Atmos'fair 2024

Development and validation of an on-line formaldehyde analyser for long-term air monitoring

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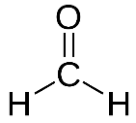
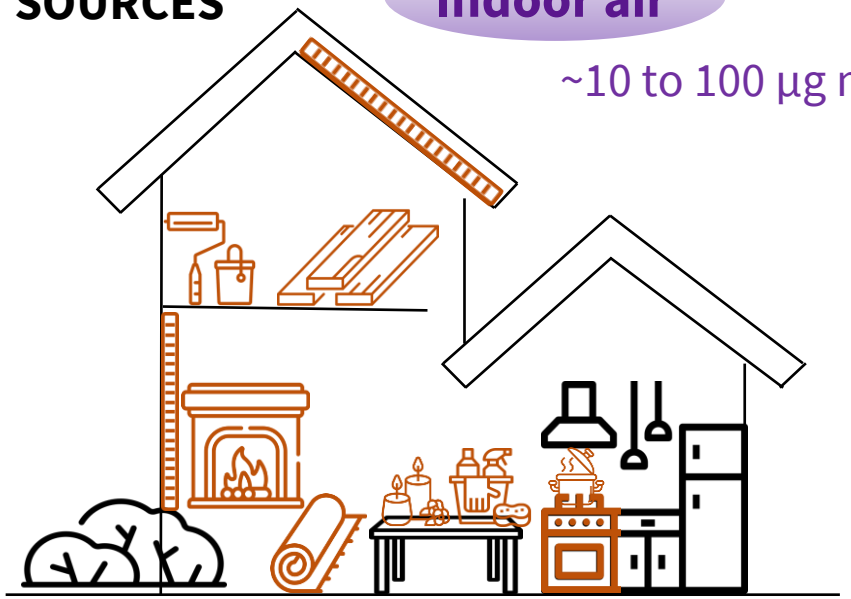
Formaldehyde sources

FORMALDEHYDE	
Structure	
M (g mol^{-1})	30.03
Bp (°C)	-21°C
Henry Law's constant (atm^{-1})	2.5 10^3
Odour threshold (µg m^{-3})	50–500

SOURCES

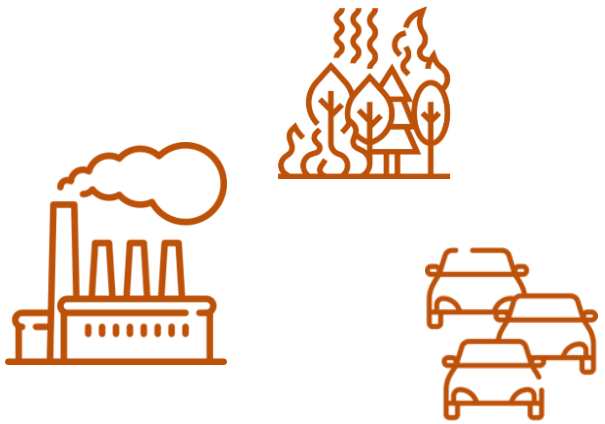
Indoor air

~10 to 100 µg m^{-3}



Outdoor air

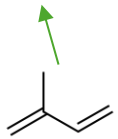
~ <1 to 10 µg m^{-3}



In-situ formation:

VOCs (alkanes or alkenes) oxidation by radicals

CH_4

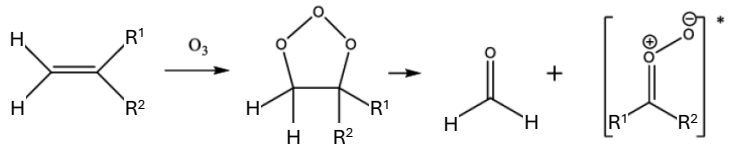


Methane, isoprene, most abundant hydrocarbon emission into the atmosphere

$OH\cdot$ and $NO_3\cdot$

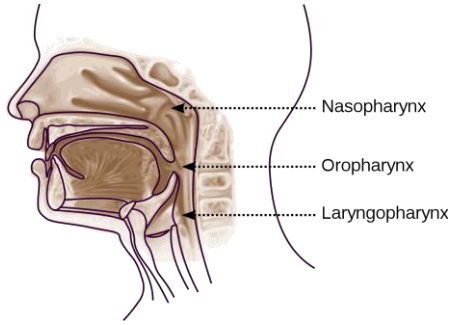
ex: terpenes used as fragrance in consumer products

alkene ozonation



Salthammer, T., *Building and Environment*, **2019**

Formaldehyde health effect and legislation



Nasopharyngeal cancer

HEALTH EFFECT

children (<3 years) asthma

olfactive and ocular symptoms

nasal irritation

short-term respiratory and ocular irritation, nausea, headache etc.

