purity \cdot \left(\frac{V_{m_{gas}}}{M_{m_{comp}}}\right) \cdot f_{dil1} + X_{res}$ (> 30-50 nmol/mol)

2nd dilution: $X_{RGM} = \left(q_m \cdot purity \cdot \left(\frac{V_{m_{gas}}}{M_{m_{comp}}}\right) \cdot f_{dil1} + X_{res}\right) \cdot f_{dil2} + X_{res}$ (< 30 nmol/mol)

Permeation dynamic method: uncertainty

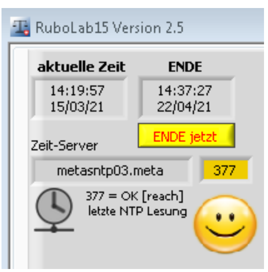
Main contributors to the uncertainty of the RGM amount fraction generated

$$X_{RGM} = q_m \cdot purity \cdot \left(\frac{V_{m_{gas}}}{M_{m_{comp}}}\right) \cdot f_{dil1} + X_{res}$$

Permeation rate (step 1)

$$q_m = \frac{\Delta m}{\Delta t}$$

- Balance sensitivity: < 1.5 % ($u(S) = 3 \cdot 10^{-5}$ g)
- Buoyancy variations: < 1 % ($u(b) < 3 \cdot 10^{-7}$ g)
- Chamber temperature variations: negligible ($u(T) < 0.00026$ °C)
- Chamber pressure variations: negligible ($u(P) < 0.002$ hPa)
- Noise of the system > 75 % ($u(SC) < 0.004$ %)



- PC time synchronized through a Network-Time-Protocol (NTP) server with the Swiss official time given by **atomic clocks** at METAS photonic, time and frequency lab (**negligible**; $u(t) < 1 \cdot 10^{-18}$ s)

- Others: leaks, wall reactions…

Permeation dynamic method: uncertainty

Main contributors to the uncertainty of the RGM amount fraction generated

$$X_{compound} = q_m \cdot purity \cdot \left(\frac{V_{m_{gas}}}{M_{m_{comp}}}\right) \cdot f_{dil1} + X_{res}$$

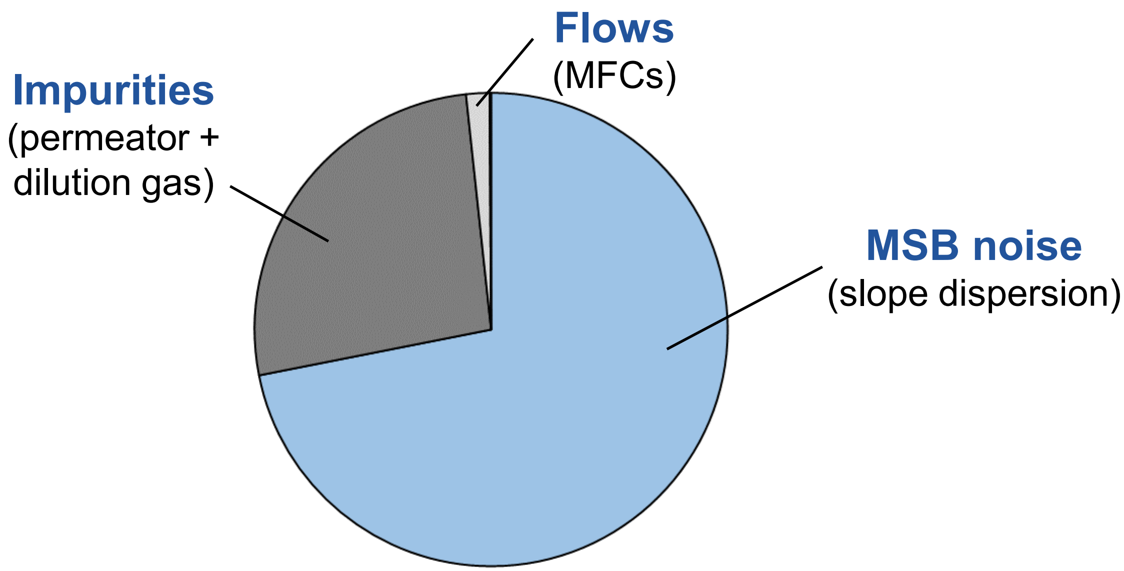
Step 2

- Impurities: variable
- Molar mass, molar volume: negligible (at 10^{-6} nmol/mol level)
- Dilution flow: 4-10 % ($u(q_v) < 0.2$ %)
- Residuals in dilution gas: variable
- Others: leaks, wall reactions…

