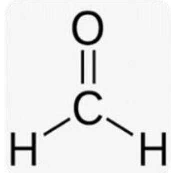
ACTRIS - CiGas side-by-side interlaboratory comparison of new and classical techniques for formaldehyde measurement

Thérèse Salameh[1], E. Stratigou[1], E. Tison[1], S. Dusanter[1], V. Gaudion[1], S. Sauvage[1], M. Jamar[1], R. Tillmann[2], F. Rohrer[2], B. Winter[2], T. Vera[3], F. Bachelier[4], V. Daele[4], A. Grandjean[5]

[1]IMT Nord Europe - France, [2]FZJ - Germany, [3]CEAM - Spain, [4]ICARE - France, [5]CHROMATOTEC - France

Introduction

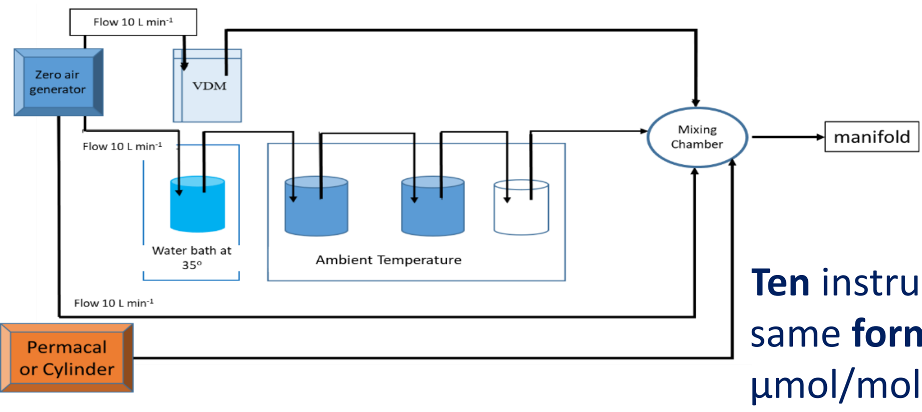
Formaldehyde

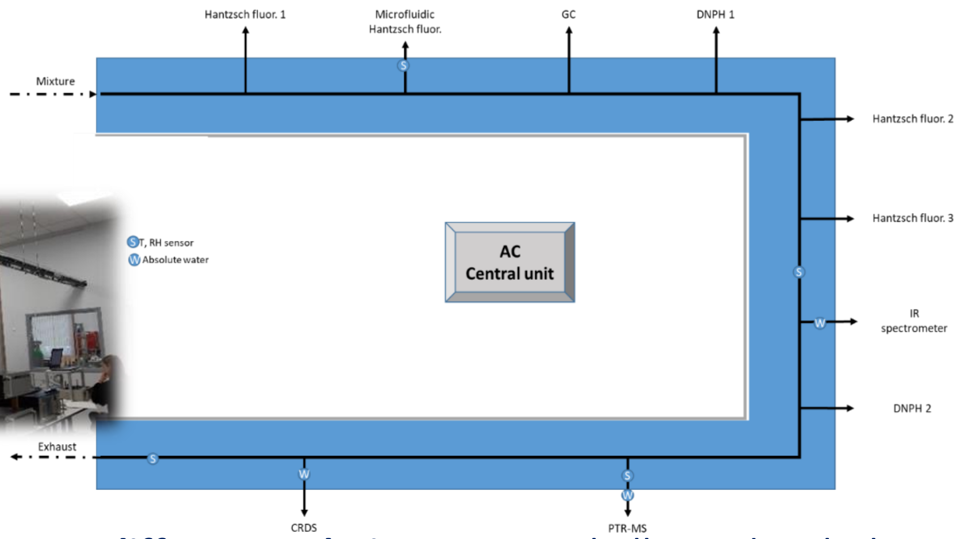


- Important hazardous air pollutant, classified as carcinogenic to humans by the International Agency for Research on Cancer (IARC)
- Emitted directly by many anthropogenic (building materials, industry) and natural sources, and formed as a secondary product from volatile organic compounds (VOCs) photo-oxidation; a significant source of radicals in the atmosphere resulting in ozone and secondary organic aerosols formation
- Routine measurements of formaldehyde in regulatory networks within Europe (EMEP) and USA (EPA Compendium Method TO 11A) rely on sampling with DNPH (2,4-Dinitrophenylhydrazine)-impregnated silica cartridges, followed by analysis with HPLC (High-performance liquid chromatography) => **need to evaluate new and classical measurement techniques at nmol/mol amount fractions**

Side-by-side interlaboratory comparison: 30/05 - 08/06 2022, CiGas IMT NE unit, Douai – France

Objectives: Evaluation of the metrological performance of measurement techniques: repeatability, limit of detection, linearity, potential drift, etc. ; Determine advantages/drawbacks of the techniques; Develop recommendations about best practices.