30 **60** **100** **370** **610** **740** **2500** **37 000** **µg.m⁻³**

EXPOSURE LIMITS (France/EU)

chronic exposure

30 min /day

General public

professional exposure 8 hours /day

professional exposure 15 min /day

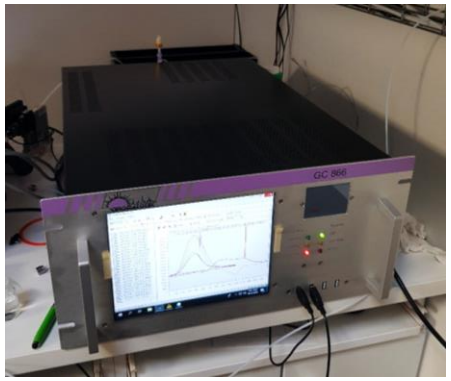
Workers in :

- chemical industries
- furniture/textile/plastic industries
- funeral, veterinary, hospital (anathomopathology), etc.

World Health Organization, **2010**

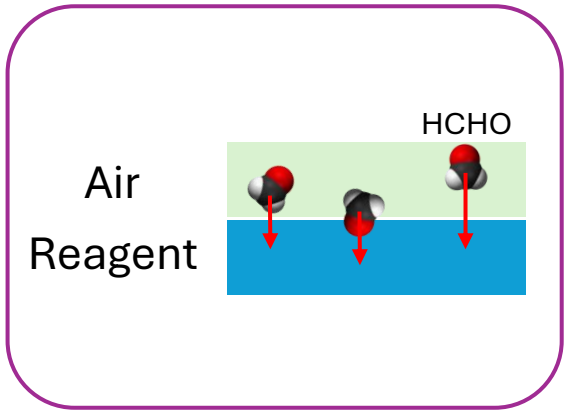
Analytical technique		Detection range (µg m^{-3})	LOD (µg m^{-3})	Temporal resolution	Weight (kg)	Price (k€)
Optical spectroscopy (IR/UV)	FTIR	0 – 12 300	1.2	< 1 min	20	≈ 55
	CRDS	0 – 37 000	**0.2**	< 0.03 – 5 min	21	≈ 70 – 80
Chemical method coupled to spectroscopy	Hantzsch fluorimetry	**0 – 1230**	1.2	1 – 120 s	6.5	≈ 20
		0 – 3690	**0.2**	90 s	20	≈ 35
Separation techniques	off-line DNPH HPLC-UV ISO 16000-3	0 – 15 000	0.6	**hours/days**	> 40 kg	≈ 70
Mass spectrometry	SIFT-MS	0 – 5000	0.5 – 9	**<2 s**	**220**	**≈ 300**
Electrochemistry	sensors	**0 – 2 500 000**	**6 – 12**	< 30 s	**2 – 3**	**≈ 6**

Principle of the on-line formaldehyde analyser: airmoF

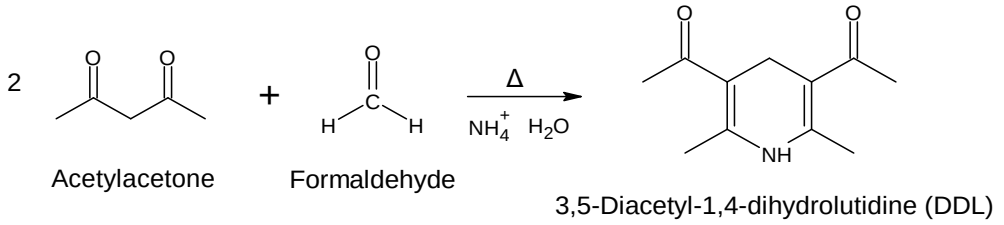


- Sampling by transfer of formaldehyde from the air to the liquid reagent
- Derivation reaction forming 3,5-diacetyl-1,4-dihydrolutidine (DDL)
- DDL fluorescence detection