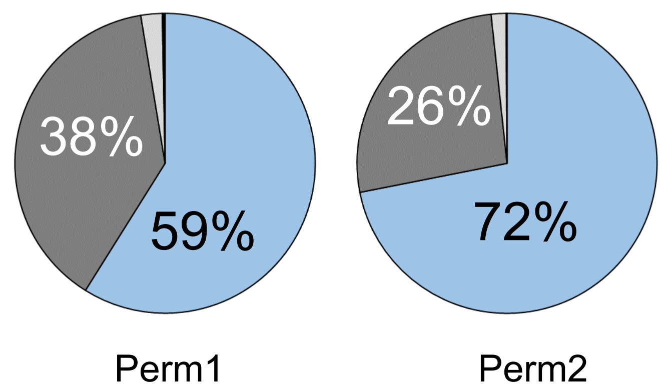
Permeation dynamic method: uncertainty

$U(X_{RGM}) = k \cdot u_c(X_{RGM})$

$$\frac{u_c(X_{RGM})}{X_{RGM}} = \sqrt{\left(\frac{u(q_m)}{q_m}\right)^2 + \left(\frac{u(q_v)}{q_v}\right)^2 + \cdots +}$$



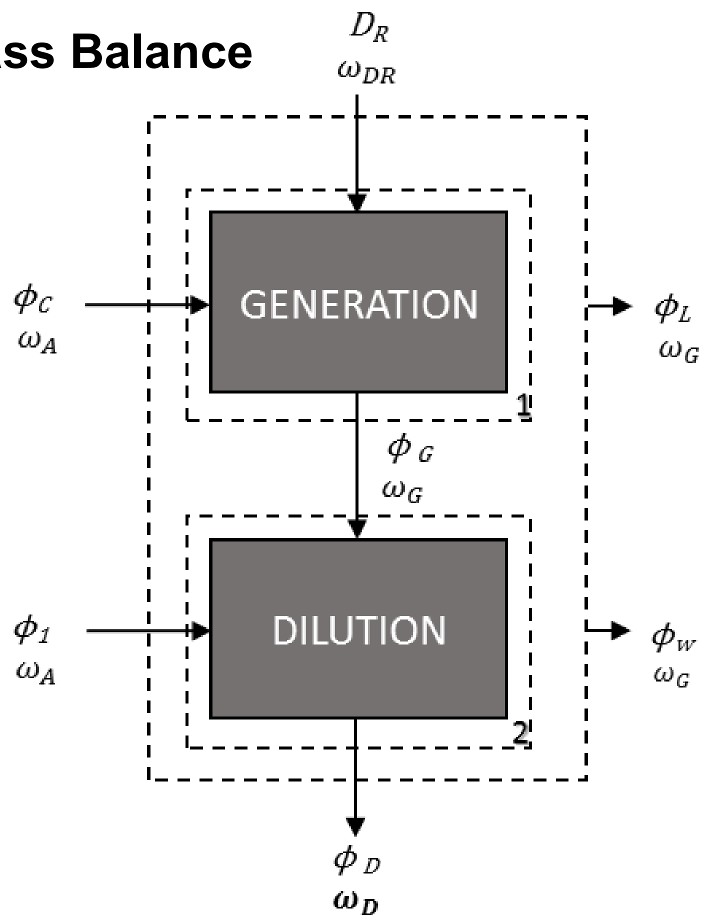
Permeator	Dilution steps	Amount fraction (nmol/mol)	Uncertainty (k = 2)
Perm1	2	31.3	1.9%
Perm2	1	345.9	1.6%



