TDLS system to measure CO$_2$:N$_2$ gas mixtures with 0.12 % accuracy

DLS
LAB

A.Nadezhdinskii, Ya.Ponurovskii, I.Popov, Yu. Shapovalov, D.Stavrovskii, I.Vyazov

A. M. Prokhorov General Physics Institute of RAS, 38 Vavilov str., 119991, Moscow, Russia, E-mail: Nad@nsc.gpi.ru

L.Konopelko

D.I.Mendeleyev Institute for Metrology, Moskovsky pr. 19, St.Petersburg 190005, Russia

A.Kuzmichev

Moscow Institute of Physics and Technology, Institutskii per., Dolgoprudnii 141700, Russia

Introduction

Accuracy is one of recent challenges for Tunable Diode Laser Spectroscopy (TDLS). Several TDLS applications require measurement accuracy at level 0.1 %. In [1, 2] we've considered possibility to achieve this level. Present paper is next step.

Green house gases in atmosphere measurements require accurate gas mixture standards. International inter-comparison campaign is performing to achieve this goal. As result accurate instruments are necessary for the campaign. Additional requirement – primary standard: after development no calibrations.

Goals of present work: develop TDLS system with required accuracy to measure automatically CO_2:N_2 gas mixtures and investigate accuracy achieved.

[1] L.Konopelko, A.Nadezhdinskii, Accuracy in TDLS. TDLS as gas mixtures primary standard, Abstracts of TDLS 2009, Zermatt, Switzerland, p.76.
[2] http://www.dls.gpi.ru/rus/conf/TDLS2009/Posters/D2_TDLS%20primary%20standart.pdf

Analytical line selection
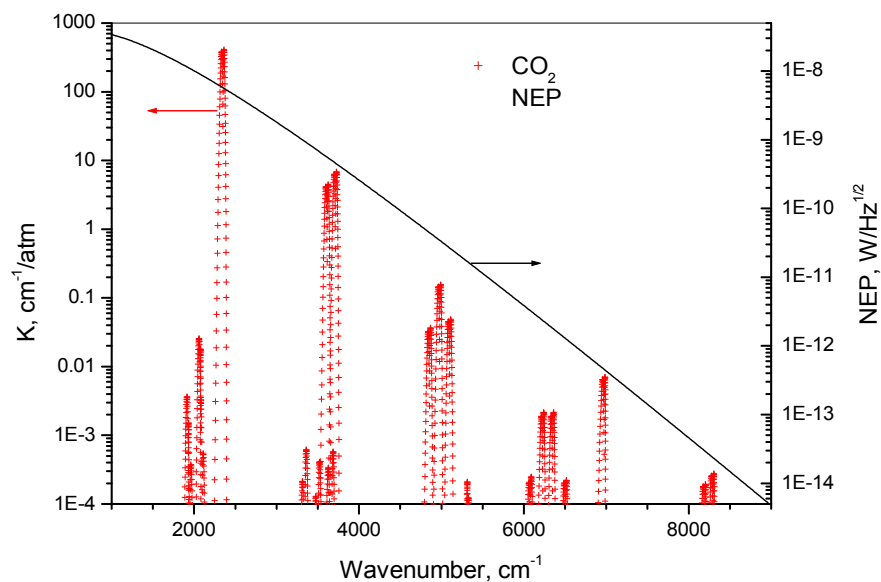
To select analytical line modeling was performed based on HITRAN 2008.

When signal (absorbance – red) to noise ratio (black) is considered one can that band near 1.44 μ can be considered. Important – in this spectral range both commercially PD and DL are available. DL has lifetime – 60 years.
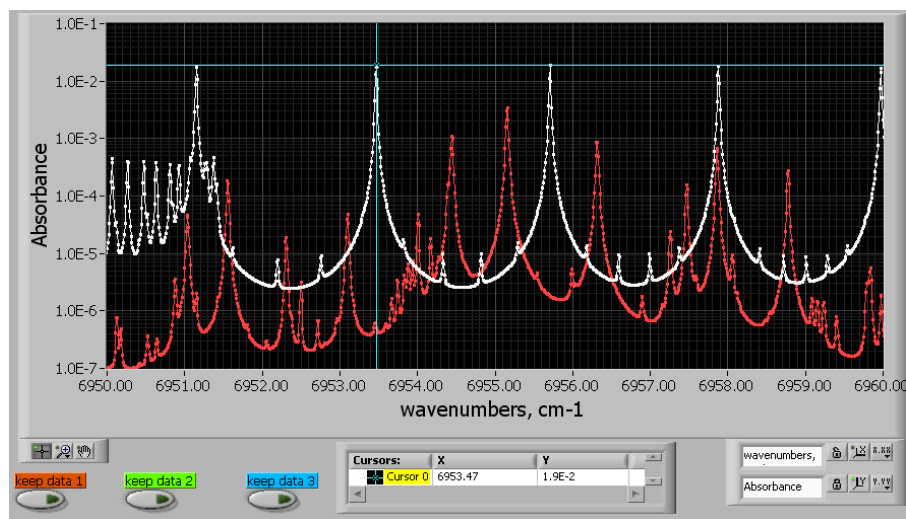

Requirements to analytical line: strong absorbance and absence of interference with water having strong absorbance here.
CO_2 and H_2O absorbance in spectral range under consideration – white and red, respectively.
L = 39 m, P_0 = 100 mBar, C_{CO2} = 1000 ppm, C_{H2O} =10 ppm.
Analytical line is marked by blue cursor. Weak lines near analytical one are due to $^{16}O^{12}C^{17}O$.