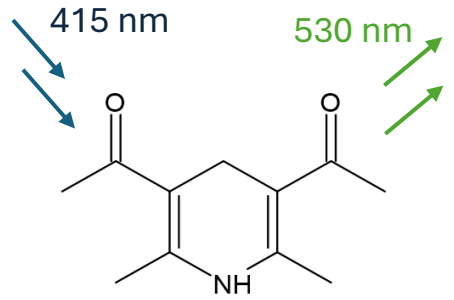
1. Uptake



2. Reaction



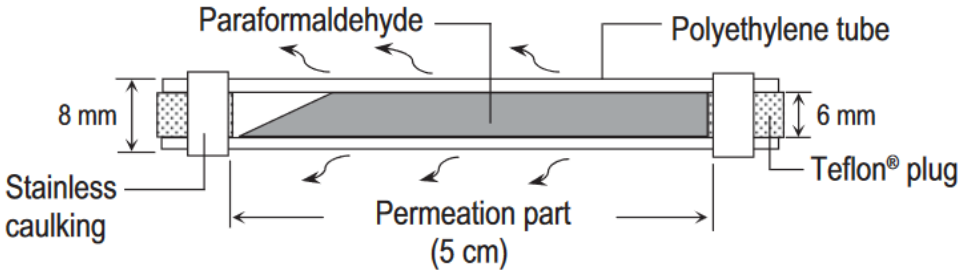
3. Detection

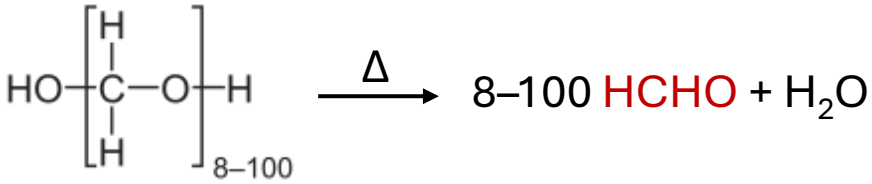


- Formaldehyde-specific
- On-line

Formaldehyde gas standard: permeation tube

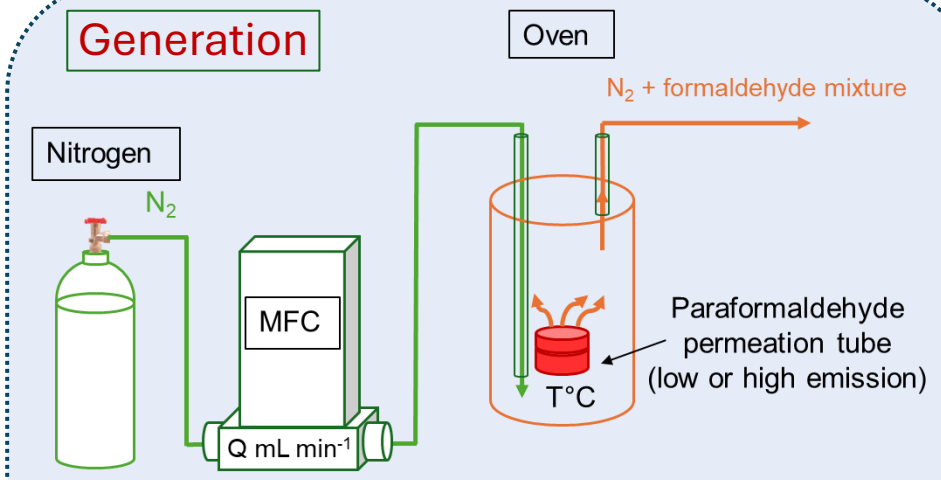
- Mechanisms: paraformaldehyde depolymerisation and permeation through membrane





