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Development and characterization of a toluene permeation tube in a dynamic gas generation system for calibration of an online gas chromatography at ppb level

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INTRODUCTION

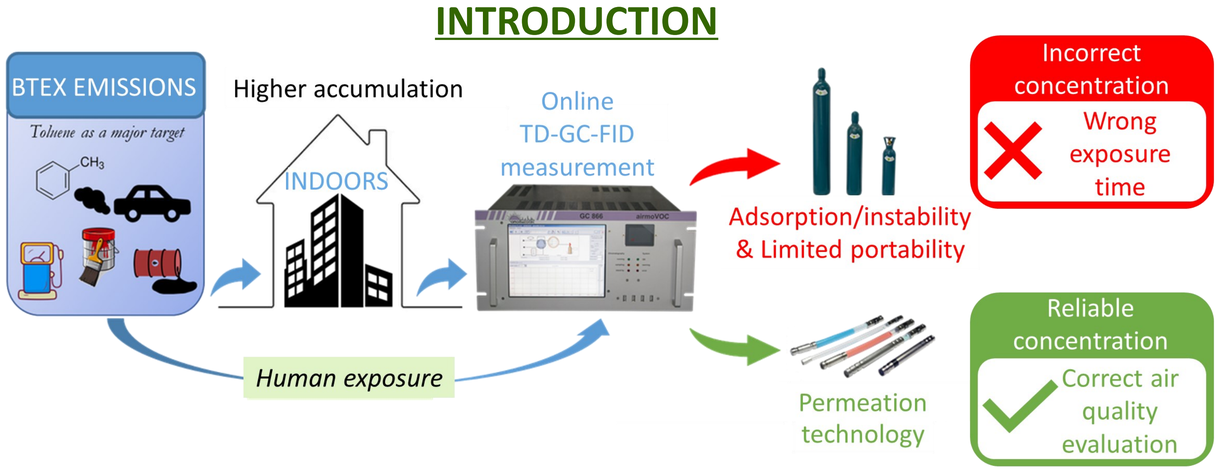

Figure 1: *Improving indoor BTEX exposure assessment through reliable quantification using permeation technology and online TD-GC-FID.*

- **BTEX (benzene, toluene, ethylbenzene and xylenes)** contribute to ozone and secondary organic aerosol formation [1]. **Indoor toluene** concentration (few to tens of ppb) often exceeds **outdoor** levels (sub to few of ppb) [2]. **Gaseous pressurized cylinders** suffer from adsorption, instability, and limited portability, while **permeation technology** (dynamic standard) can be efficient for in-situ calibration at trace levels (Figure 1).
- Advantages of using **real-time GC-based methods** for analysis of emissions from permeation devices *outweigh* those of the **weighing method** (Figure 2).

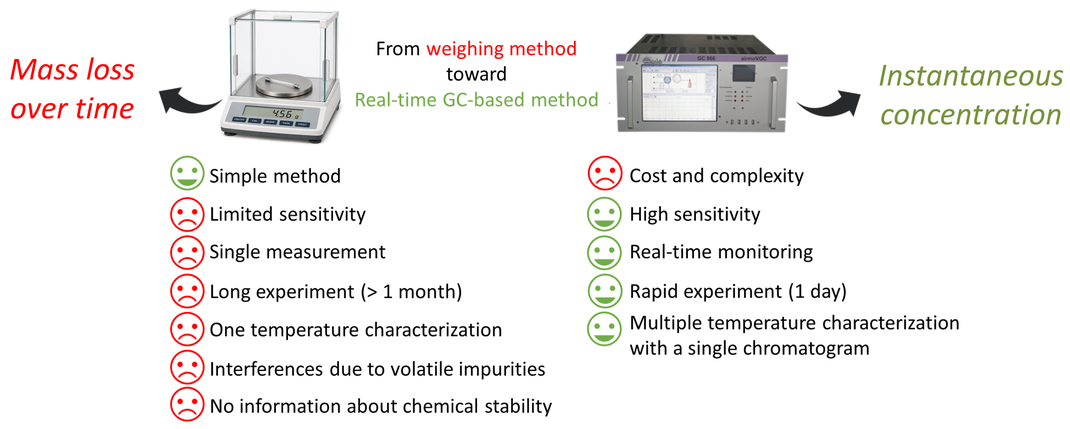

Figure 2: *Advantages and drawbacks of weighing versus real-time GC methods for permeation characterization.*

- Trace quantification using analytical tools like Thermodesorption-Gas Chromatography-Flame Ionization Detector (TD-GC-FID) coupled to a gas generator depends on calibration quality [3]. ***A toluene permeation tube was designed together with a gas generator that contains it and produces toluene at low-ppb concentrations using suction approach.***

METHODOLOGY

- **Toluene permeation tube**

TOLUENE
PTFE permeation tube
(6 mm OD, 4 mm ID)

- **Gas generation system**

Temperature of the permeation tube is regulated at ±0.1°C. All the flow rates of dry zero-air are controlled with permeation oven with **Mass-Flow Controllers (MFCs).** MFC3 is used to **suck a portion of the flow of MFC1** using a pump.
The mixture is mixed using a mixing chamber and delivered to an **analyzer (online TD-GC-FID)** for analysis (Figure 3).