Diffusion method

Diffusion dynamic method

Mass Balance



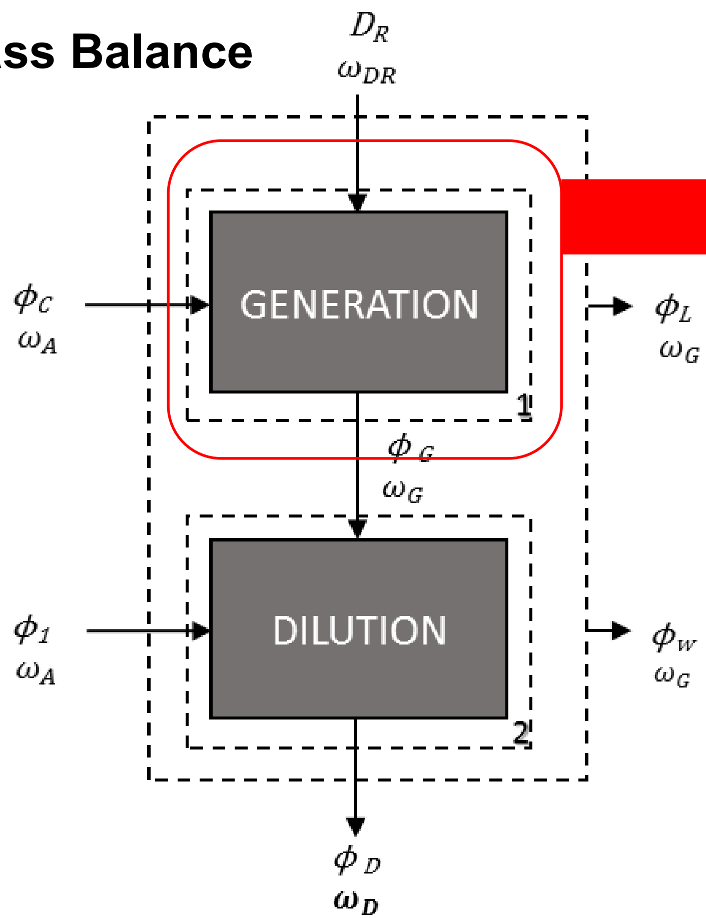
Pv = 1-70 kPa @ generation T (26 °C)

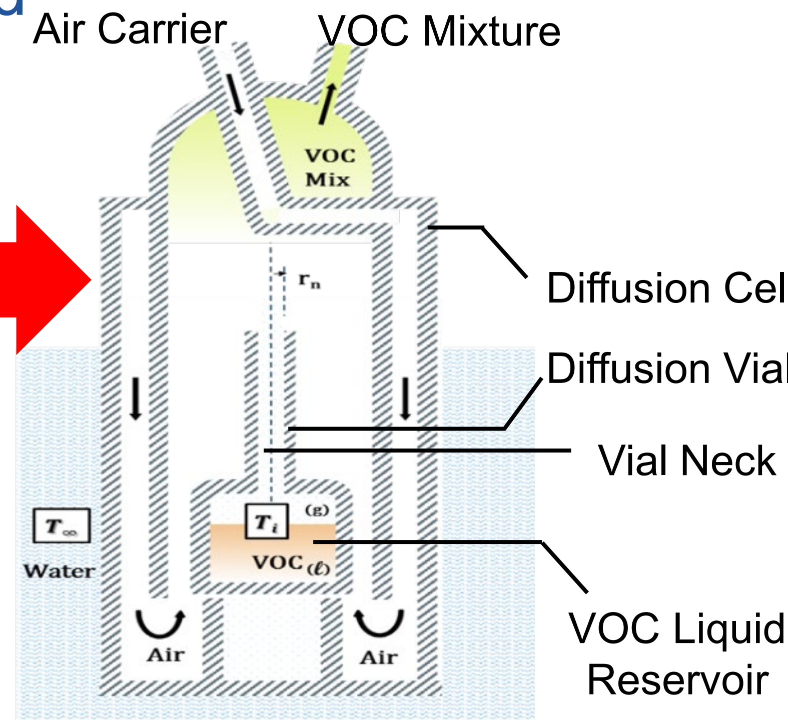
- ✓ Fick's law of diffusion
- ✓ Perfect gas assumption

