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Quantification of minor trace-gas pollutants in air by variable pressure infrared diode laser spectroscopy

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Abstract

We recently developed a new protocol for the measurement of minor trace-gas pollutants in air : variable pressure infrared diode laser spectroscopy (Dusanter et al., Applied Optics, vol.41(24), pp. 5142-5147, 2002). Instead of scanning the laser emission around the feature of interest at a fixed pressure and adjusting the 2f absorption line to a calibrated spectrum, we stabilize the laser emission at the center of the line and measure the change in 2f intensity while the pressure increases inside the cell from 0 to about 20 Torr. The resulting curve of intensity versus pressure is in the low pressure range a straight line, with a slope proportional to the volume fraction of the absorbant. This procedure has been compared to the standard one, on the same instrument, and has been shown to lead to the same detection limit. However, it benefits from its ability to quantify heavier species with no isolated line, such as 1,3-butadiene, from its simplicity in the data analysis phase, and from its lower sensitivity to variations of the baseline. We will present in this poster our results on 1,3-butadiene, formaldehyde and acetaldehyde, as well as our ongoing work toward an automated field instrument.

Context & Objectives

Because of the increasing need of selective and sensitive instruments, we recently enlist in the R&D field for atmospheric research. By their complementary abilities -atmospheric chemistry and spectroscopy- our laboratories^{1,2} have collaborated to build a tunable diode laser spectrometer. This work was realised within the CERLA for an ulterior technology transfer.

The main aims of this work was focused on the quantification of pollutants heavier than those usually measured by TDLAS. These compounds usually display congested absorption spectrum. We have selected 1,3-butadiène -a potentially carcinogenic compound with a high photochemical reactivity- as a good pretender.