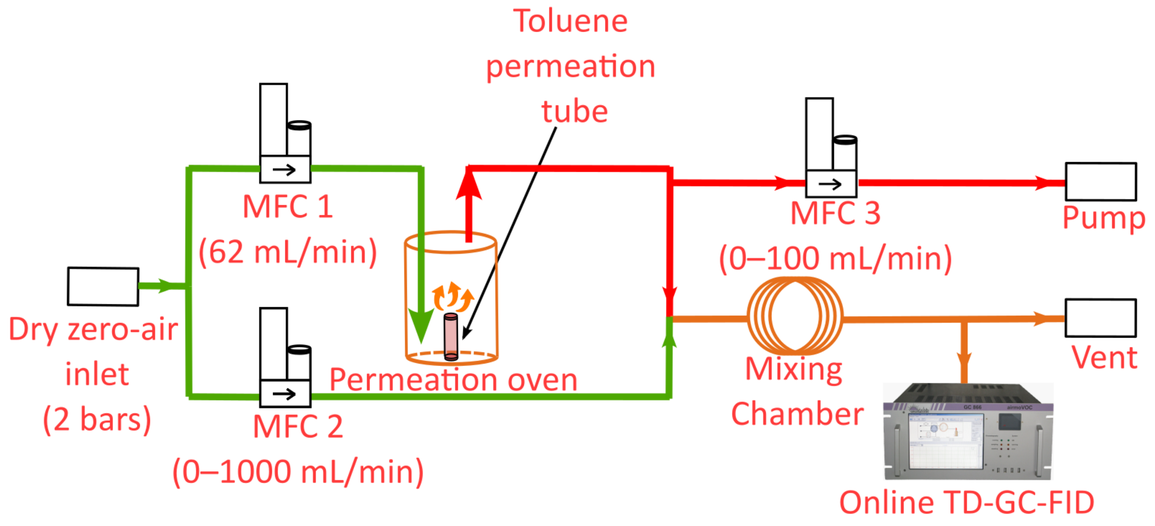

Figure 3: *Generation setup of toluene emissions coupled to an online TD-GC-FID analyzer for chromatographic analysis.*

- **Online TD-GC-FID**

Principle (Figure 4):
→ *preconcentration* (adsorbent trap),
→ *separation* (chromatographic column),
→ and *detection* (FID).

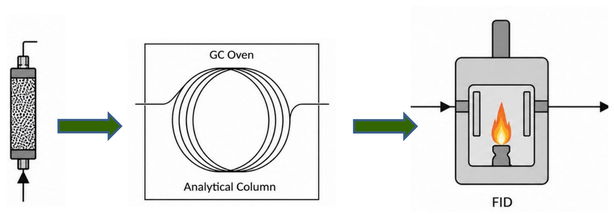

Figure 4: *Setup of online TD-GC-FID.*

RESULTS AND DISCUSSION

- **Permeation stability of toluene permeation tube**

→ Continuous measurement of the concentration for ***T°-range = 40–70°C*** after 24-hr equilibration period in the permeation oven (Figure 5).

→ **Evaluation of the emission rate ER(T) at 40°C** based on **Equation (1)** after attaining stability.

ER(T = 40°C) = 90.64 ± 3.69 ng/min (RSD = 0.94%)

$$Equation\ (1): C(toluene) = \frac{ER(T)}{F} \times \frac{22.4}{M} \times \frac{T}{273}$$

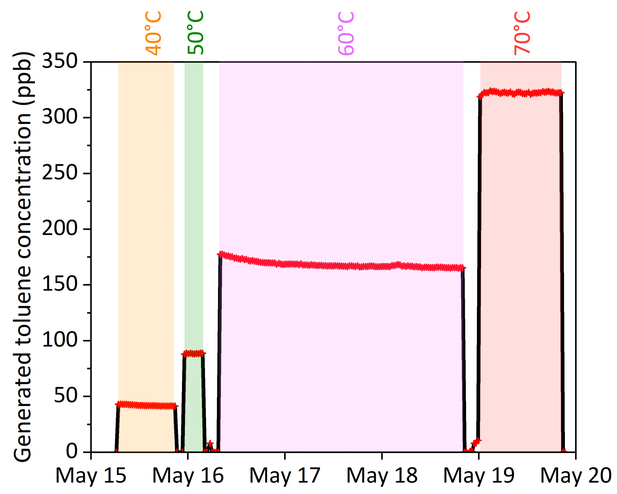

Figure 5: *Generated concentrations of toluene (in ppb) at 4 different temperatures (40°, 50°C, 60°C, and 70°C) for consecutive six days (total flow = 624.4 ± 12.66 mL/min).*

- **Concentration range of emitted toluene**

→ Concentration can be modified by **varying T, MFC1 & MFC2 flow rates**, and **sucking MFC3 flow rate.**

→ **4.2 ppb** (minimum at 40°C)
4.1 ppm (maximum at 70°C)

☺ Advantage of using the extra MFC3 (up to 84% portion of MFC1 flow is sucked out): obtaining a concentration down to **4.2 ppb**.