Instrument block scheme and view
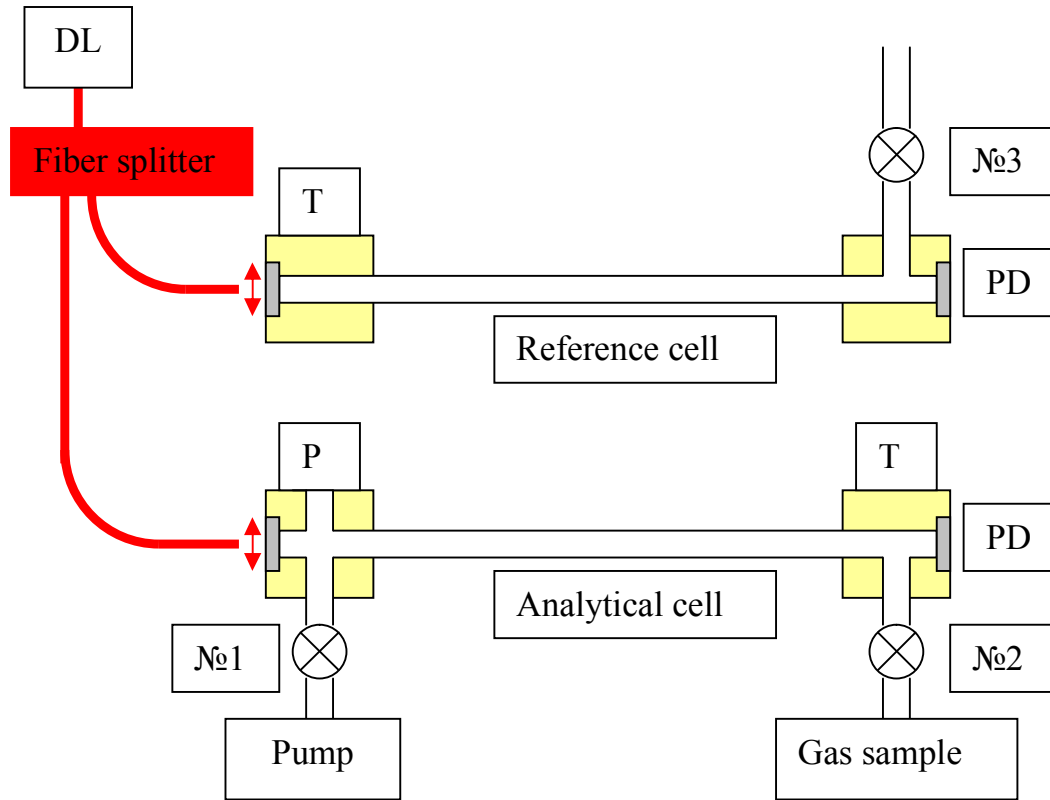
Instrument block scheme.
Reference is filled with pure CO_2.
Analytical is filled with gas sample under investigation.
Signals of two PD as well as temperature and pressure sensors are measured simultaneously.
Pressure 0 – 100 mBar with accuracy 0.07 mBar.
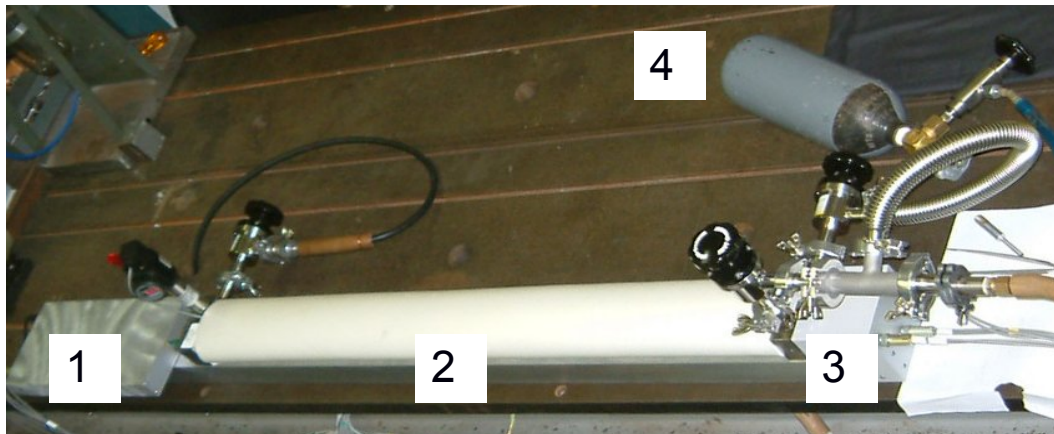
Instrument view.
1 – DL module, 3 – PDs module, 4 – gas mixture under investigation, 2 – gas cells in thermo-isolated cover.
Temperature in both cells is the same within 0.1 ^oC, its accuracy 0.2 ^oC.

CO_2 sample preparation

Raw CO_2 sample was investigated using FFT. Absorption observed belongs only to CO_2 and H_2O.
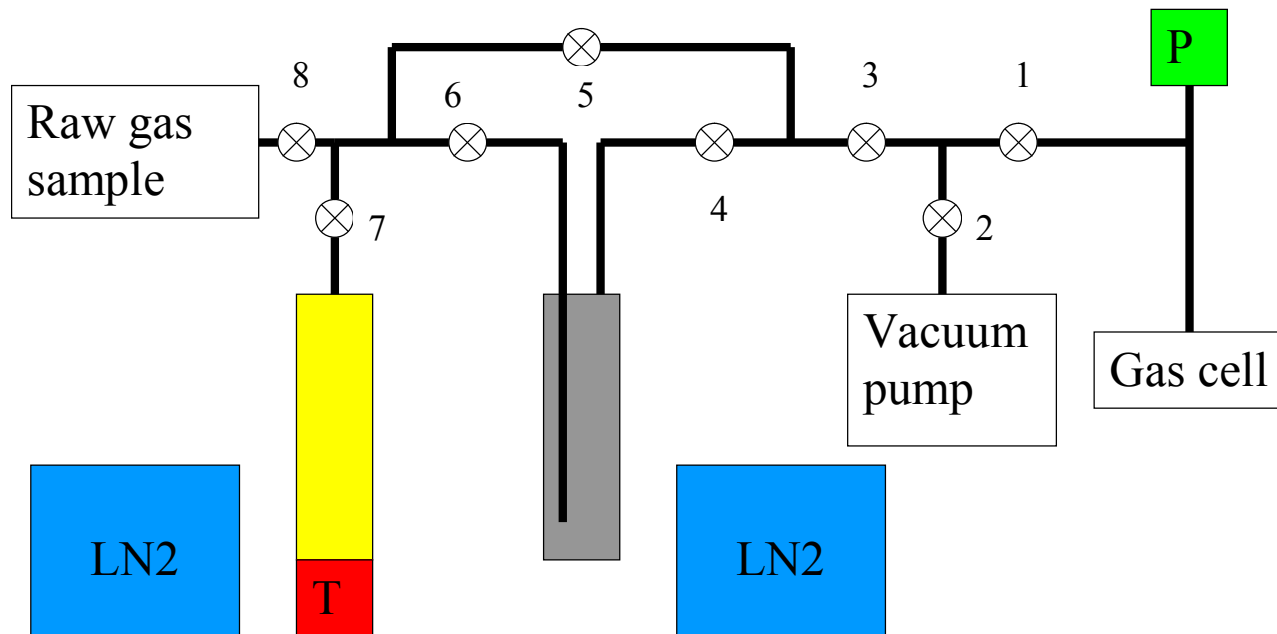
Cryogenic purification was used to improve the sample purity. Final sample passed 5 stages of purification.

