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Formaldehyde monitoring by variable pressure infrared diode laser spectroscopy

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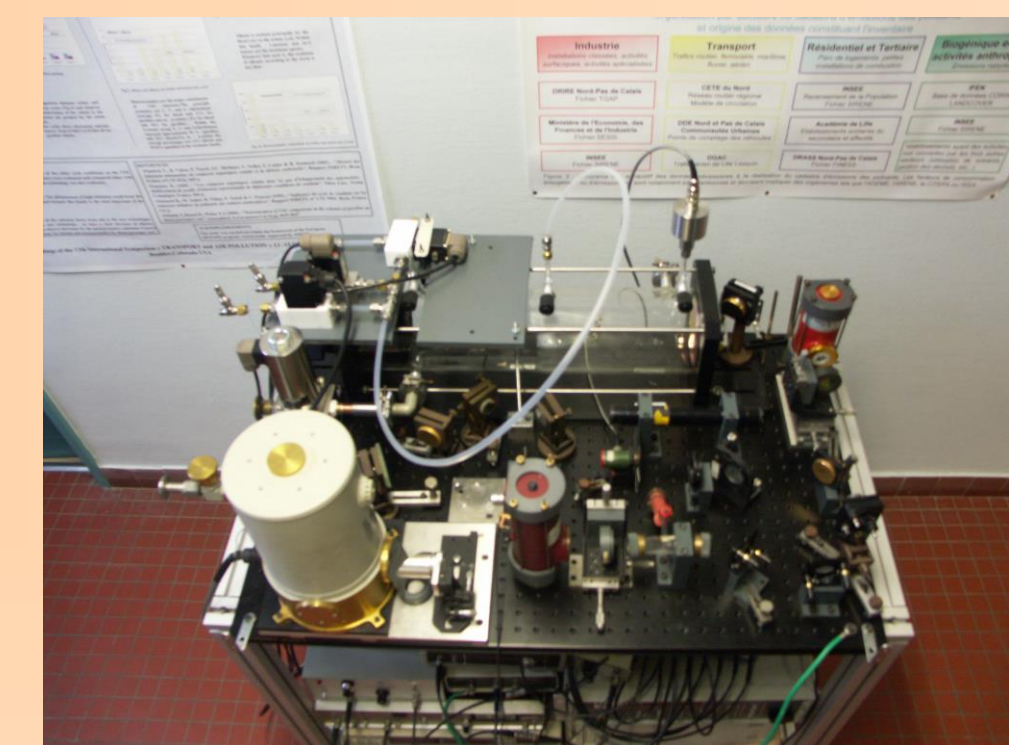
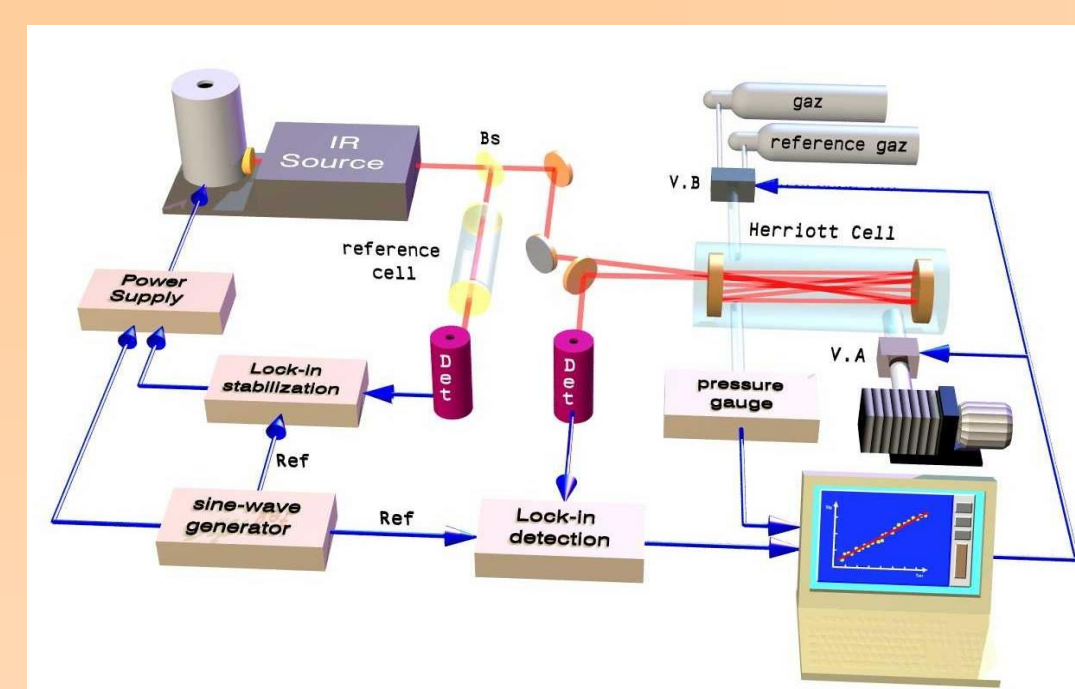
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Context and objectives