Formaldehyde gas standard: permeation tube

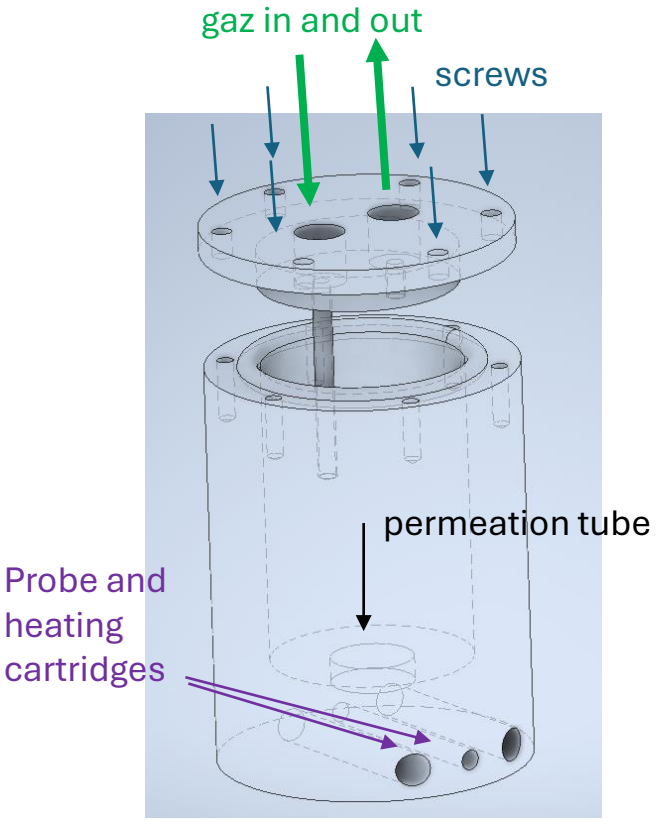
Generation

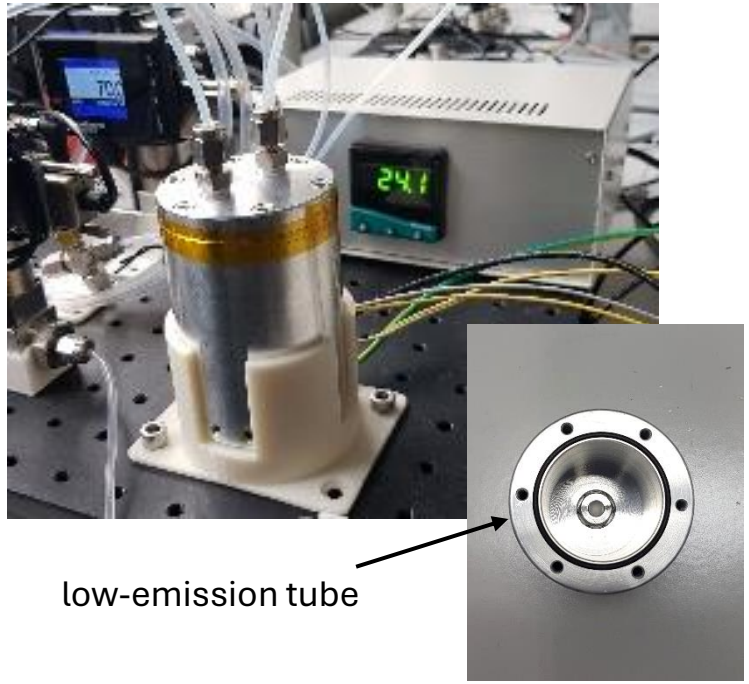


Oven temperature: 35 → 70 °C
Flow rate (Q): 30 → 100 mL/min

Certification method

DNPH/HPLC-UV (ISO 16000-3)
no mass-certification (water weight loss error)