The sample purity: light fraction (N_2, O_2, Ar – pressure above frozen sample) < 0.016 mBar, heavy fraction (H_2O in cells was measured using 1.392 DL) < 0.016 mBar, other possible impurities 100 time less.
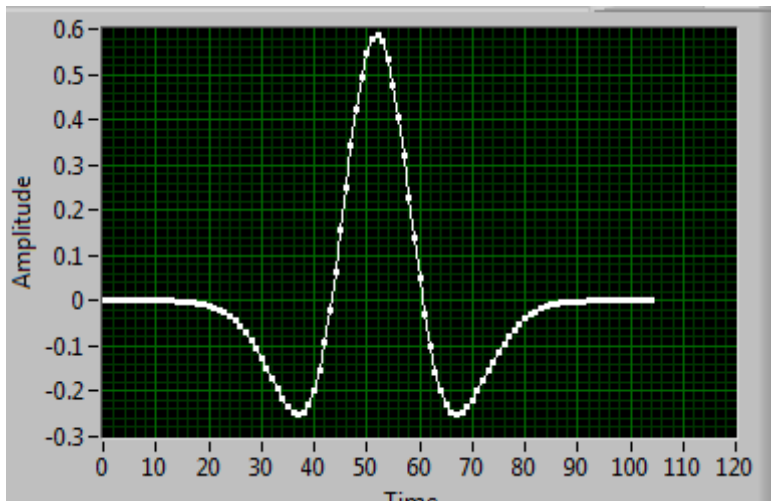
System operation
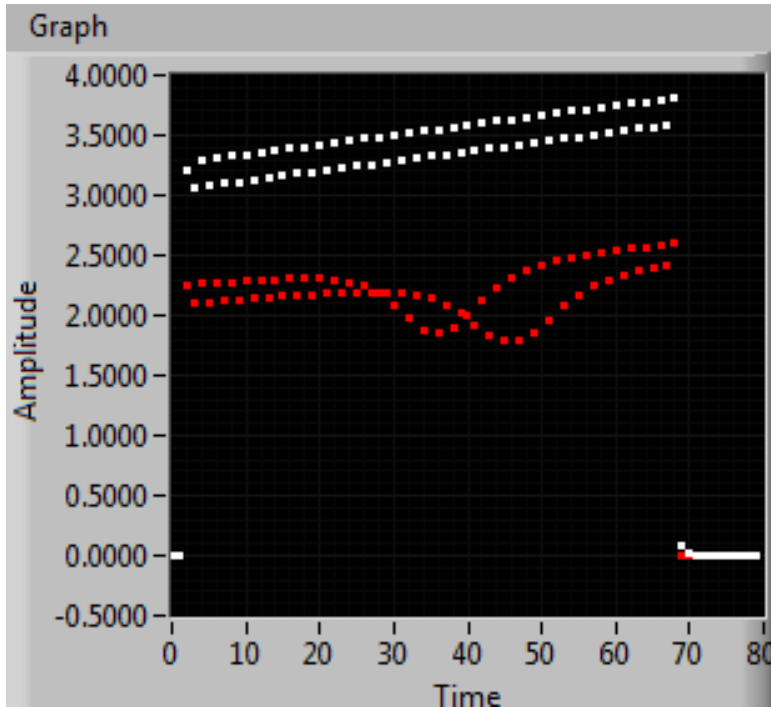
PD signals in two channels

Red - reference cell was filled with 63.37 mBar pure CO_2. Analytical line can be observed.

White - Analytical cell was pumped out. No absorption in analytical line.

Autocorrelation function of reference channel.

Correlation function of reference and analytical channels has the same shape and amplitude proportional to concentration in gas mixture under investigation.