Interest in measurements of formaldehyde, as well as other carbonyl compounds, has grown recently as it is typically present around the ppbv level in outdoor urban air, and at much higher concentrations indoors, and because it is thought to be allergenic, carcinogenic, and responsible for respiratory diseases. Formaldehyde measurements are also of importance for troposphere modeling studies as it is often included in the chemical mechanisms. Because of the high spatial and temporal variability of formaldehyde concentrations, it is necessary to develop portable, real-time, selective and sensitive instruments.

The spectrometer

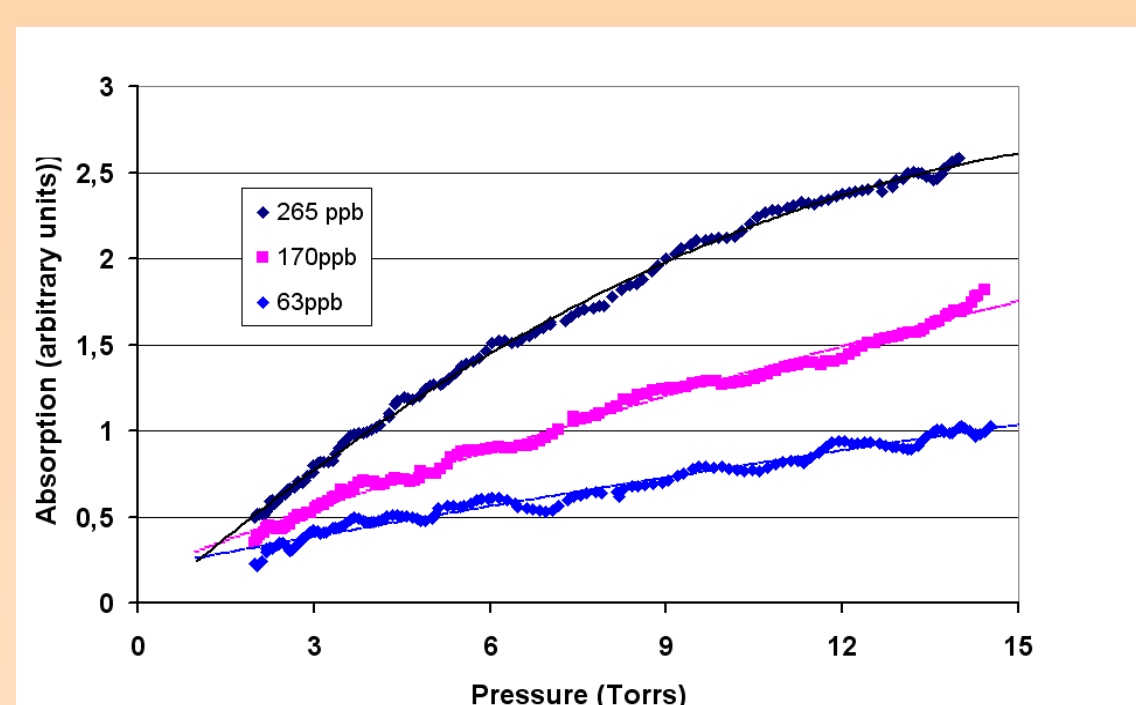


Characteristics : total weight ~ 80 kg, size (L x l x h) 100 x 60 x 100 cm, autonomy ~10 h (detectors IN_2 holding time), automated operation using LabView™ software, calibration point provided with permeation device