Partners

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Methods & Results

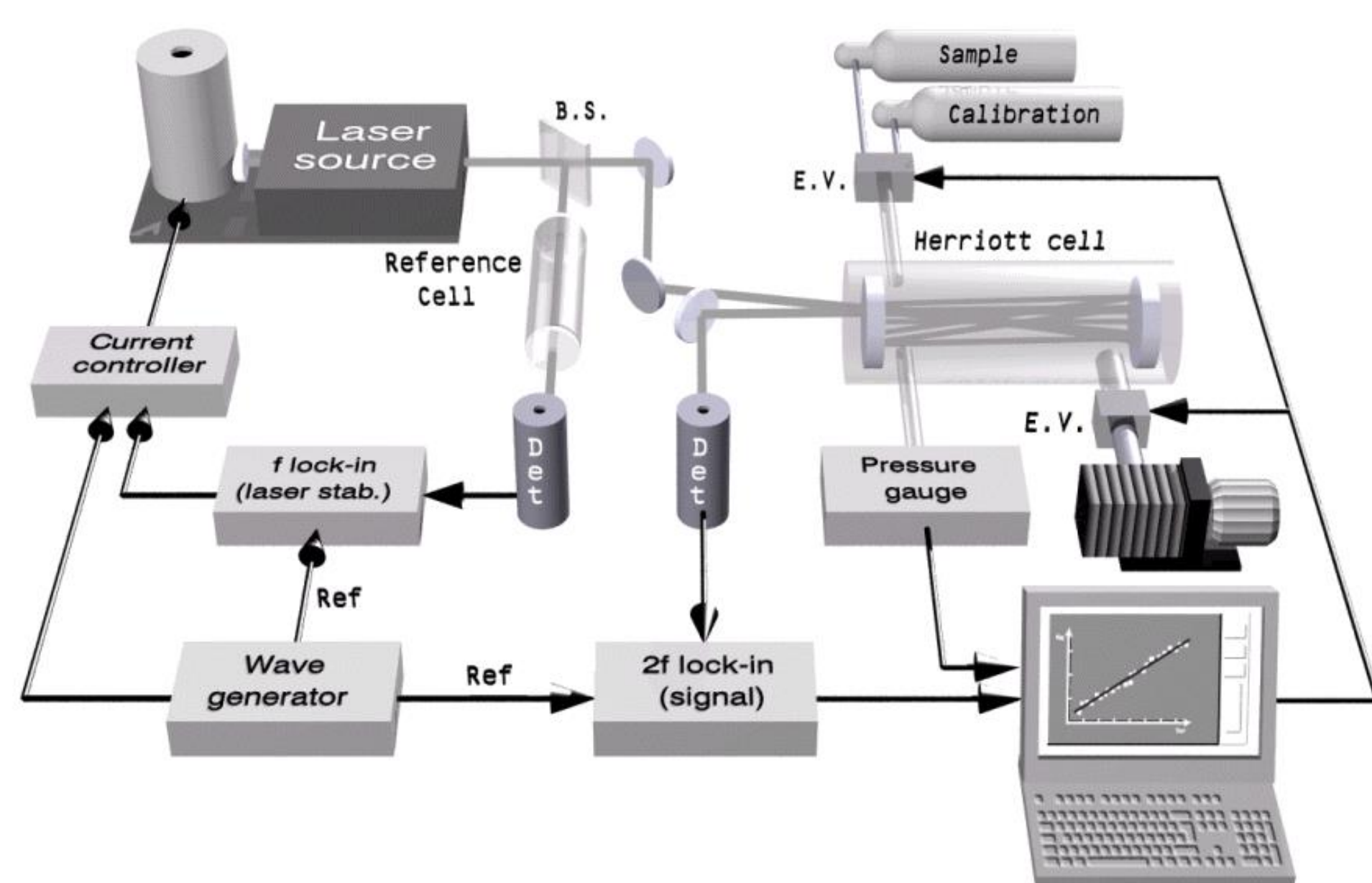


Fig.1 : Experimental set-up. (BS : beamsplitter ; EV : electromagnetic valve)