Ten instruments belonging to **seven different techniques** were challenged with the same **formaldehyde gas mixture generated either from a cylinder** (5.2 ± 0.26 µmol/mol) **or from a permeation system, in different conditions:** amount fractions: 2-17 nmol/mol; RH=60%; w/ & w/o O_3 (50 nmol/mol); ambient air

Preliminary results

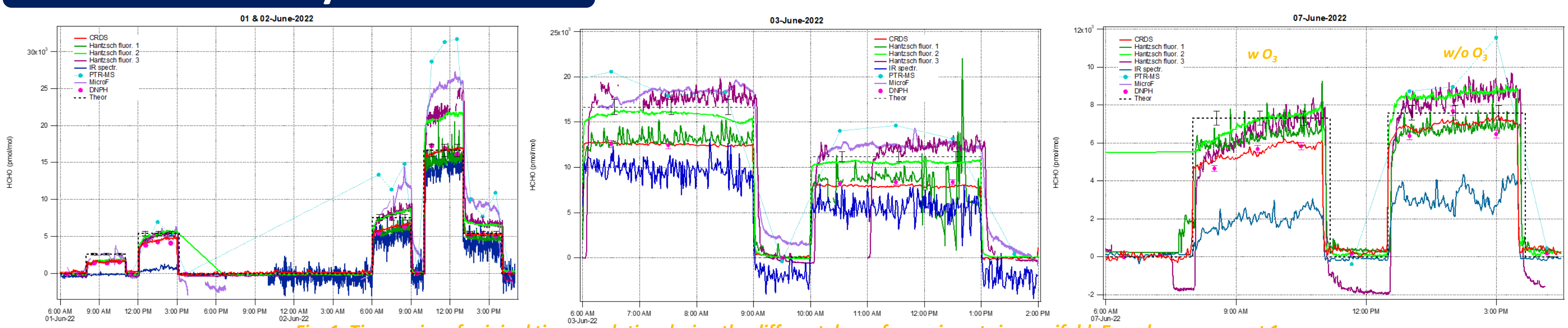


Fig. 1: Time series of original time resolution during the different days of experiments in manifold. Error bars represent 1σ.

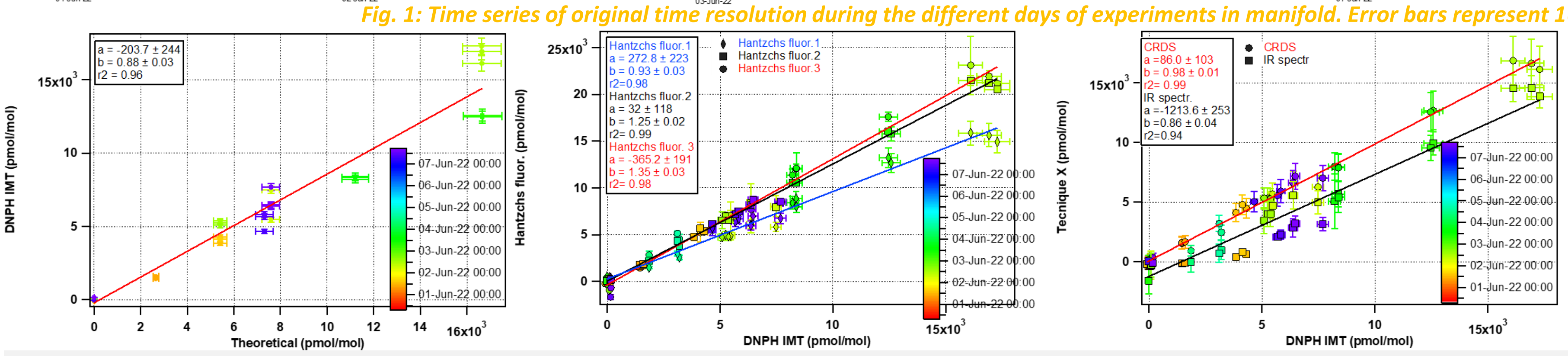


Fig. 2: Correlations of DNPH (ref. technique) with theoretical values, and correlations of techniques with ref. technique. Symbols correspond to the respective technique, color coding of symbols corresponds to the date, color coding of the regression lines correspond to each technique. Error bars represent 1σ.

DNPH, Hantzsch-fluorimetry-based instruments and CRDS -based instrument: more robust for measuring formaldehyde, time series stable regardless the generation way ; IR-spectrometry-based instrument not suitable for measuring low amount fractions; PTR-MS and microF techniques: overestimation of the HCHO amount fractions; Possible losses of 4-17% of HCHO under typical ozone conditions.

Conclusions & perspectives

Evaluation of many online and off-line techniques for formaldehyde measurements at nmol/mol levels. Preliminary analysis suggests significant promise, however, there remain some discrepancies between instruments to be addressed (impact of water vapor levels, internal calibrations especially for Hantzchs techniques, lack of a SI traceable calibration standard, etc.). QA/QC measures are crucial to provide high quality formaldehyde measurements for outdoor and indoor ambient measurements.

Acknowledgements

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For further information: https://www.metclimvoc.eu; *therese.salameh@imt-nord-europe.fr*

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