- ✓ Convective transport
- ✓ Turbulence for enhanced mixing

Diffusion dynamic method

Mass Balance

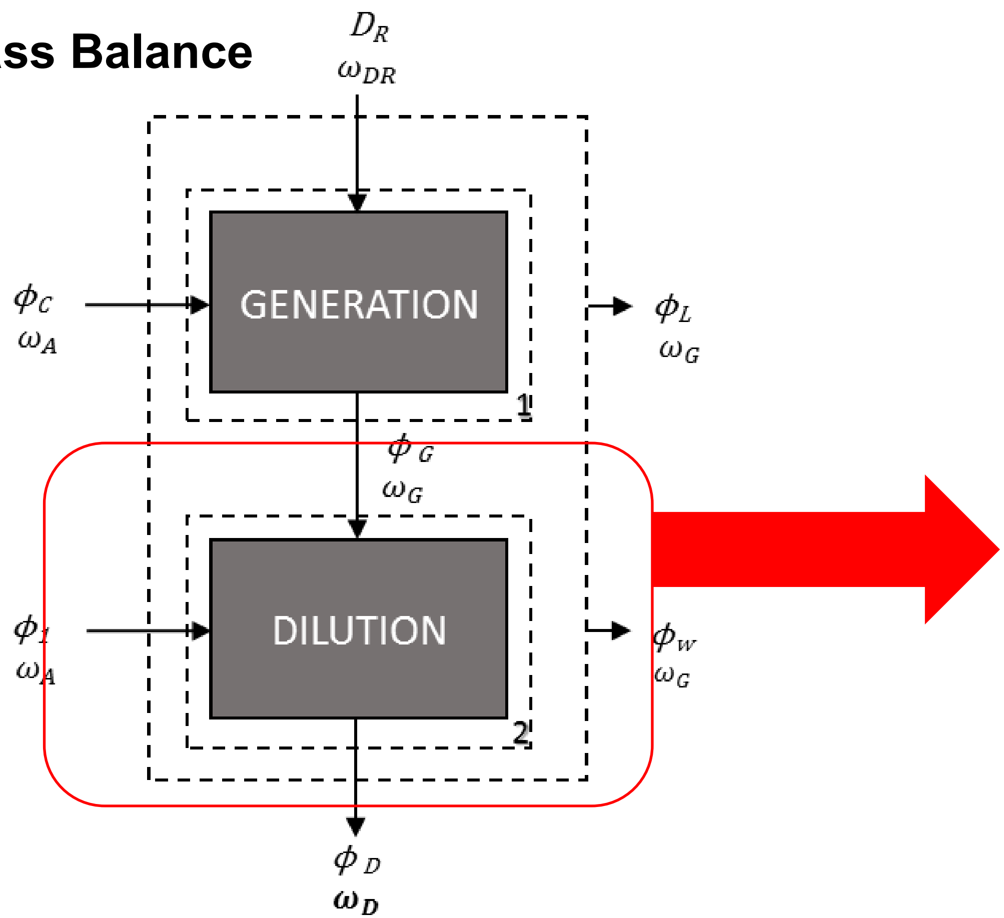


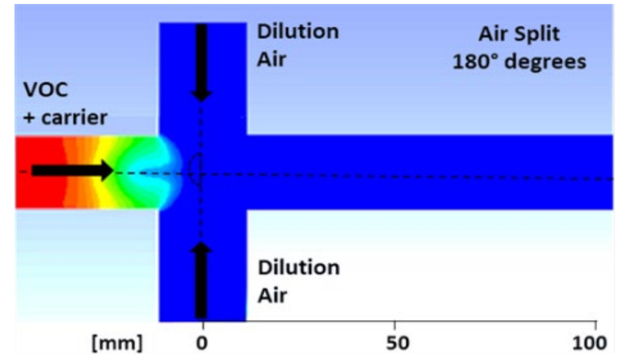


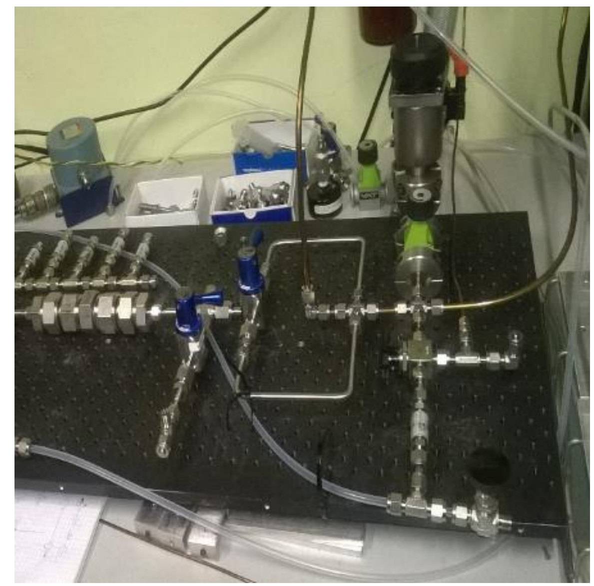
Lecuna et al, 2018

Diffusion dynamic method

Mass Balance





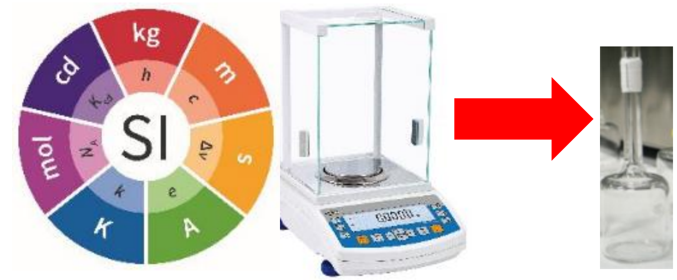


Sassi et al, 2015

Diffusion based - **Primary device**

Gravimetric Method

Primary = Directly traceable to SI (kg)



- ✓ **Average Diffusion rate**

$$D_{R,average} = \omega_{VOC}\left(\frac{\Delta m + \Delta m_B}{\Delta t}\right)$$

Mass evaporated (corrected for buoyancy) over a period of time

- ✓ **Actual Pressure Correction**

$$D_{\mathrm{R,actual}} = D_{\mathrm{R,average}} \frac{\ln\left(1 - \frac{p_{\mathrm{VOC}}}{p_{\mathrm{actual}}}\right)}{\ln\left(1 - \frac{p_{\mathrm{VOC}}}{p_{\mathrm{mean}}}\right)}$$

Corrected to account for pressure variations

