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Benjamin Hanoune, Bernard Lemoine

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Application of a variable pressure infrared spectrometer for formaldehyde measurements in indoor and outdoor environments

B. Hanoune, Physicochimie des Processus de Combustion et de l'Atmosphère, UMR CNRS/USTL 8522, FR CNRS 2416, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, France

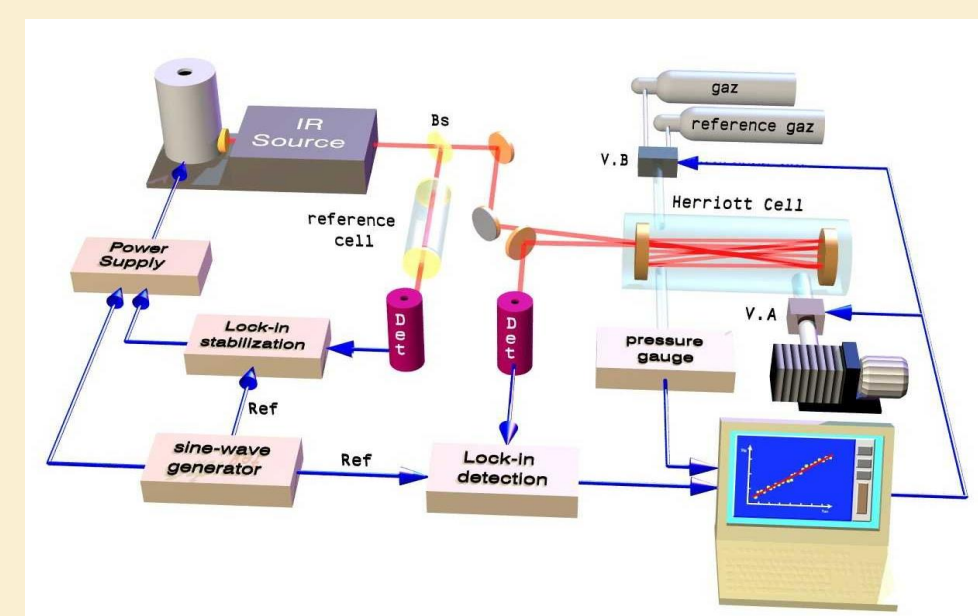
B. Lemoine, Laboratoire de Physique des Lasers, Atomes et Molécules, UMR CNRS/USTL 8523, FR CNRS 2416, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, France

Context and objectives

Interest in measurements of formaldehyde 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.

We developed a mobile diode-laser based instrument that provides near real-time measurements of formaldehyde, together with an acquisition procedure that allows a reduced gas consumption while retaining the sensitivity of the standard measurement procedure.

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

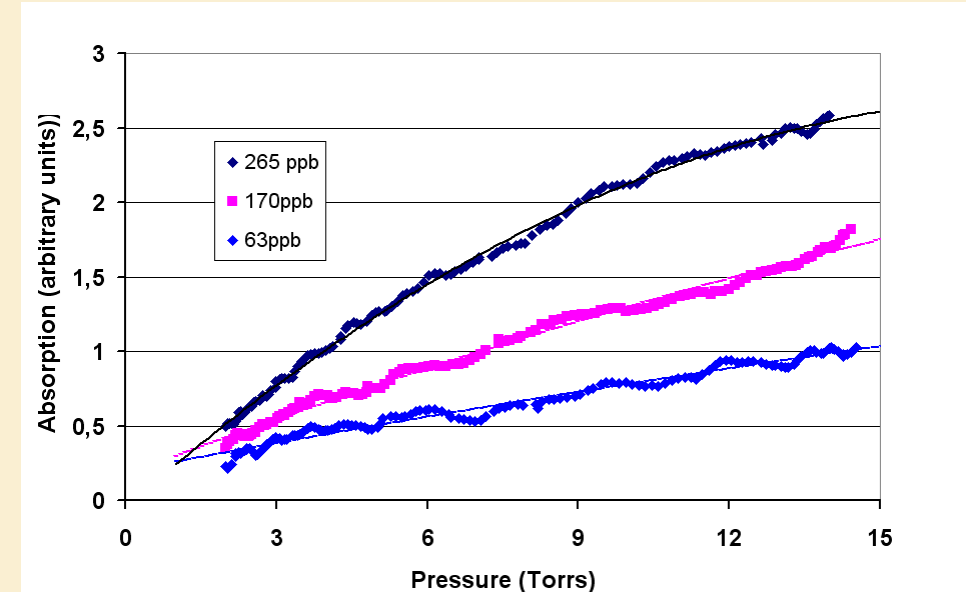
Diode laser : H_2CO , 2800 – 2840 cm^{-1} , 10-kHz sinewave modulation