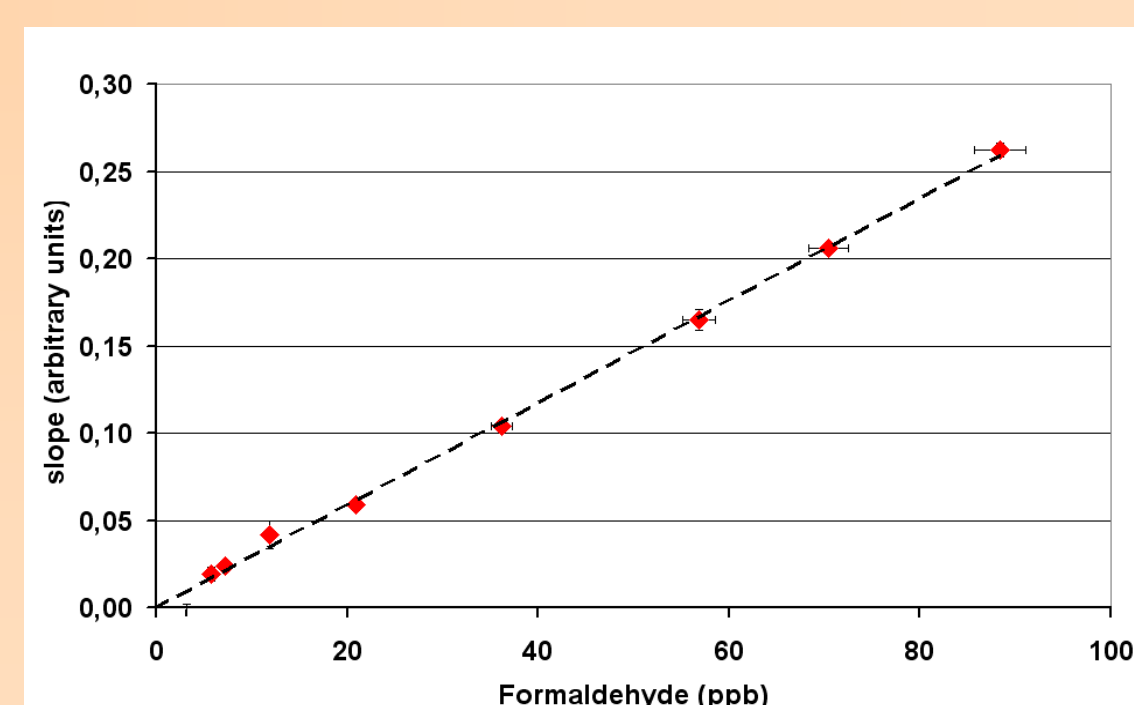
Performances : time resolution 20 s, measurement range : 1 - 1000 ppbv, detection limit : 3 ppbv in 1 acquisition

Principle of variable pressure spectroscopy

We reported in 2002 a new protocol for the determination of mixing ratio of trace gases in the atmosphere by tunable infrared diode laser spectroscopy, which we called « variable pressure spectroscopy ». Instead of scanning the emission frequency around the absorption line and comparing the full profile of the sample to the profile of a calibrated mixture at the same pressure, we lock the laser frequency on the top of the spectral line, and record simultaneously the $2f$ signal and the pressure P as the sample flows into or out of the low pressure long path (30 m) absorption cell. The rate of increase of the signal versus the pressure is proportional to the volume fraction of the absorber. One calibration point is sufficient to determine the absolute volume fraction.



Absorption vs. pressure (H_2CO , 2830 cm^{-1})