System channels test

In present case we are measuring concentration of gas mixture under investigation in analytical cell with respect to primary standard pure CO_2 in reference cell. Requirement: both channels have to be similar with high accuracy.
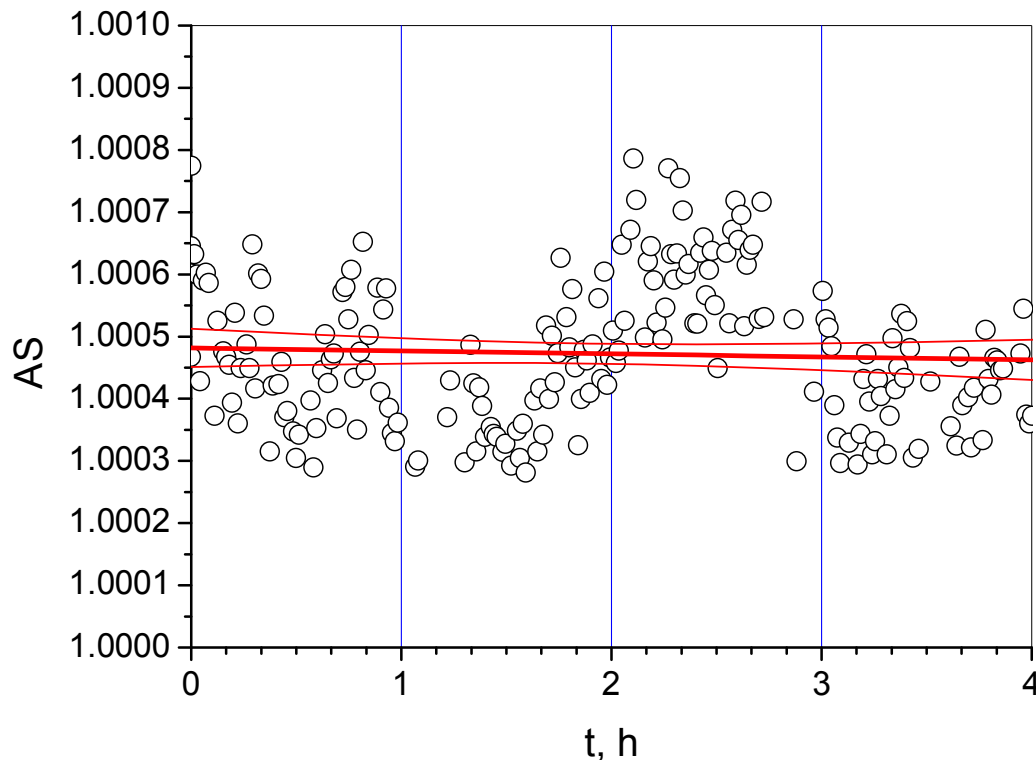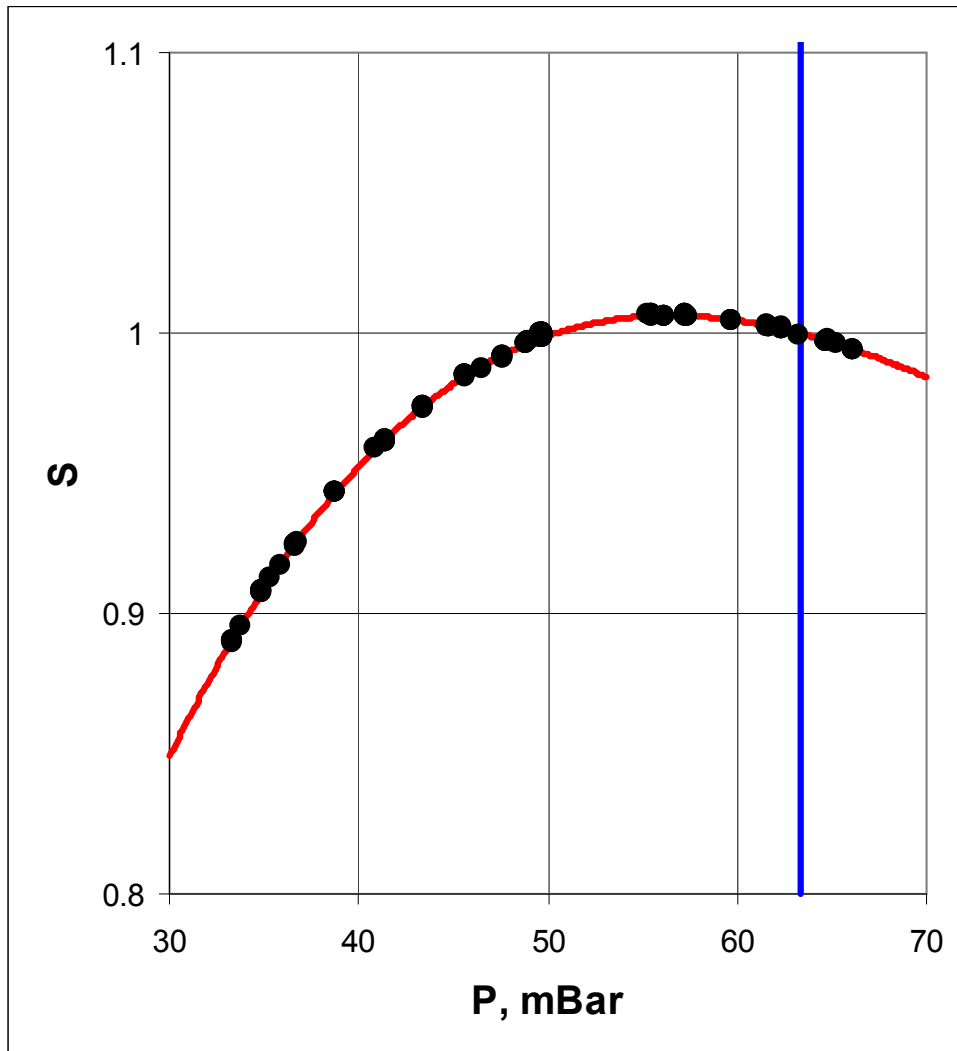

System channels test.

Both cells were filled with the same pure CO_2 at the same pressure.

Prediction: result obtained has to be 1.

Left – test result of long term system operation.

Channels are equal within 0.05 %, std = 0.011 %, drift is less than 7 ppm/h.

Analytical signal pressure dependence

Reference cell was filled with pure CO_2 pressure 63.37 mBar (blue vertical line).

Analytical cell was filled with the same pure CO_2 at different pressures (black circles).

Prediction: result obtained at the same pressure has to be 1.

At small pressures signal is proportional to pressure (molecules number in cell). At high pressures signal has to be reducing due to line broadening (we are measuring line second derivative).

