

## EMRP project [3]

### Objectives:

- Development of spectrometric techniques for accurate quantification of biomarkers in human breath

### Instrumentation for breath analysis:

- OPO-based CRDS
- fibre-based TDLAS
- TDL/QCL-based AS

### Validation and spectrometric parameters:

- measurement method – recommendation and standardization
- line strengths evaluation
- multi-component spectra measurements

### Outcome: (lab-based and -validated)

- Methodology for accurate, interference-free, calibration-free breath analysis

### Interfering components:

- moisture, hydrocarbones
- gas handling
- cross validation by gravimetric mixtures

### Dissemination and Impact:

- symposion on breath metrology
- liaisons with academic and industrial research groups

## At PTB

### Calibration-free TDLAS:

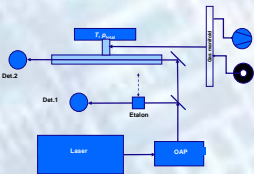
$$\phi(\nu) = \phi_0(\nu) \cdot \exp[-k(\nu - \nu_0) \cdot n \cdot L]$$

$$S = \int_{-\infty}^{\infty} k(\nu - \nu_0) d\nu$$

$$A_{\text{line}} = \int_{-\infty}^{\infty} A(\nu) d\nu = - \int_{-\infty}^{\infty} \frac{\phi(\nu)}{\phi_0(\nu)} d\nu = S \cdot n \cdot L$$

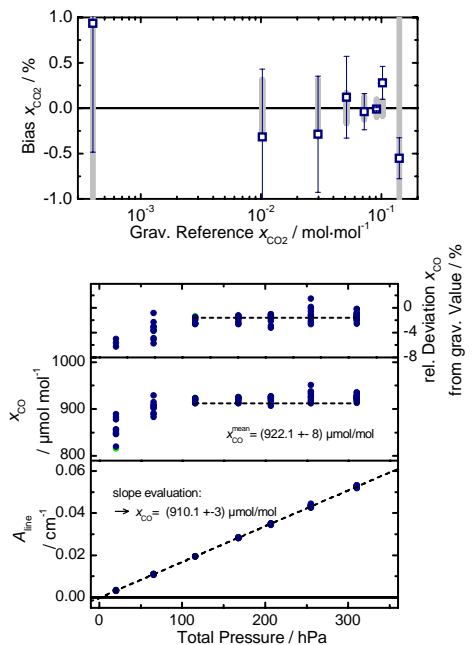
$$p_{\text{species}} = x_{\text{species}} \cdot p = n \cdot k_B \cdot T$$

$$x_{\text{species}} = \frac{A_{\text{line}} \cdot k_B \cdot T}{S \cdot p \cdot L}$$

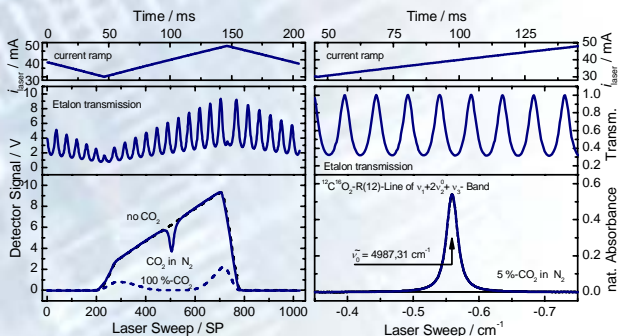


We employed direct absorption spectrometry to determine the amount of substance fraction ( $\text{CO}$ ,  $\text{CO}_2$ ) in gas mixtures, probing e.g. the R(12)-ro-vibrational line of  $\text{CO}_2$  in the combination band around  $2 \mu\text{m}$ . The feasibility of calibration-free measurements were earlier demonstrated for applications of room air monitoring and vehicle exhaust emission tests spanning a dynamic range of amount of  $\text{CO}_2$  fractions from  $0.0004$  to  $0.14 \text{ mol}\cdot\text{mol}^{-1}$ . The respective budgets showed relative uncertainties of the SI-traceable amount of carbon dioxide fractions from  $\pm 3.3$  to  $2 \%$ . A 2-channel-laser-spectrometer setup, operated with a DFB-laser diode emitting around  $4987 \text{ cm}^{-1}$ , was used to measure the integral absorbance of the completely resolved R(12)-line of  $\text{CO}_2$  [1]. Results with a QCL-operated setup has been obtained for  $\text{CO}$  [2]. The QCL was operated in the intra-pulse-chirp mode to probe the P(1) line of  $\text{CO}$  in the fundamental vibration band at  $4.6 \mu\text{m}$ .

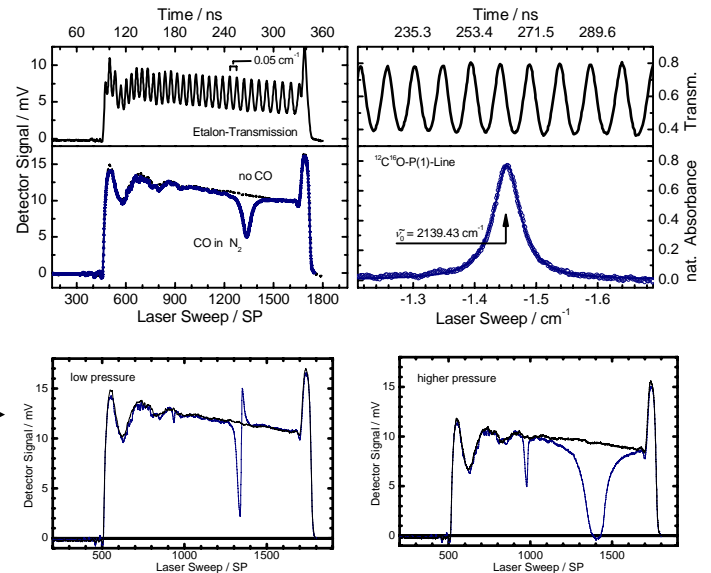
For the EMRP project, a link towards breath analysis shall be made. The measurement method (TILSAM [4]), based on lab experiments, shall be standardized and validated against gravimetric standards [3].



### TDLAS - From raw data to processed data:



### QCLAS - From raw data to processed data:



Interesting effects observable in QCL-AS →

[1] J. Koelliker Delgado et al., VDI-Bericht 1959, p. 303 (2006)  
 [2] O. Werhahn (Hrsg), Abschlussbericht QUANSYS-Teilvorhaben FKZ 13N8123, Braunschweig 2006  
 [3] The research within this EURAMET joint research project receives funding from the European Community's Seventh Framework Programme, ERA-NET Plus, under the IMERA-Plus Project - Grant Agreement No. 217257. The collaboration with partners from DFM (DK), LNE-CNAM (FR), NMI (NL), and IPQ (PT) is acknowledged.  
 [4] EURAMET project No 934; <http://www.euramet.org>, search for project ref. 934