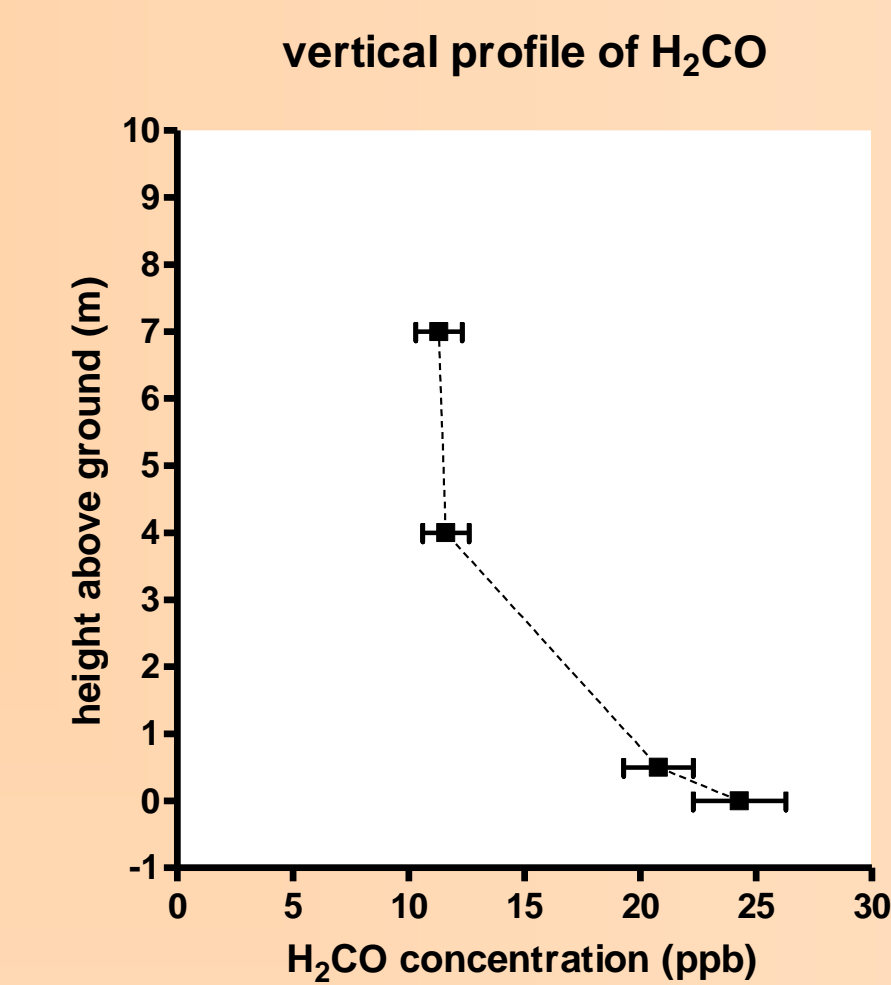


Calibration curve

Outdoor formaldehyde measurements

Sampling sites : parking lot outside laboratory, Villeneuve d'Ascq

Methodology : direct measurements from outside air with a teflon sampling line



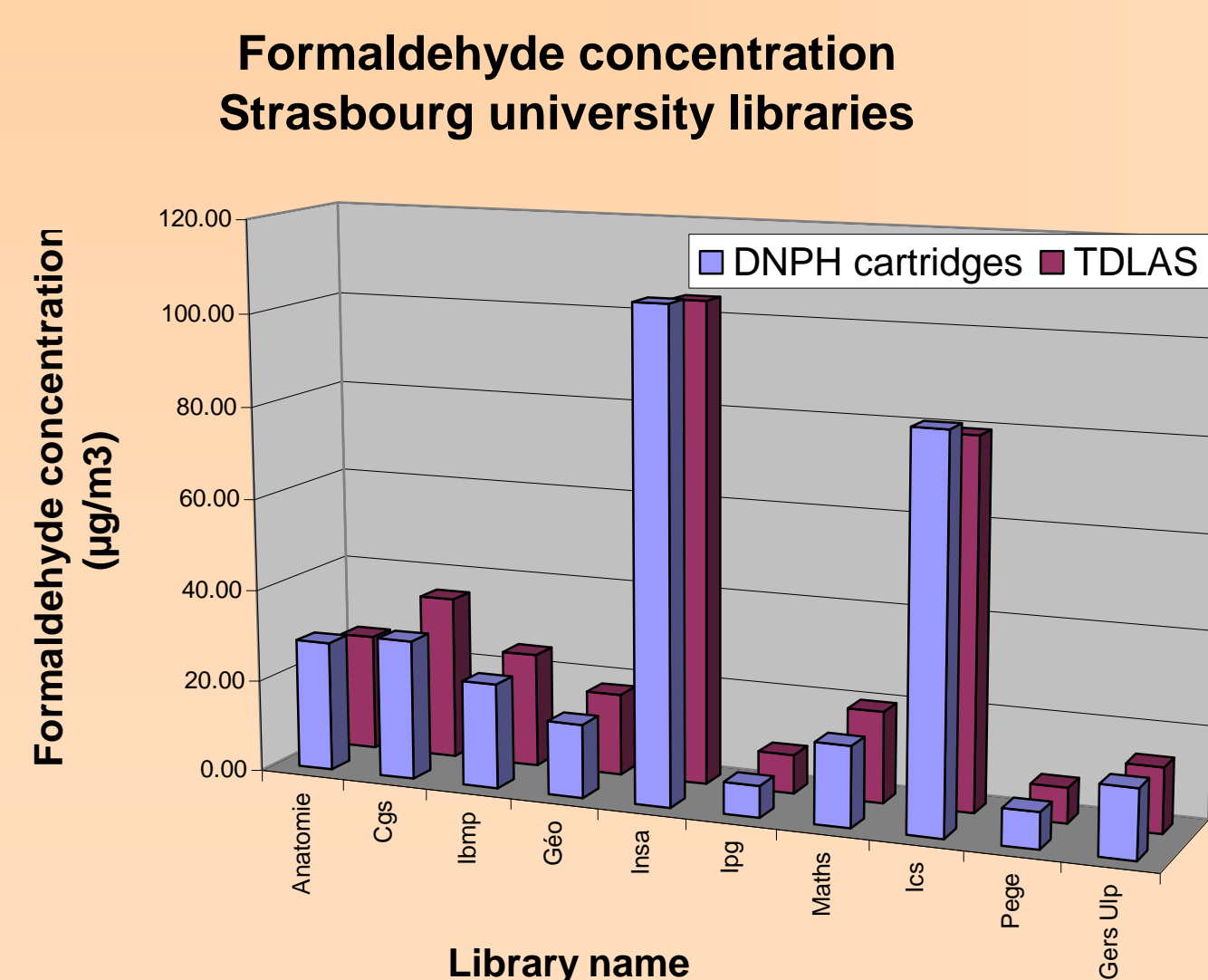
Vertical profile of H_2CO outside laboratory