Sassi et al, 2011

Diffusion rate Uncertainty

Propagation of uncertainty GUM
JCGM 100:2008 (E) by BIPM

X	[X]	x2	u(x)	u%(x)	SI [%]
Δm	g	0.01	3.81E-04	3.8%	100.0%
Δt	days	7	255	0.0%	0.0%
p_{mean}	Pa	98000	58	0.1%	0.0%
p_{actual}	Pa	101325	58	0.1%	0.0%
p_{VOC}	Pa	32154	643	3.0%	0.0%
ω_{VOC}	$g.g^{-1}$	1.0	0.0	0.1%	0.0%
dp_{actual}	Pa	0	50	0.0%	0.0%
dT_{actual}	K	0	0.02	0.0%	0.0%
D_R	$\mu g.min^{-1}$	0.96	0.036	3.8%	(k = 1)

$$u(\chi_{VOC}) = U(u(D_R), u(\phi_{dilution}))$$

Contribution to u(x)

$$Cx_i = \left(\frac{df}{dx_i}\right)^2 u^2(x_i)$$

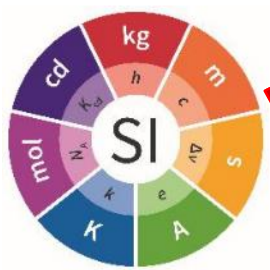
Significance Index (SI)

$$SI_i = \frac{Cx_i}{Max\ Cx_i}$$

Diffusion based - **Working standard**

Portable generation

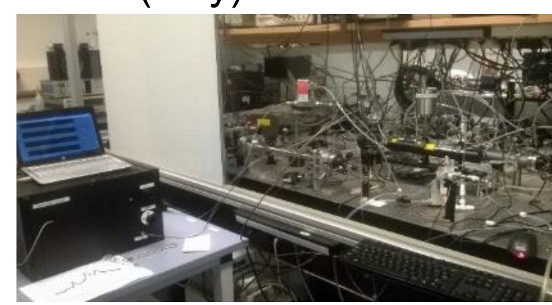
Working standard = Traceability to SI trough a primary standard



PRIMARY or TRANSFER STANDARD

WORKING STANDARD

Transportable device in INRIM (Italy)