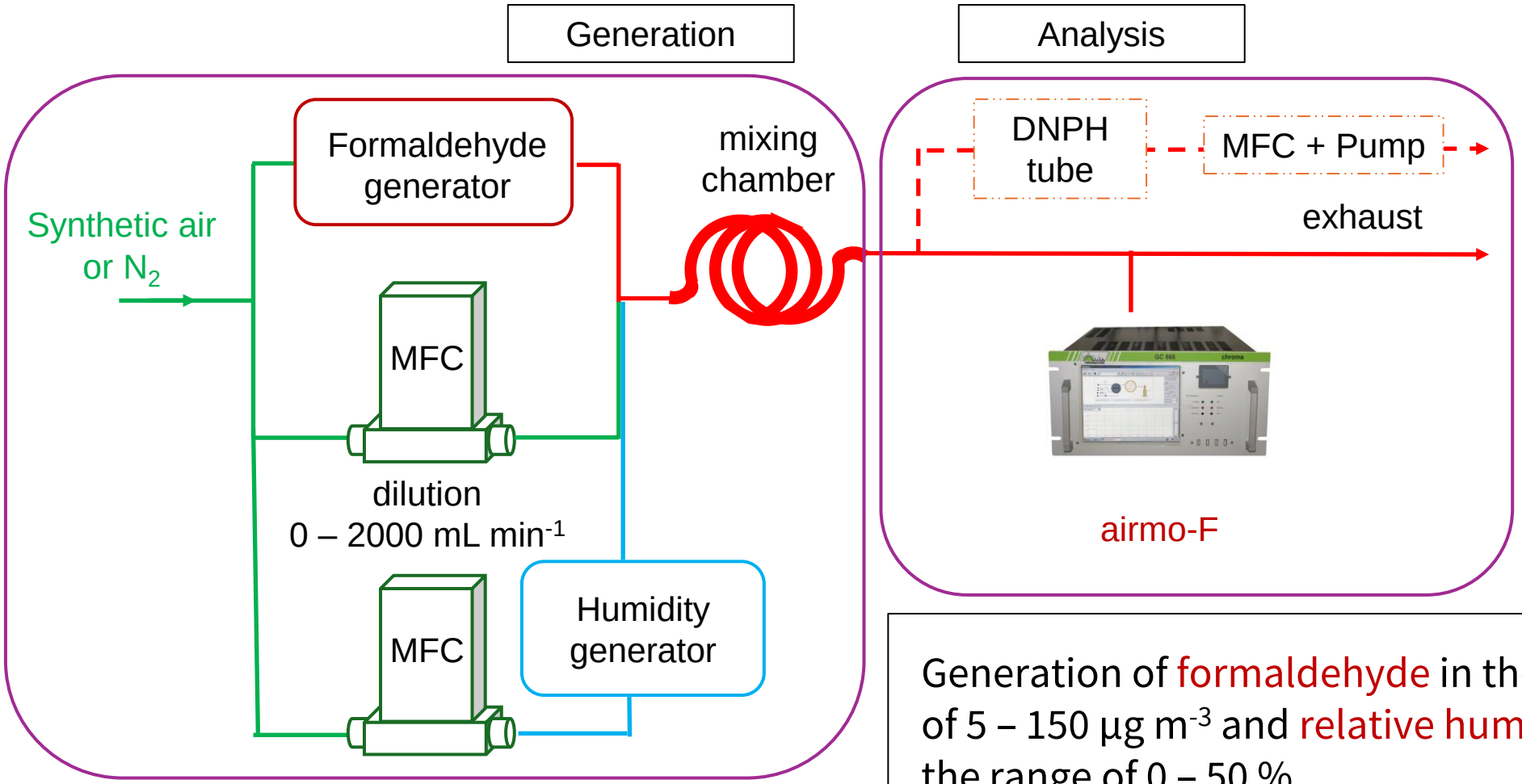




→ **8.3 to 464 µg m^{-3}**

Grandjean A., *Microchemical Journal*, **2024**

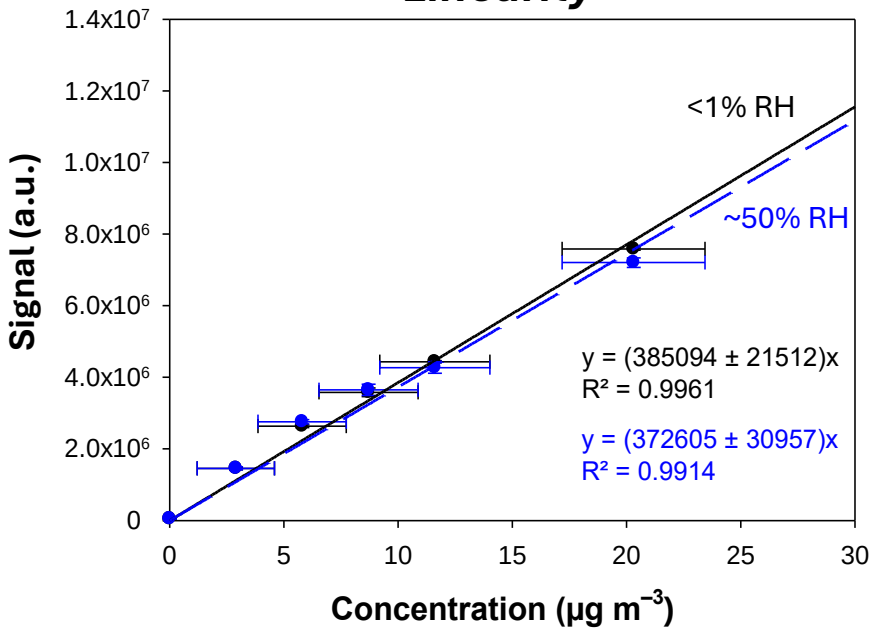
Laboratory experiments set-up



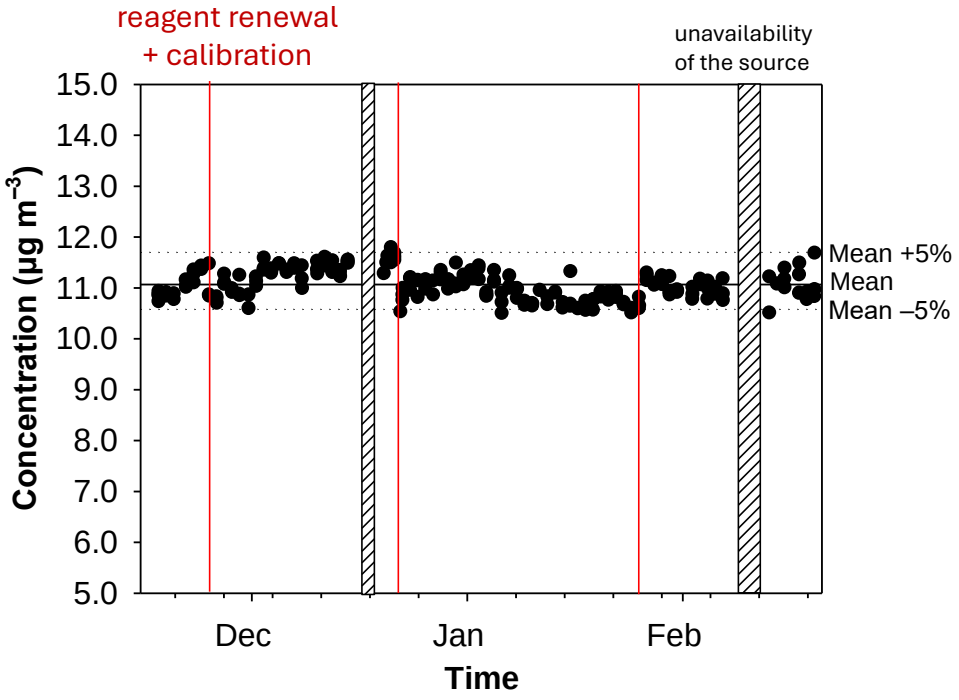
Generation of formaldehyde in the range of 5 – 150 µg m^{-3} and relative humidity in the range of 0 – 50 %

Method validation