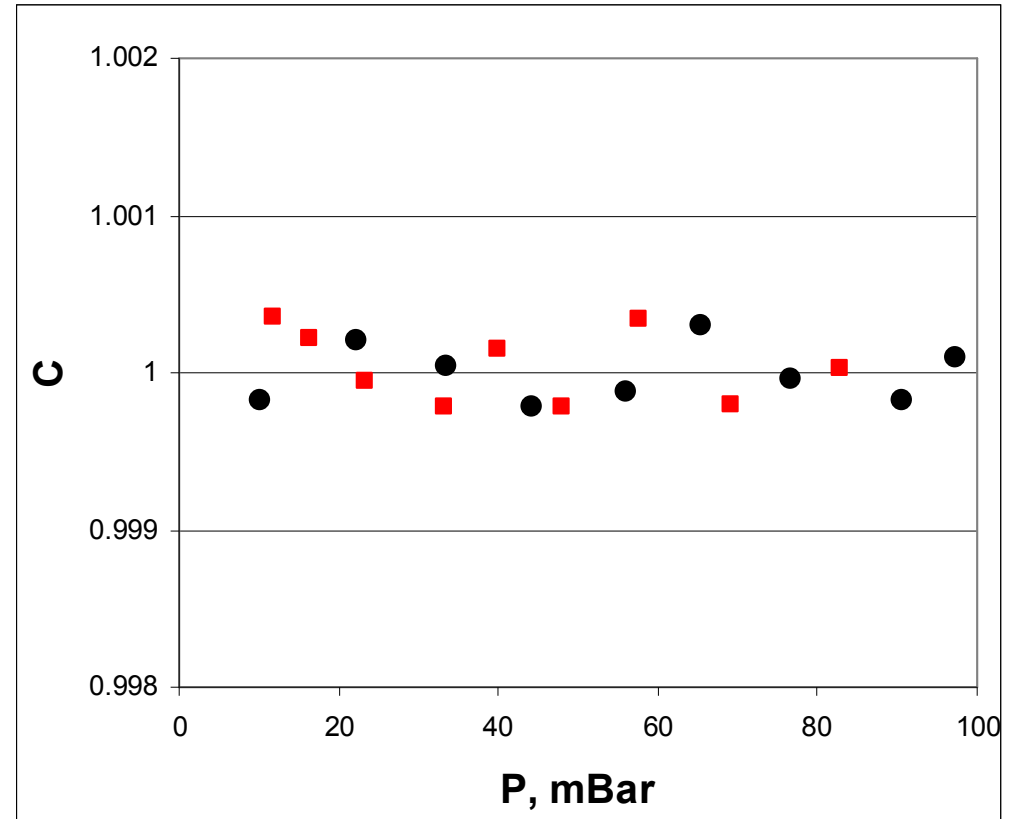Dependence observed was fitted by 4-th order polynomial F4(P) (red curve).

Calibration test

As pressure – P and analytical signal – AS are measuring continuously, concentration – C can be calculated using F4(P) determined in previous slide:

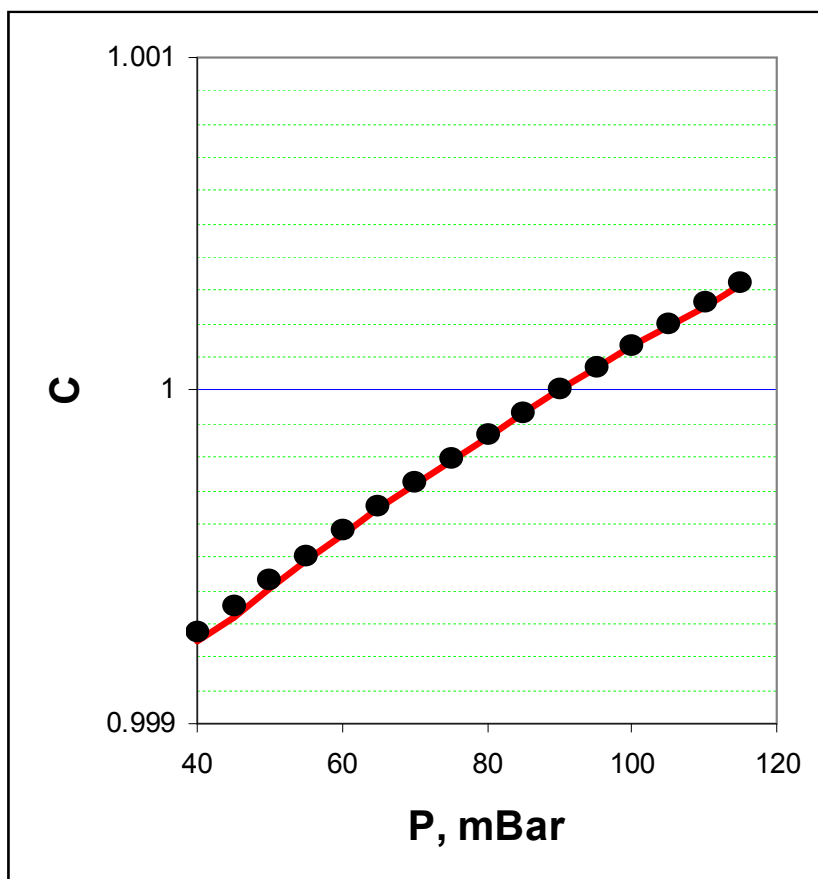$$C = \frac{AS(P)}{F4(P)}$$
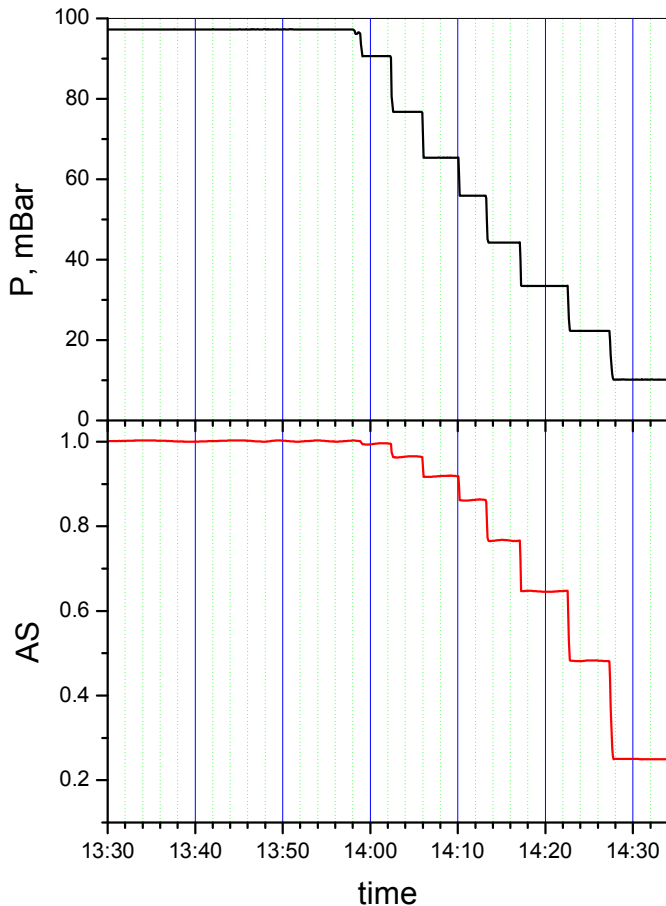
Pressure in analytical cell (black) and analytical signal (red) time dependence.