- **Temperature dependence of ER(T)**

→ Two models to explain the temperature dependence (Figure 6):

1. ***Arrhenius-type*** model [4]

$$ln\ ER(T) = -\frac{E_a}{R}.\frac{1}{T} + ln\ A$$

2. ***Antoine-Fickian*** model [5]

$$ln\ ER(T) = A' + \frac{B}{T}$$

$$-\frac{E_a}{R} = -7270;\ ln\ A = 27.92$$
$$B = -7270;\ A' = 27.92$$

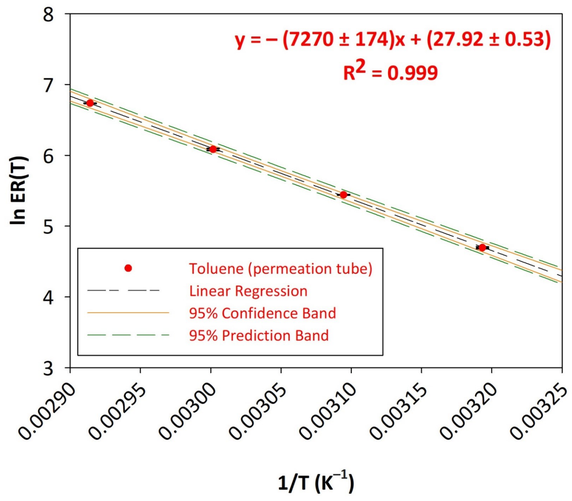

Figure 6: *Temperature dependence of emission rates of toluene at 4 different temperatures (40°, 50°C, 60°C, and 70°C) and its linear fit. Vertical error bars correspond to the uncertainty calculated from the errors of the three MFC flow rates.*

- **Accuracy of measurements on online TD-GC-FID**

→ Measured and generated concentrations are **linearly correlated** (**R^2 = 0.999,** Figure 7).

→ Online TD-GC- FID is ***accurate and precise*** (repeatability ***< 2% RSD at 5 ppb***).

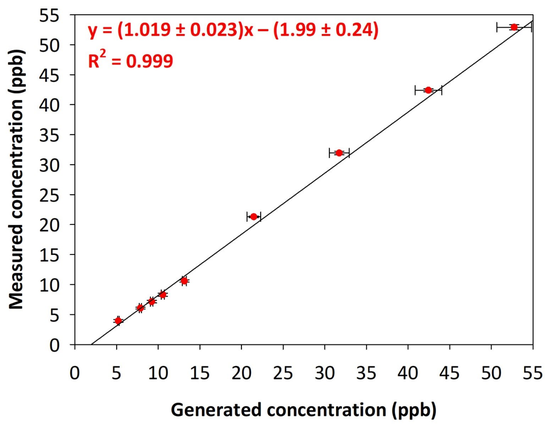

Figure 7: *Measured concentration versus generated concentration of toluene at 40°C. Vertical error bars correspond to the standard deviation of n=10 measurements in ppb.*

CONCLUSION

- Successful fabrication of toluene permeation tube and gas generation system.
- The temperature dependence was explained using two models.
- Concentrations from **ppb to ppm levels (3 orders of magnitude)** were attained by adjusting the **oven temperature**. In addition, **MFC flow rates** can also vary (dilution and sucking).
- Online TD-GC-FID has **high accuracy** in the detection of toluene generated concentration.
- Strong potential for **extension to other BTEX and other VOCs** that are not available in a pressurized cylinder.

ACKNOWLEDGEMENTS

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[1] G. Li, S. Deng, J. Li, J. Gao, Z. Lu, X. Yi, J. Liu, Air Qual. Atmos. Health 15 (2022) 1941–1952.
[2] ATSDR, Toxicological profile for toluene, U.S. Dep. Health Hum. Serv., Atlanta (2000).
[3] N. Baimatova, B. Kenessov, J.A. Koziel, L. Carlsen, M. Bektassov, O.P. Demyanenko, Talanta 154 (2016) 46–52.
[4] R. Aoyagi, T. Arakawa, K. Iitani, K. Mitsubayashi, Y. Sekine, Y. Kaifuku, Discover Applied Sciences 7 (2025) 1–11.
[5] A. Grandjean, A. Becker, C. Kustner, M. Wolf, C. Sutter, R. Severac, J.P. Amiet, D. Bazin, S. Le Calvé, Microchemical Journal 206 (2024).