Linearity

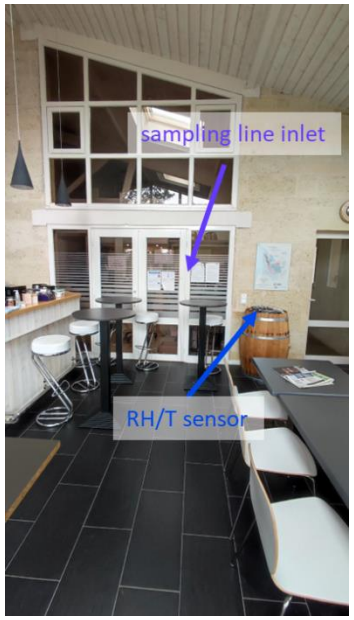


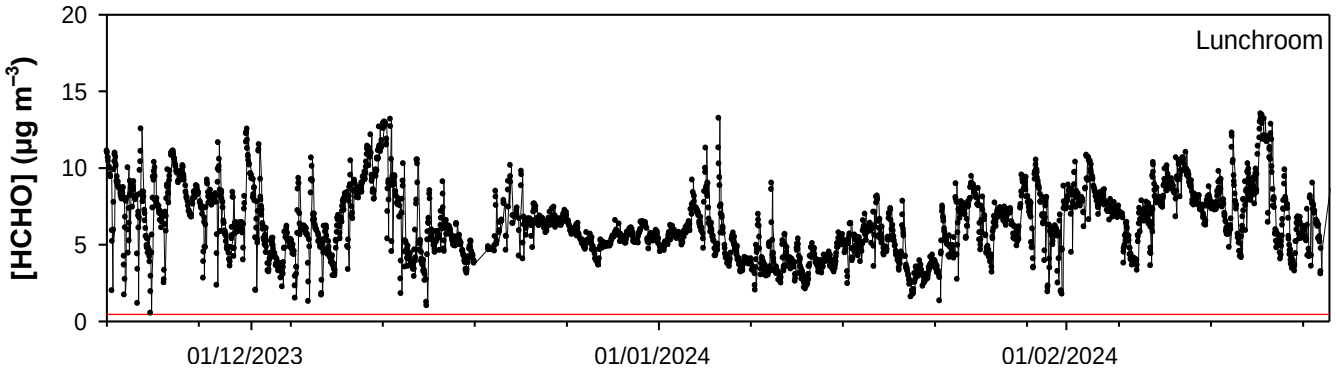
Reproducibility



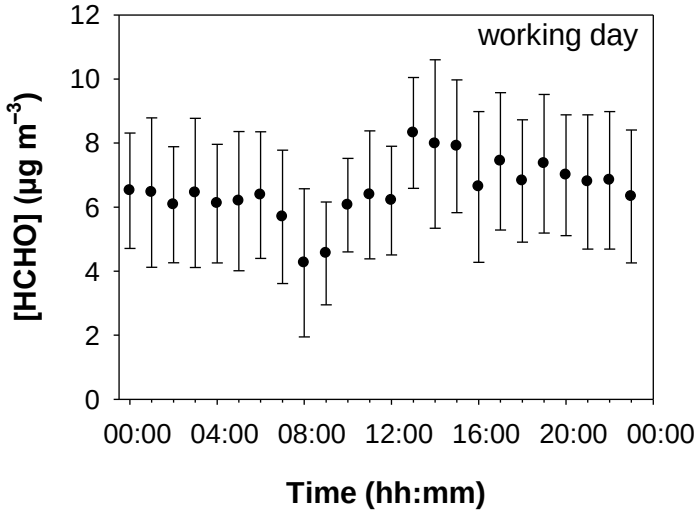
- Linearity: $R^2 > 0.99$ in humid and dry conditions
- Repeatability at 11 µg m^{-3} ($RSD_{n=10}$): 1.9%
- Reproducibility at 11 µg m^{-3} ($RSD_{3\ months}$): 2.6 %
- $LOD_{US\ EPA;\ <1\%RH}$ = 0.19 µg m^{-3}