Results of concentration for pure CO_2 sample obtained for two calibration runs. Prediction C = 1. **_Accuracy 0.03 % was demonstrated._**

Temperature dependence

Analytical signal temperature dependence is due to several facts.

Absorbance is determined by molecules number density. So pressure presented in pictures is pressure corresponding 296 K.

For Foigt line and measurement procedure in use F4(P) depends on ratio of Lorentz to Doppler widths - WHH_L/WHH_D. Both are temperature dependent.

Collision broadening is determined by molecular interaction leading to temperature exponents:

0.25 - quadruple - quadruple interaction (self broadening);

0.3 - Van-der-Vaals interaction (broadening by N_2).

Results of temperature dependence modeling for pure CO_2. F4 was obtained at 296 K. Figure shows result of measurement for 298 K. Red curve is result of procedure considered above. Temperature dependence can be around 0.1 % for 2 K. For correction procedure considered it can be reduced to 0.01 %

***All options considered above are doing automatically.***

Calibrated gas mixture preparation

Analytical cell was filled with P_{CO2} = 10.19 mBar of pure CO_2. Than pure N_2 was added up to total pressure P_0 = 62.12 mBar.

By definition gas mixture concentration of this sample is:

$$C_0 = \frac{P_{CO2}}{P_0} = 16.41\%$$

Filling the cell with N_2 press CO_2 from optical path of the instrument to connecting tubes of vacuum system leading to smaller analytical signal just after filling. Due to molecular diffusion analytical signal approached to constant value. To be sure about gas mixture homogeneity it was remained in the cell for 1 day.
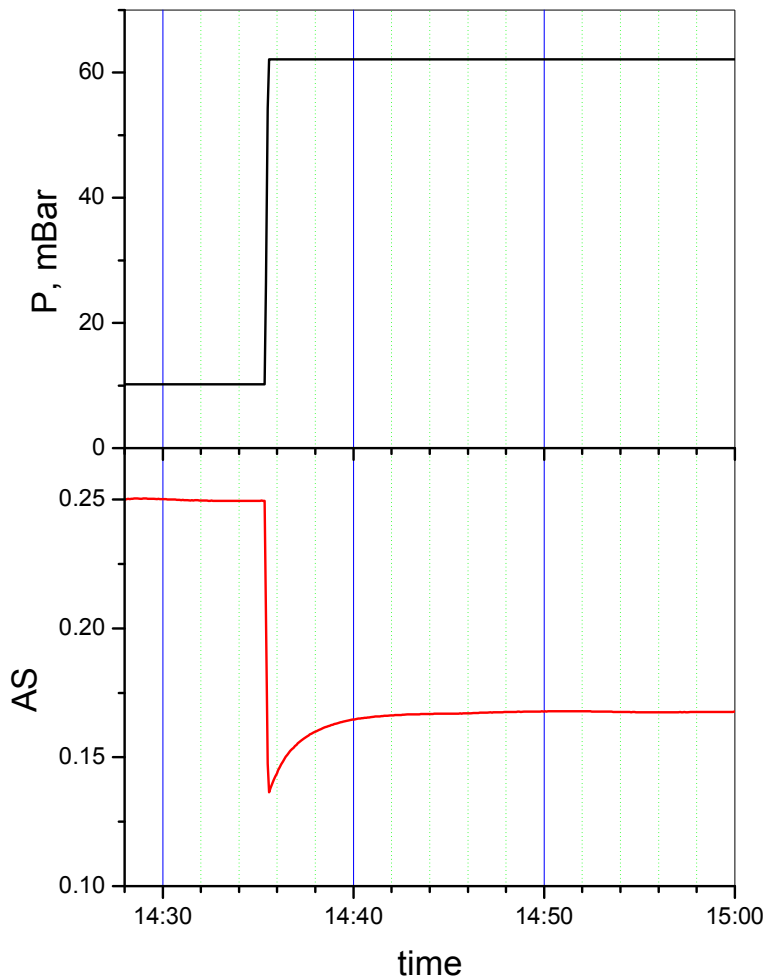
Concentration pressure dependence
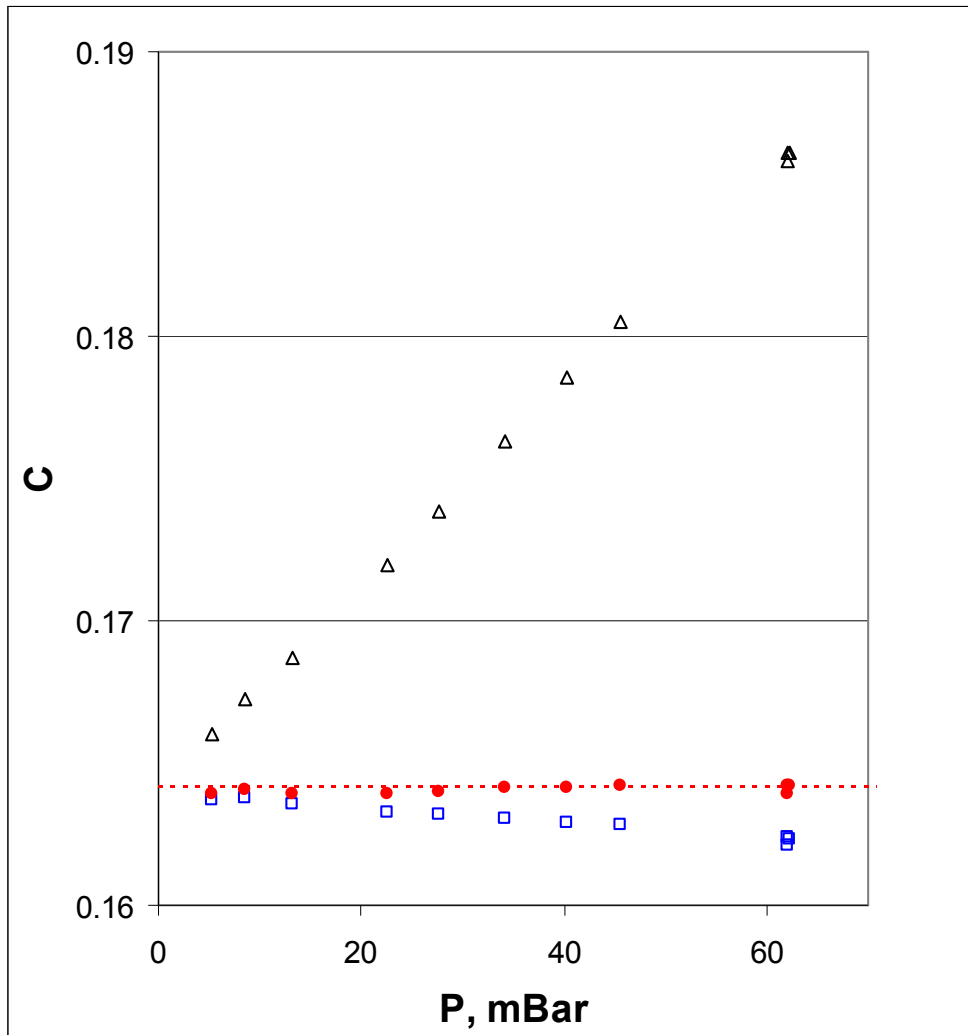
Concentration of calibrated gas mixture prepared was measured at different pressure (black triangles). Linear dependence can be observed with intercept close to C_0 (red dashed constant). It is due to the fact that analytical signal pressure dependence is function of ratio of collision broadening to Doppler width. When gas mixture is measuring corrected pressure dependence has to be used:

$$F4_{corrected}(P) = F4(xP)$$

$$x = \frac{\gamma_{self} C + \gamma_{N_2}(1 - C)}{\gamma_{self}}$$

Blue squares - γ_{air} from HITRAN,
Red solid circles - γ_{N2} as measured in present work.

Instrument developed operation

Example of one calibrated mixture measurement.
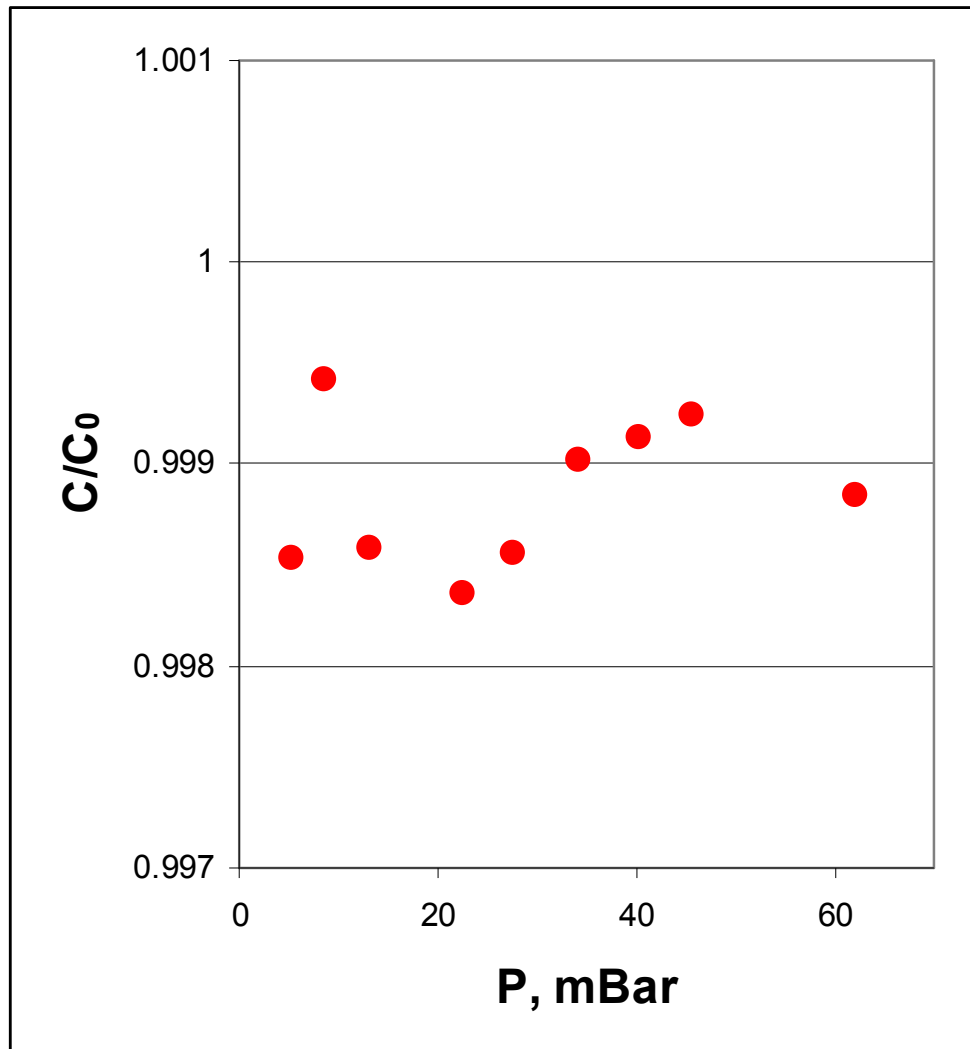
Using instrument and software developed several calibrated CO_2:N_2 gas mixtures were measured.