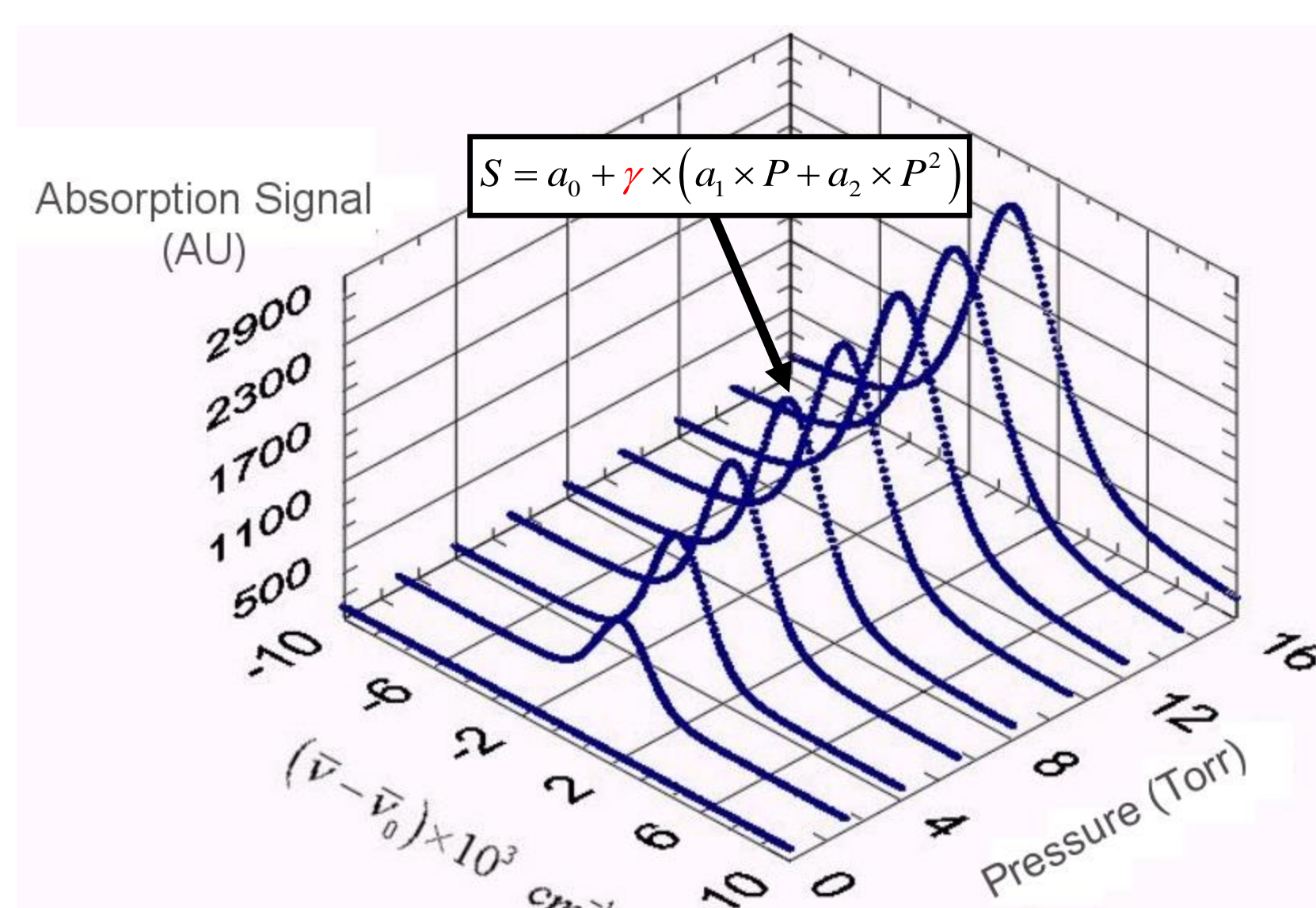


Fig.2 : Behavior of an absorption line when the pressure increase

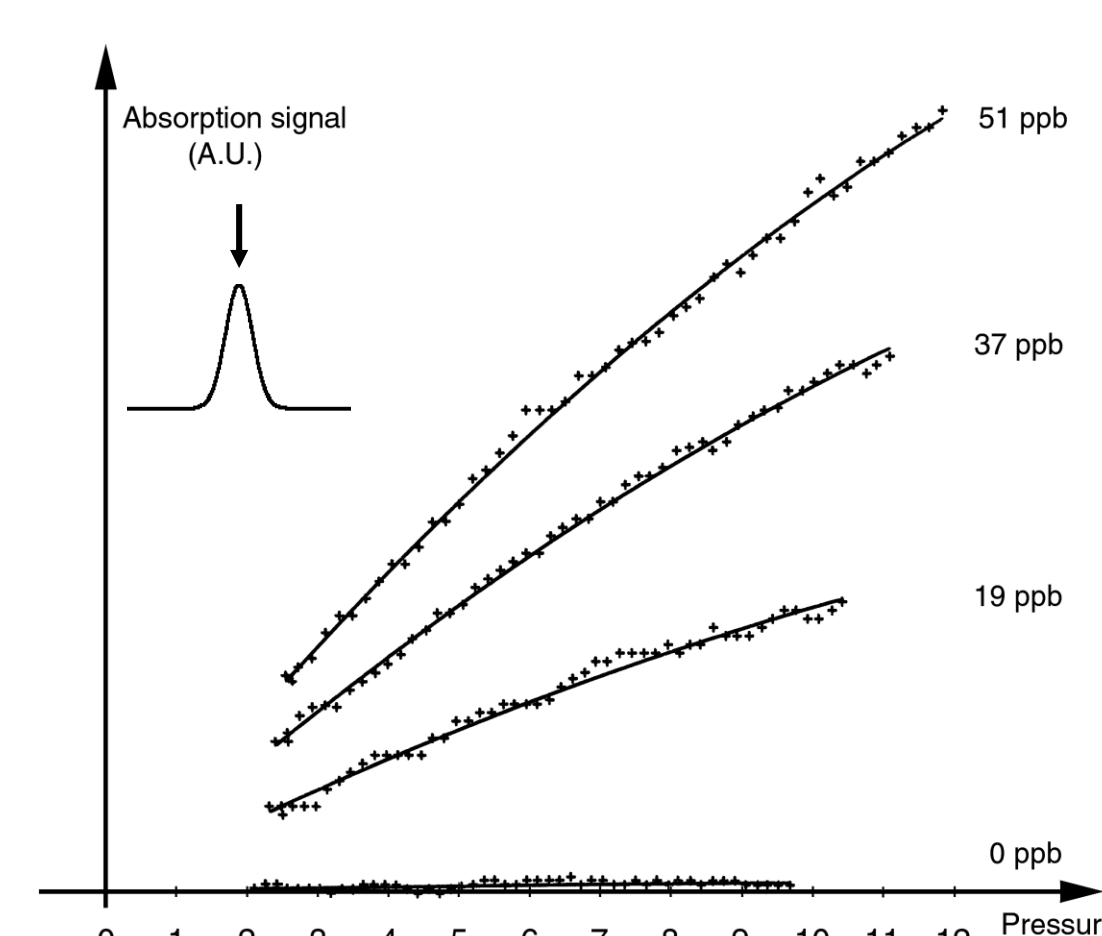


Fig.3: Typical curves of N₂O signal increase with pressure for several mixing ratios