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

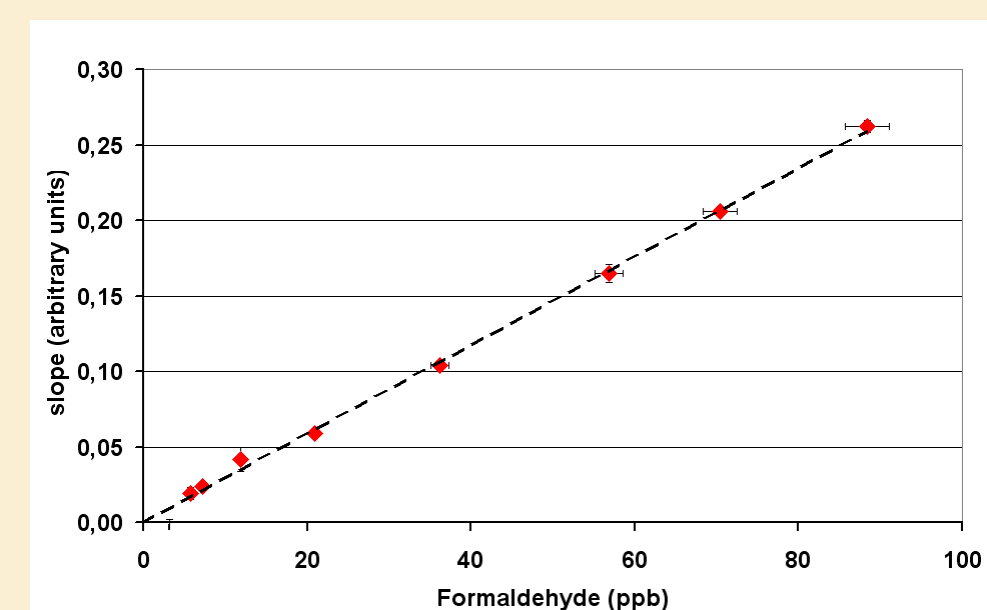
Principle of variable pressure spectroscopy

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 absorption 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 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})



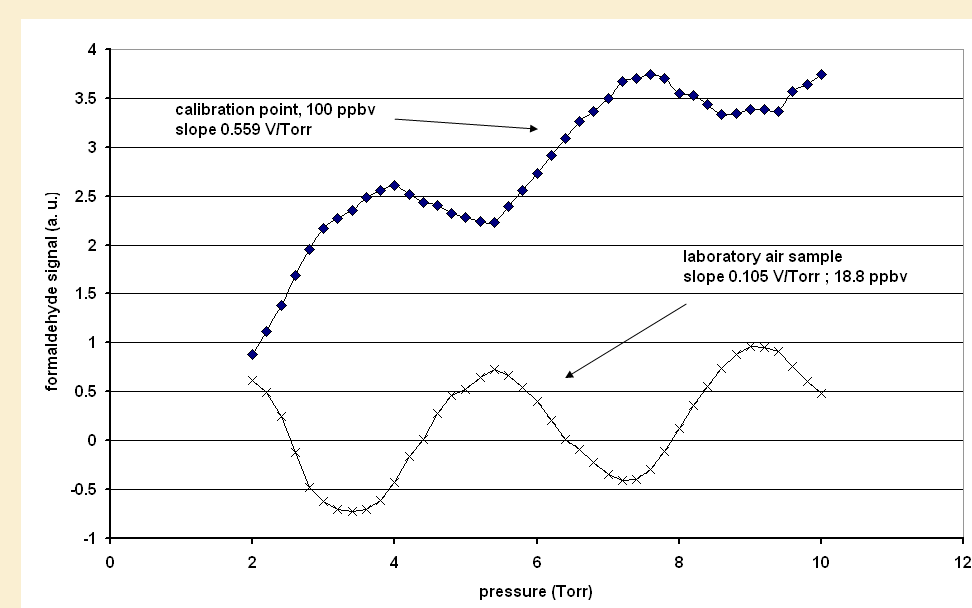
Calibration curve

Analysis procedure

Individual acquisitions signal S vs. pressure P are analyzed between 2 and 10 Torr as:

$$S = a + b \cdot P - c \cdot P \cdot P + d \cdot \sin(e \cdot P + f)$$

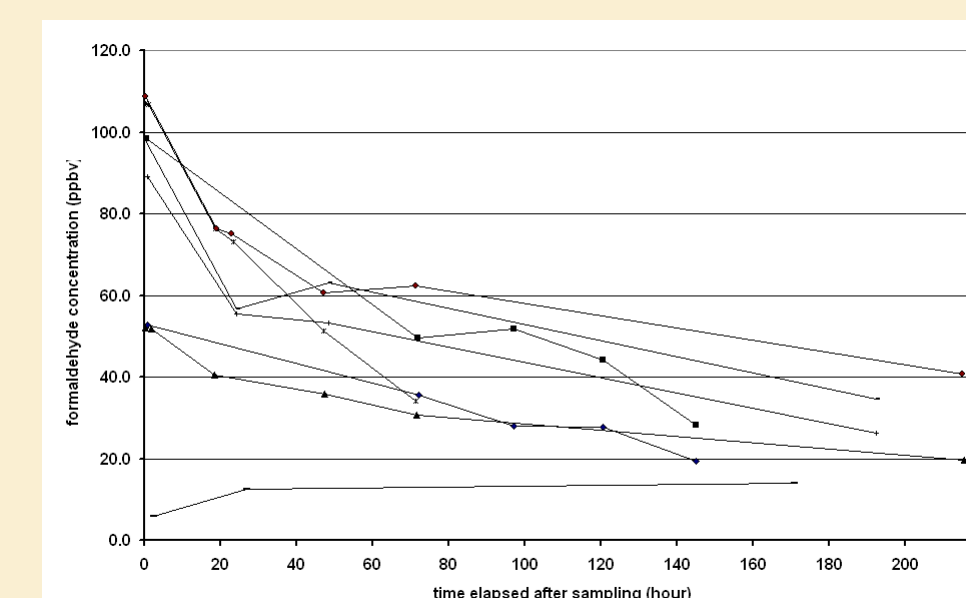
offset \equiv baseline fluctuations
 slope \equiv concentration
 pressure pseudo-fringes
 curvature \equiv line-broadening



Stability of formaldehyde samples in Tedlar bags

When feasible, measurements are performed by directly injecting the sample gas into the absorption cell. When it is not possible to bring the spectrometer close enough to the sampling point, air samples are collected into Tedlar bags. Synthetic formaldehyde-in-nitrogen samples and real air samples were analyzed over 9 days to check for stability. There is equilibration between the formaldehyde level inside the bag and the storage room formaldehyde level, but the evolution is less than 10 % if the measurement is performed less than 5 hours after sampling.