Field application – indoor, winter

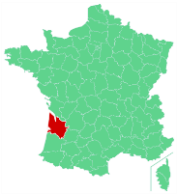


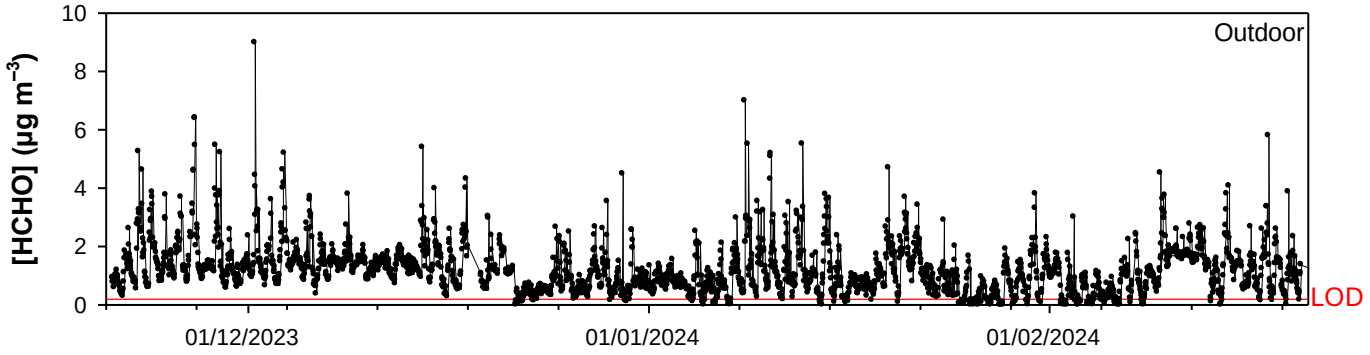


- Stable concentration during vacation
- 8AM: manual ventilation → concentration decrease
- 1PM: lunchtime, human activity → concentration increase