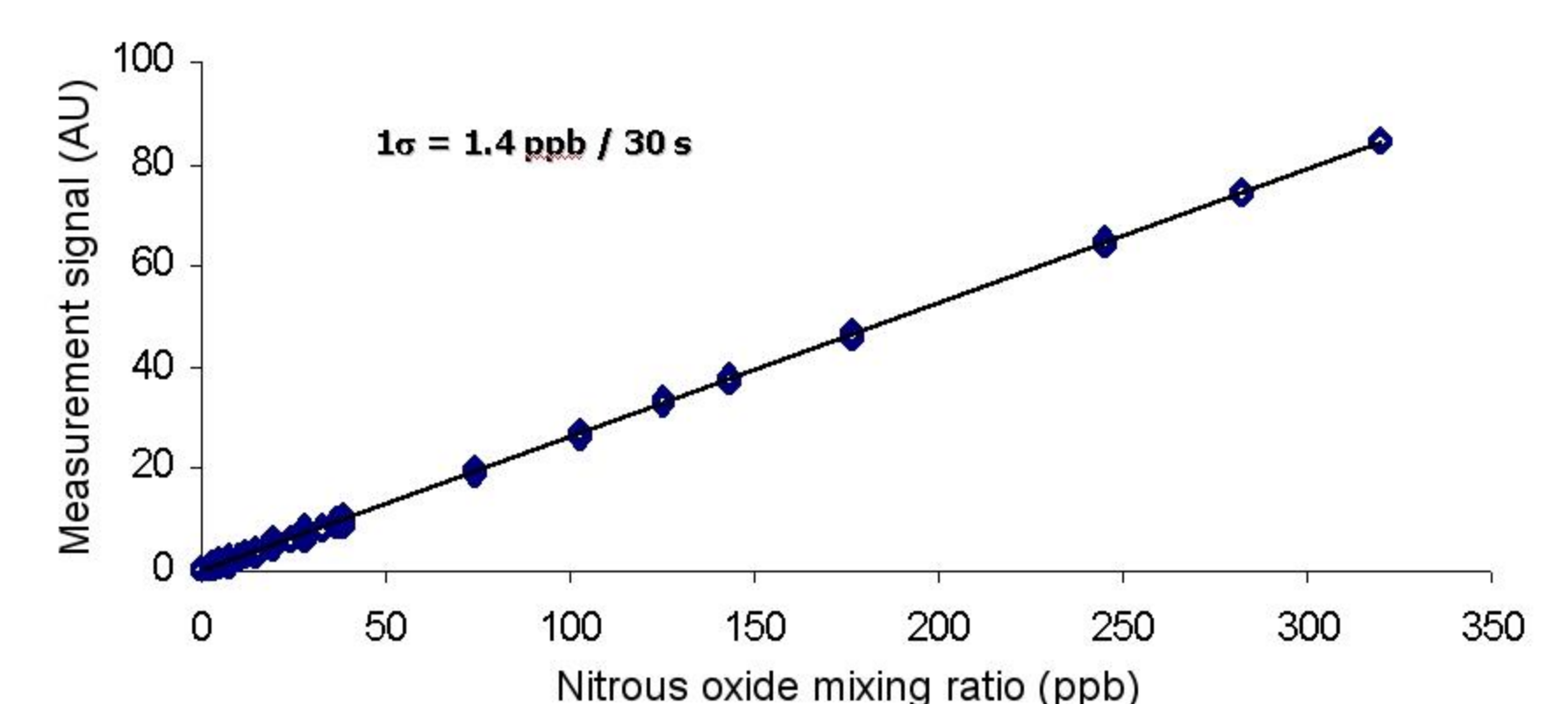


Fig.4: Calibration curve for N₂O

We developed an original protocol for trace gas quantitative determination, which retains most of the features of the classical method (synchronous 2f detection, long path absorption cell, low total pressure). Instead of scanning the emission frequency of the diode around a spectral line at a fixed pressure, we measure the rate of increase of the signal as the pressure of the sample increases inside the cell (fig.2). By locking on a line with a conventional first derivative procedure and measuring only the peak intensity S of the 2f signal, this will translate in a plot of S versus P as a straight line showing for higher pressure a small downward curvature (fig.3).