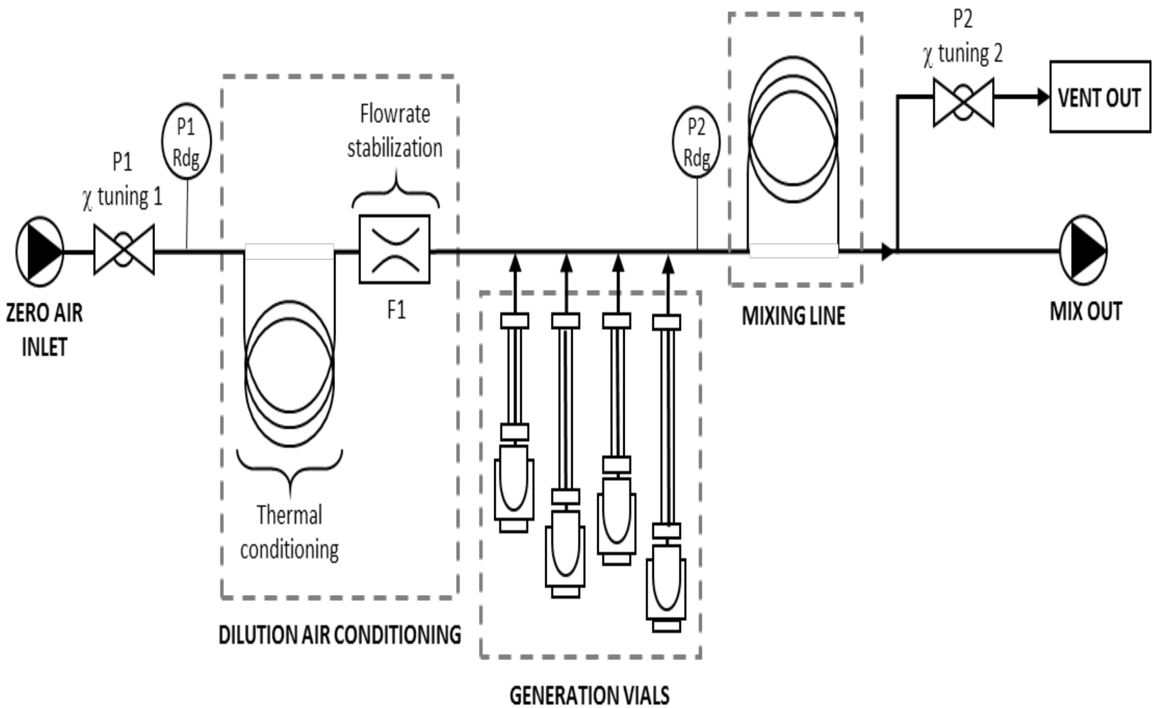


Transportable device in VSL (Netherlands), 2017

Diffusion based - **Working standard**

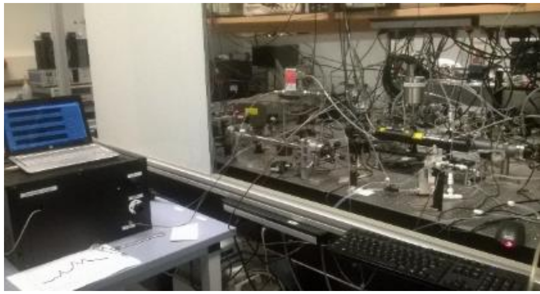
Portable generation

Working standard = Traceability to SI trough a primary standard



Demichelis et al, 2018

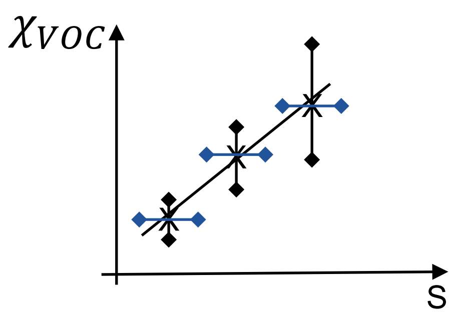
Transportable device in INRIM (Italy)