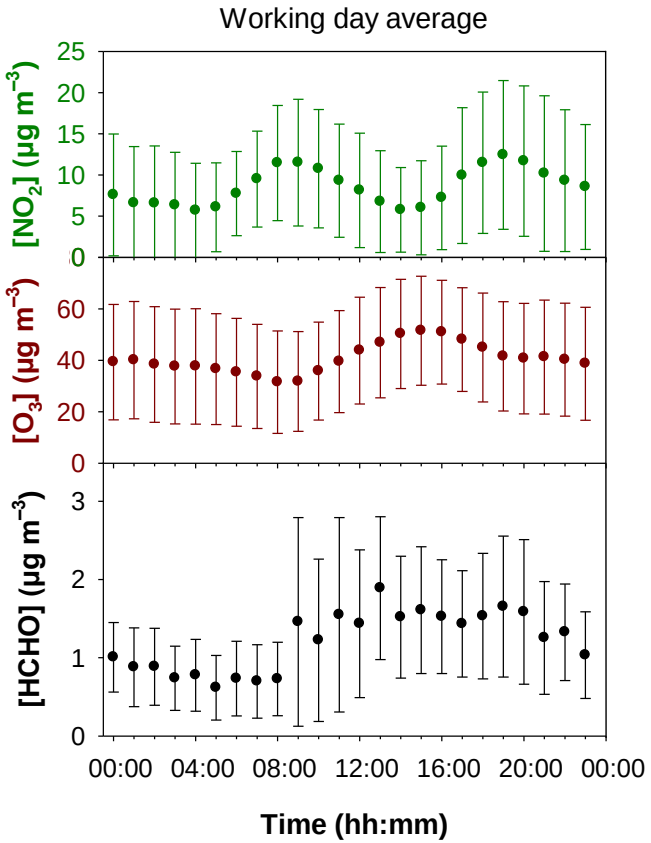


Field application – rural, winter

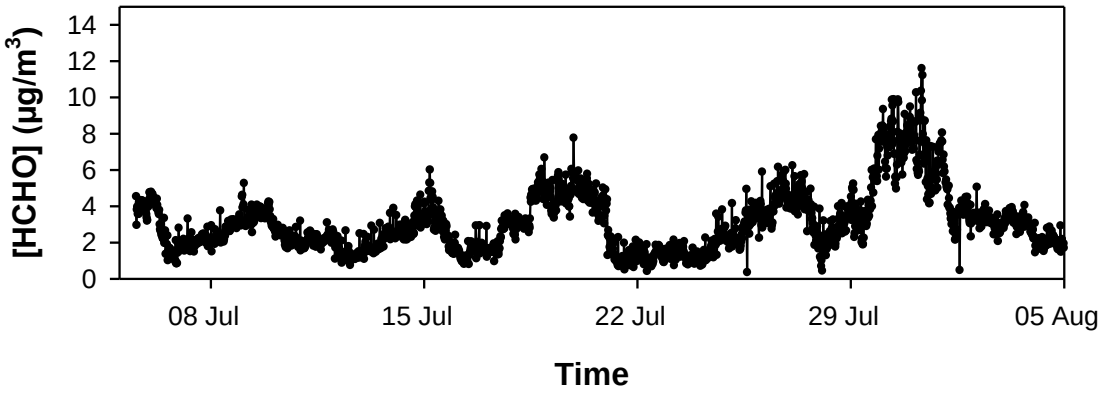


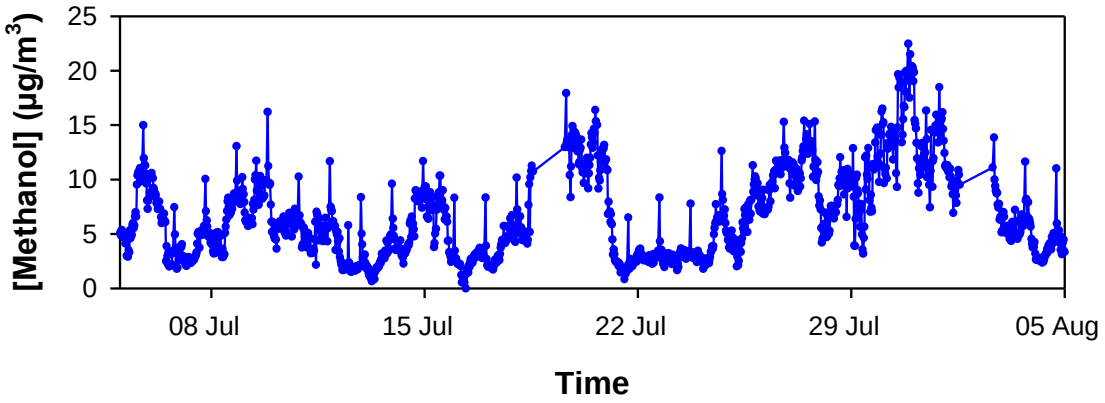


- **3-month** outdoor air **measurement**: rural area near a highway
- acquisition frequency enough to observe **daily variation**
- Diurnal variation correlated with ozone concentration → in-situ formation
- Disturbed trend at commute hours→ primary emissions + in-situ formation



Field application – remote, summer



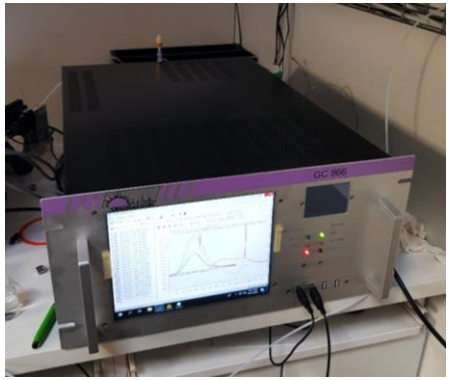


- Most measurements mostly between 1 and 5 µg m^{-3}
- no diurnal trend observed
- correlation with methanol

Conclusion

- Sensitivity ✓ LOD <µg m^{-3} → 0.19 µg m^{-3}, suitable for outdoor air levels
- Selectivity ✓ formaldehyde-specific, no water interference
- Repeatability ✓ < 2% at 11 µg m–3 (RSDn=10)
- Reproducibility ✓ reproducible results over 3–4 months
- Low maintenance ✓ monthly reagent renewal
- Robustness ✓
- Fully automatic ✓ peak integration
- Field applicability ✓ rural, remote, indoor
- Portable version : microF with LOD at 1µg/m3 in automatic
  - →adapted for indoor air study

airmoF



microF

Thank you for your attention

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jean-philippe.amiet@chromatotec.com