This technique is not only applicable to pollutants exhibiting well resolved thin absorption lines like N₂O but also to broad absorption peaks on unresolved background like 1,3-butadiene (fig.5). To illustrate this point, we have used our system to measure the mixing ratio of 1,3-butadiene in vehicle exhaust gases (fig.6). Butadiene is classically measured in the atmosphere or in automobile exhausts by standard gas chromatography (GC) techniques. However, as it is highly reactive, GC determination of butadiene needs to be corrected for the residence time in the canister. A sensitive and fast monitoring technique such as the one we present here is therefore of prime interest for this compound

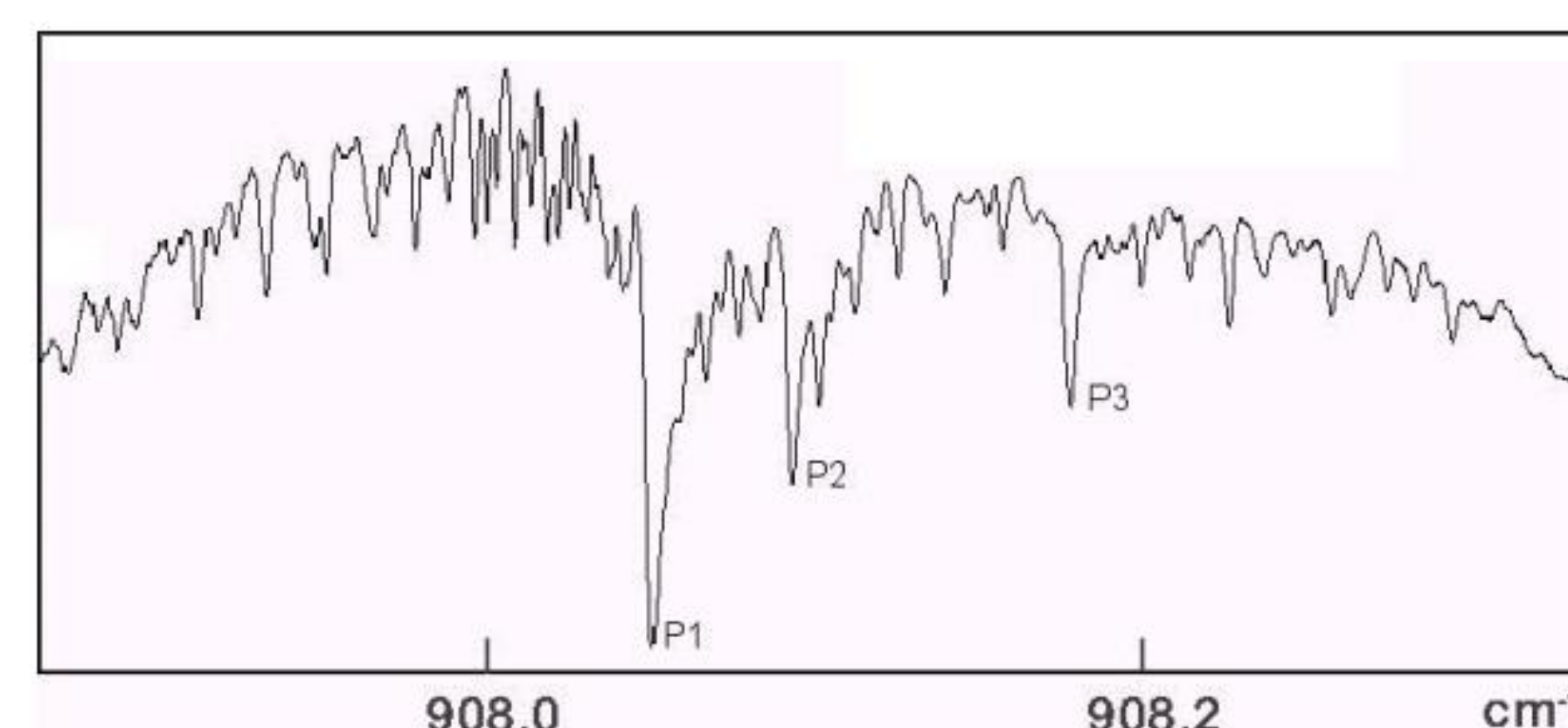


Fig.5 : Butadiene absorption spectrum around 908 cm⁻¹

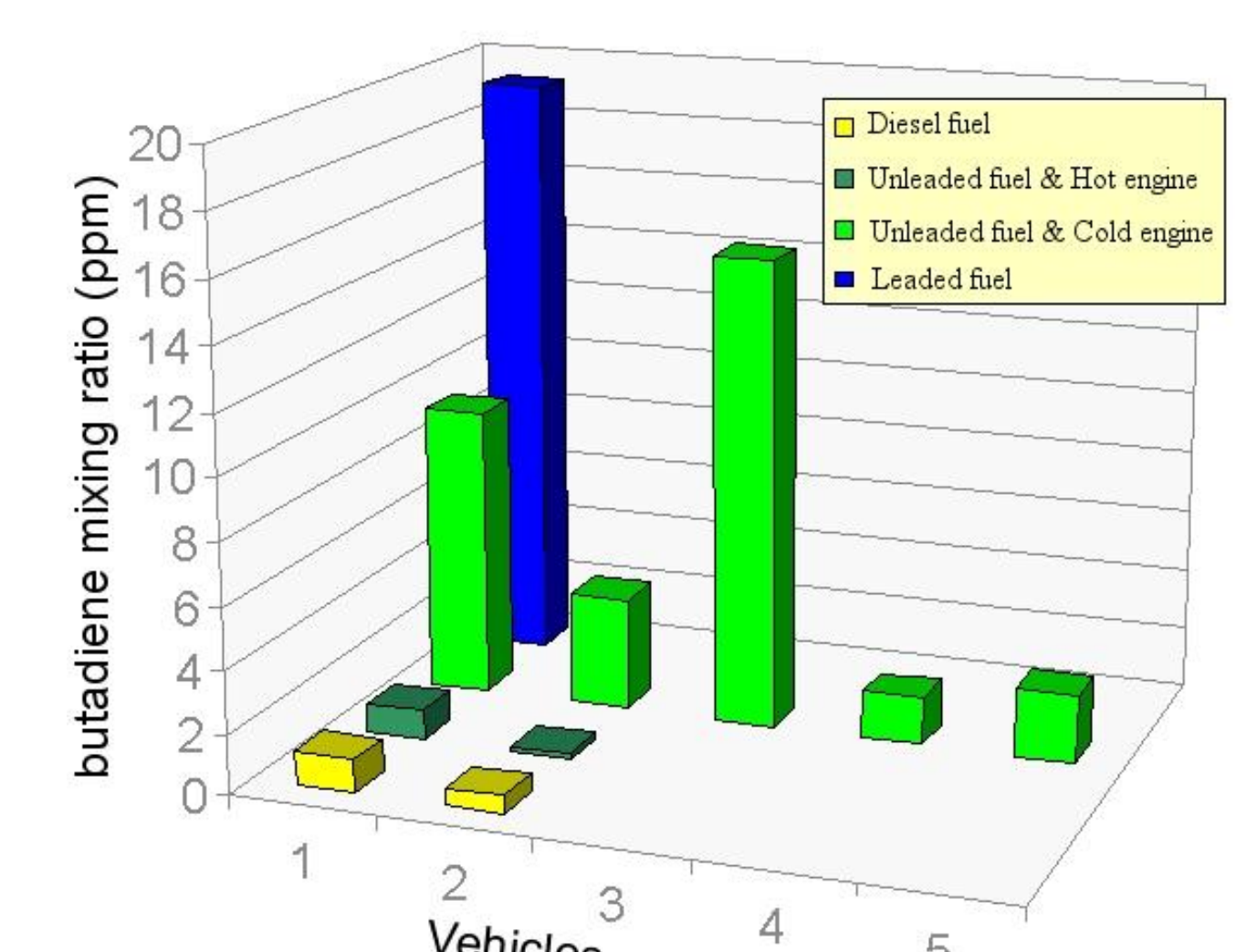


Fig.6: Butadiene measurements in vehicle exhaust gas

Finally, we have used our instrument to determine its characteristics in terms of sensibility for measurements of formaldéhyde (fig.7 & 8), acétaldéhyde and methane the sensitivities reached for these compounds are displayed in the table fig.9.