Parameters achieved for example presented:

Precision (std) – 0.04 %

Accuracy (offset) – 0.12 %

Gas mixtures measurement
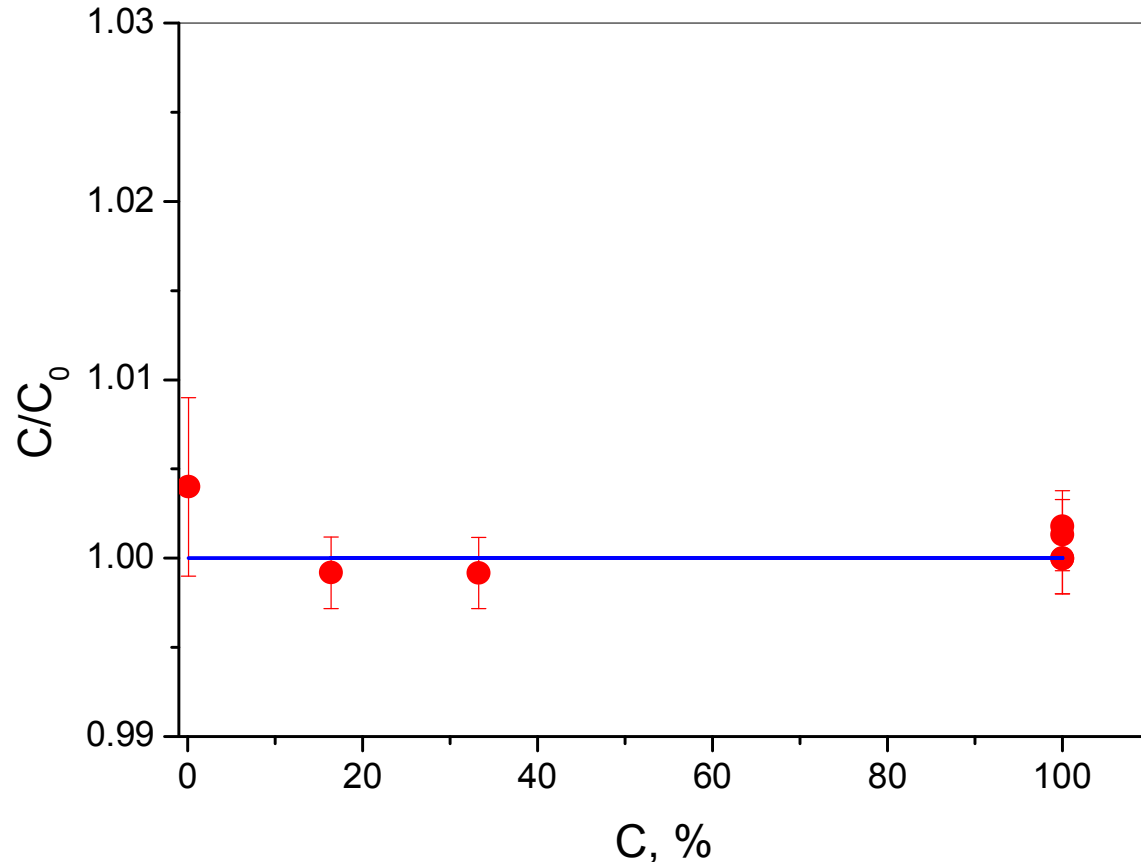
Several calibrated CO_2:N_2 gas mixtures above 10 % were prepared and measured using instrument and software developed.

Accuracy (std) = 0.11 %.

The instrument was developed for VNIIM – organization responsible for gas mixture standards in Russia. Left point in graph sample from VNIIM after isotope content correction. Error is higher because concentration is dramatically smaller.
For accurate measurements of sample with concentration less than 1000 ppm multi-pass optical cell has to be incorporated in the system under consideration.

Accuracy estimate

	Value	Error	Error %
L, cm	99.95	0.05	0.05
T, ^{o}C	20 - 25	0.2	0.007
P, mBar	0 - 100	0.07	0.07
CO_2 sample purity, %	99.98	0.02	0.02
PD non-linearity			0.02
Channels equivalence			0.05
Pressure dependence			0.11
Total			0.15

Results obtained 0.12 % accuracy of calibrated CO_2:N_2 gas mixtures measurements using TDLS instrument developed are in good agreements with accuracy estimation. ***TDLS can be considered as gas mixtures standard at 0.12 % level accuracy.***

Conclusion

Several error mechanisms of accurate measurements in TDLS were considered and their influence was minimized.

Instrument for high accurate gas mixture measurement with TDLS was optimized and developed.

Software of the instrument operation and calibration procedures were developed.

After this moment no the instrument calibration is necessary.

Using calibrated gas mixtures the instrument developed tests were performed.

Accuracy level achieved 0.12 % is in agreement with accuracy estimation.

Based on achieved accuracy and analysis performed, TDLS can be considered as high accurate gas mixtures primary standard.