Indoor formaldehyde measurements

Sampling sites : 10 university libraries in Strasbourg, France

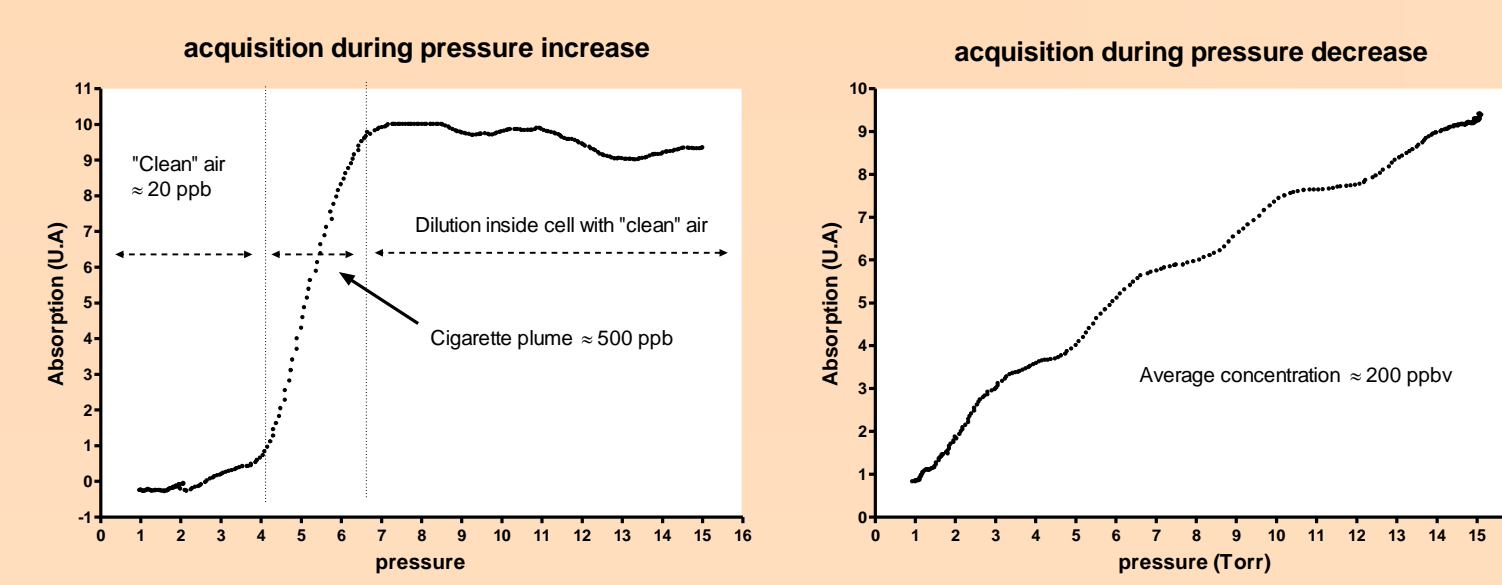
Methodology : 2 minutes air sampling in Tedlar bags, and analysis in the laboratory (less than 30 mn delay between sampling and measurement). Stability of sample in the bags is checked by repeated measurements over the next 48 hours.

Comparison with standard DNPH trapping method (2 hours sampling) / UV-HPLC measurements



Formaldehyde concentration Strasbourg university libraries

formaldehyde monitoring in cigarette smoke



Interception of cigarette smoke plume in air outside laboratory during measurement

Perspectives

Optical stability improvement (main limitation to repeatability and detection limit)
Bulk and weight reduction

Monitoring of other COVs and pollutants : acetaldehyde, 1,3-butadiene, methane...

Measurement campaigns : urban and industrial environments (Dunkerque, Lille and Reims areas), indoors and in-vehicle pollution monitoring