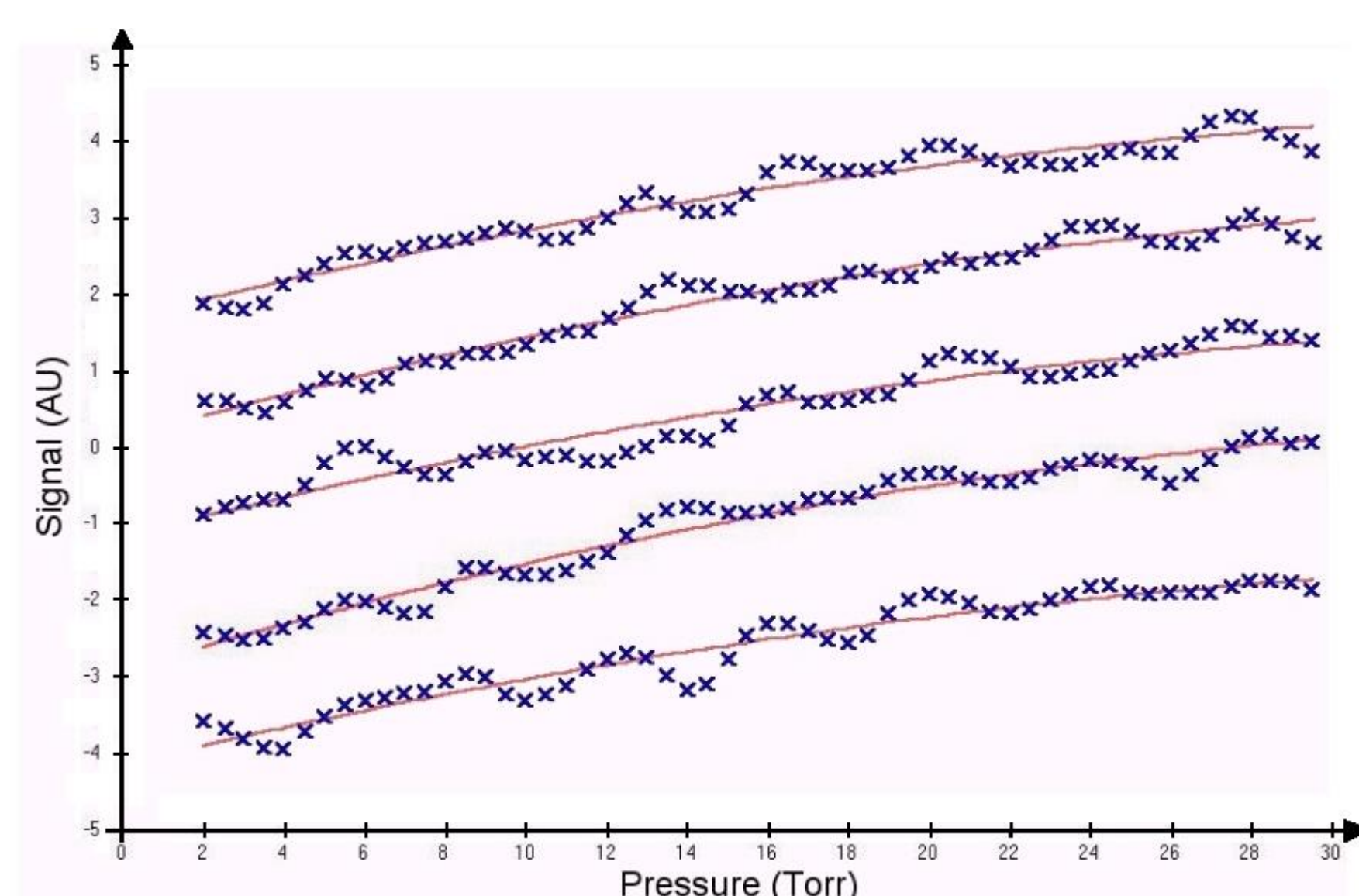


Fig.7 : Typical curves of signal increase with pressure for 57.3 ppb of H₂CO

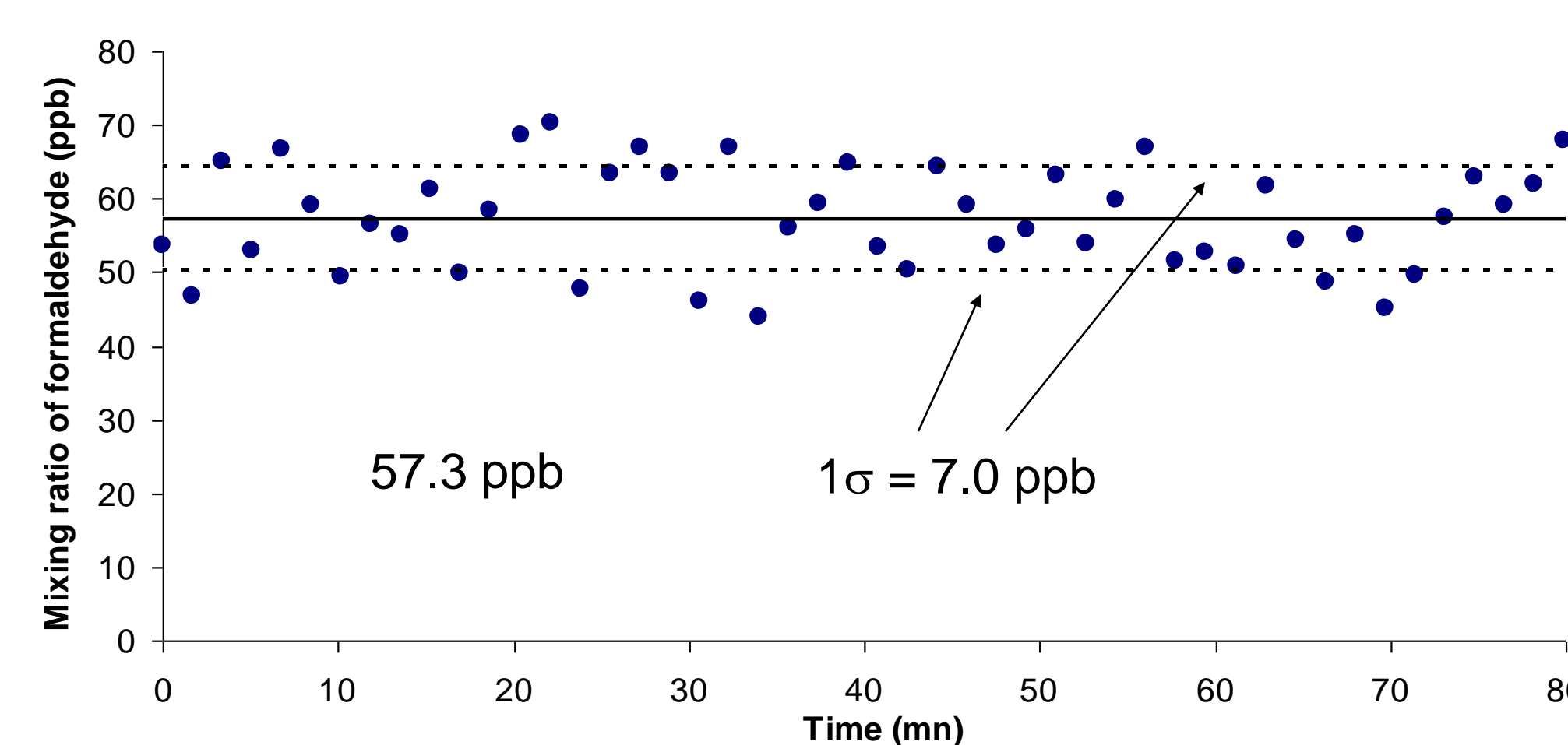


Fig.8 : Measurements of 57.3 ppb of H₂CO versus time

Compounds	Wavenumber (cm ⁻¹)	Sensitivity (1σ ppb) / 30s
Formaldehyde	near 1720 cm ⁻¹	7
	1729.5068 cm ⁻¹ (HITRAN)	7
Acetaldehyde	near 1762 cm ⁻¹	45
Methane	2828.0926 cm ⁻¹ (HITRAN)	40

Fig.9 : experimental sensitivities reached with our instrument

Conclusion & Perspectives

This new method does not require precise stabilization of the pressure inside the cell, and our technique requires a much more simple data acquisition, with no complicated cycles for data acquisition (no background subtraction) and an easier data treatment, with no complicated mathematical analysis such as fitting the shape of the line. Our method also is less demanding in terms of total sample flow (usually less than 1 SLM, whereas the classical method requires flow several times higher) and therefore on gas consumption. Unlike the conventional method, it is also unnecessary to regulate precisely the pressure in the sample cell. With all these advantages, this new system could be used more routinely for pollutants monitoring or process control, on a timescale of the order of the minute. However, working at a single absorption frequency implies that possible interferences with other species must be carefully studied beforehand, since there is no way of distinguishing between the absorption signal of the target gas and that of other species absorbing near that frequency. On the other hand, if such coincidences or near-coincidences exist, it should be possible to monitor several species with one diode, using well chosen lines of each species. Further improvements to our apparatus include eliminating the interference fringes that limit our precision and sensitivity, working with a longer optical path and/or with a cell with a smaller volume, since the acquisition time is determined by the time required to fill and evacuate the cell, and acquiring data also during the pumping of the cell.

This instrument will be shortly used for formaldehyde measurements. First, an inter-comparison with other techniques will be done at XXXXXXXXXXXXXXXX. Afterthat, it will be used to measure indoor ambient mixing ratio of formaldehyde.