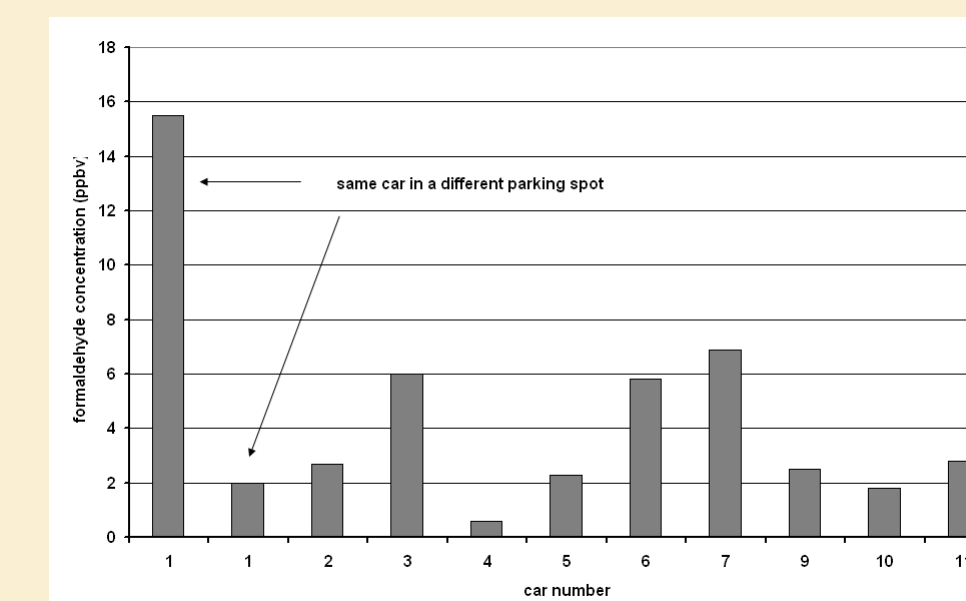
Evolution with time of formaldehyde samples in Tedlar bags



Formaldehyde measurements in cars

The concentration of formaldehyde vehicles were measured between January and March 2006. The vehicles are not representative of the car fleet in France. Concentrations measured range between 0.8 and 6.9 ppbv, with one exception at 15.5 ppbv, when the car was parked downstream from an air conditioning exhaust. This stresses both the variability between cars and the strong influence of outside conditions on the measured concentrations.

Evolution with time of formaldehyde samples in Tedlar bags

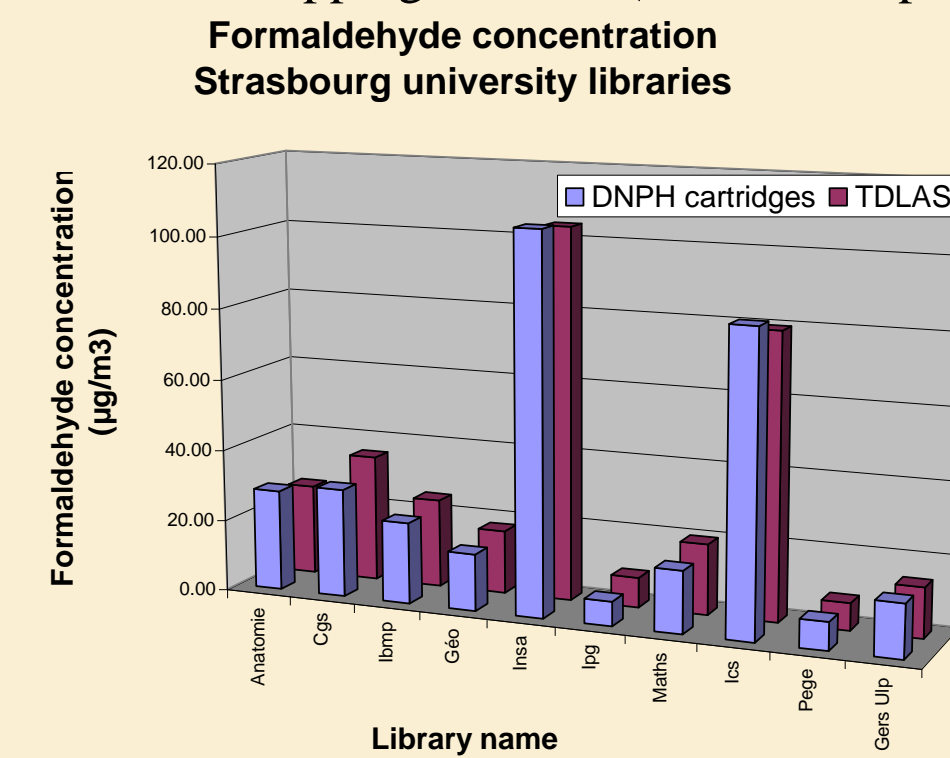


Formaldehyde measurements in university libraries

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).

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



Conclusion

- demonstrated use of the variable pressure spectrometer for formaldehyde measurements in different environments and at different levels (ppb – ppm range)
- improvements under way for thermal and mechanical stability
- monitoring of other species with the same technique : acetaldehyde, 1,3-butadiene