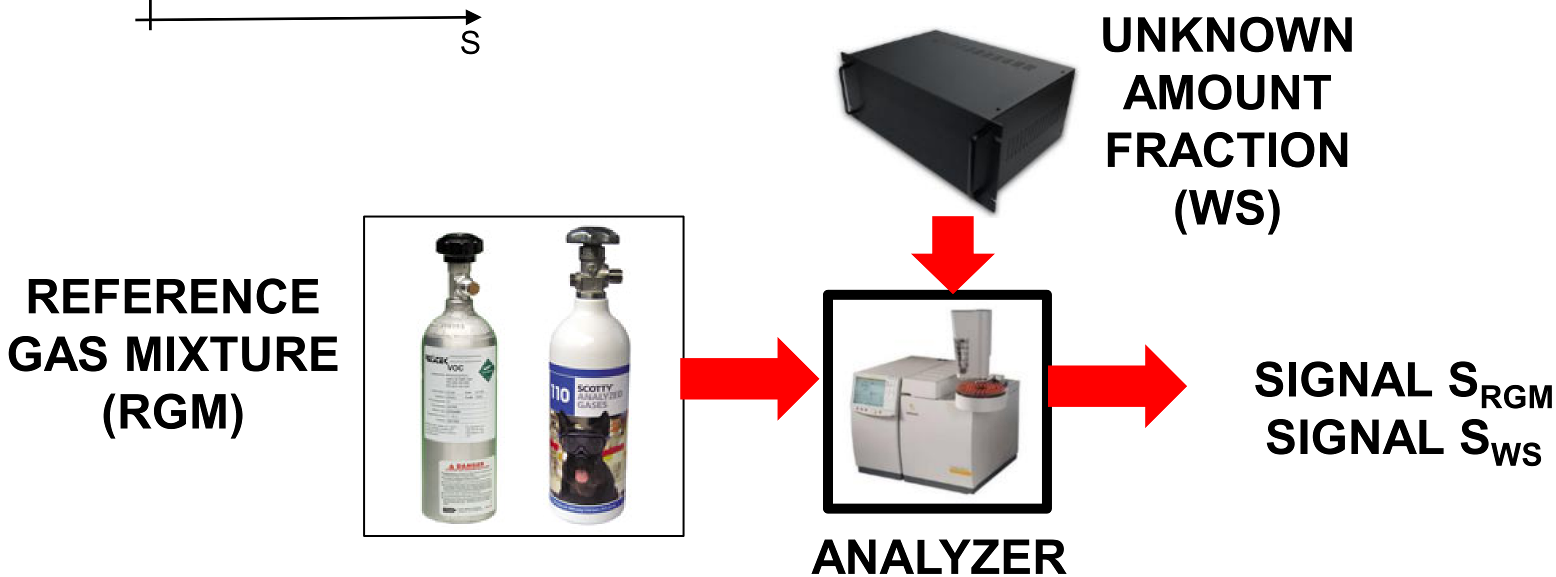
Transportable device in VSL (Netherlands), 2017

Working standard Calibration

Calibration curve of working standard, *f*

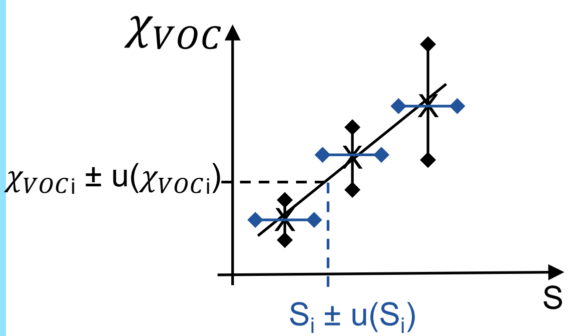


$$\chi_{VOC} = f(T, P, \phi_{dilution,} S)$$



Working standard calibration

Calibration curve of working standard, *f*



$$\chi_{VOC} = f(S, \beta, T, P, \phi_{dilution,})$$

Regression

Signal reading during calibration procedure

Influence parameters of diffusion rate

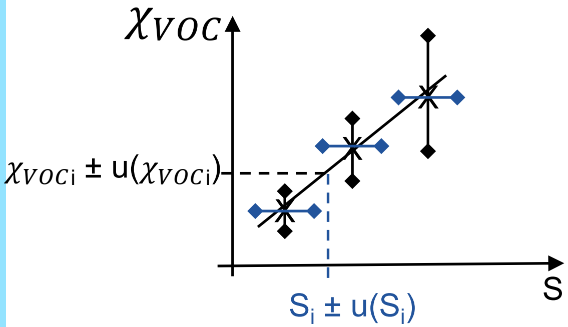
Regression: Ordinary, Weighted, Weighted total depending on system
Uncertainty of regression: Algebraic or numerical (Montecarlo) approaches

NMI reference software for regression:
CCC Software (INRIM) (Lecuna et al 2020)
XGENLINE/ XLGENLINE (NPL)

Amount fraction Uncertainty

Calibration curve of working standard, *f*

Regression



$$\chi_{VOC} = f(T, P, \phi_{dilution}, S)$$

Signal reading during calibration procedure

Influence parameters of diffusion rate

Uncertainty of the Calibration curve of working standard, *f*

$$U\,\chi_{VOC_{ws}}(T, P, \phi_{dilution}) = U(u(RGM), u(S), u(\beta_{regression}))$$

Metrology for Climate Relevant VOCs

maitane.iturrate@metas.ch
maricarmen.lecuna@polito.it

For more information, visit

www.metclimvoc.eu

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States