

# MEASUREMENTS OF THE $^{13}\text{CO}_2/^{12}\text{CO}_2$ ISOTOPE COMPOSITION USING THE TDLS TECHNIQUE

*A. Berezin, S. Chernin, A. Makkaveiskii, A.  
Nadezhdinskii, Ya. Ponurovskii, D.  
Stavrovskii*

*Natural Sciences Center of the A.M. Prokhorov*

*Moscow General Physics Institute, RAS*

*38 Vavilov street, 119991 Moscow, Russia*

*E-mail: jakov@nsc.gpi.ru*

*A. Babichev, G. Grigoriev, S. Malyugin,  
Sh. Nabiev*

*Russian Research Center "Kurchatov Institute"*

*1 Kurchatov sq., 123182 Moscow, Russia*

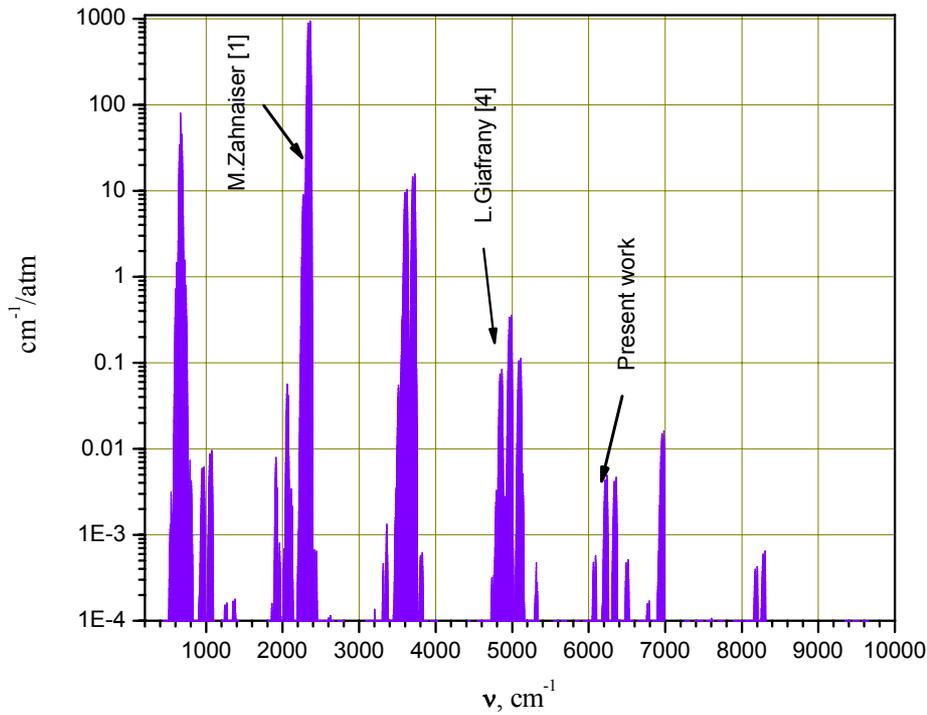
# Introduction

Isotopes abundance measurements are important now for variety of applications: Deposit oil fields and gas; control of an ecological situation and man-caused accidents, it is especial in connection with recent entrance into force of the Kyoto treaty; and several medical applications (for example, “breath-test” - an efficient method of diagnostics of gastrointestinal tract diseases), etc. Goal of present paper was instrument development for accurate absolute isotopes abundance measurements for CO<sub>2</sub> molecule.

Absorption lines R4 <sup>12</sup>CO<sub>2</sub> and P12 <sup>13</sup>CO<sub>2</sub> located near 6232.5 cm<sup>-1</sup> were chosen taking into account independence of results obtained on sample temperature [1]. Fiber pigtail Anritsu DFB DL was used to cover spectral range near 1.6 μm. We've used our traditional DL operation mode (see separate poster). “Chernin” multipass cell with total optical path of 42 m was used in the instrument analytical channel. Absorption of main isotopomer spectral line was chosen close to 0.1 to reduce influence of DL electromagnetic field spectrum on results obtained [2]. To reduce instrument operation time observed spectral lines were fitted by Gaussian profile using HITRAN [3] data to determine isotopomers partial pressure. Special procedure was developed to removed baseline (see separate poster) influence on results measured. Intercomparison campaign between Mass-Spectrometer (MS) and the instrument developed (TDLS) was performed using several gas samples having different isotopes abundance.

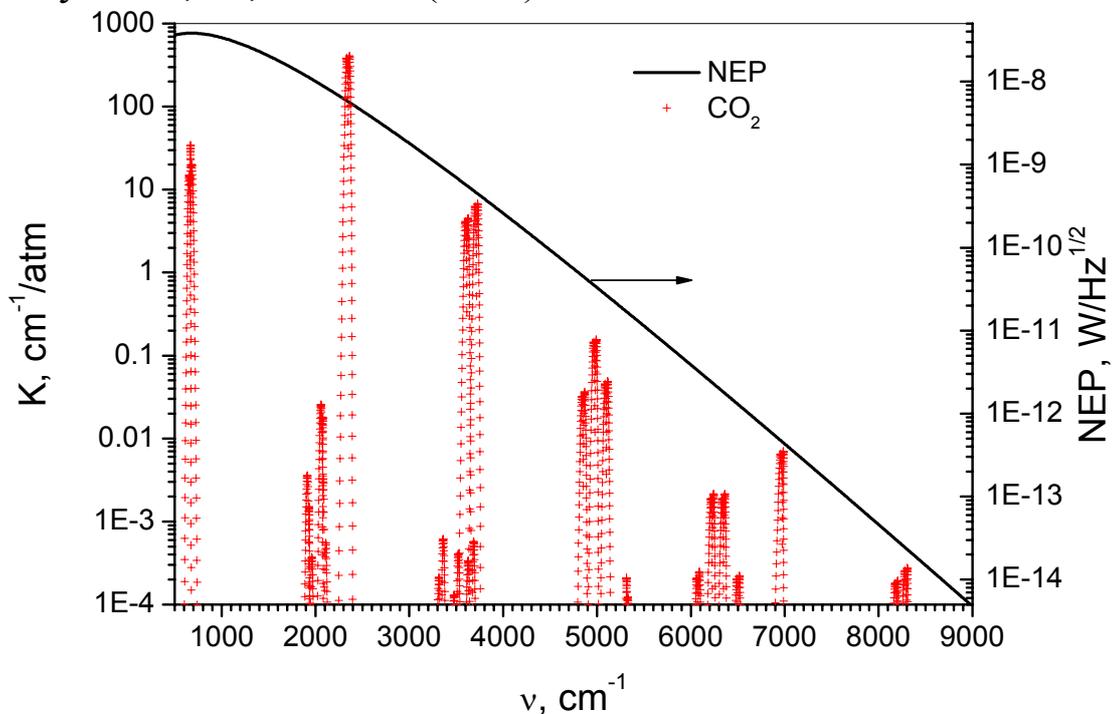
Precision achieved for present measurement is equal to 0.013 % and is caused by DL quantum noise. Analysis shows that this value can be considered as accuracy if HITRAN data are accurate enough. Achieved precision corresponds to minimum detectable absorption at level of  $1.3 \cdot 10^{-7}$ .

1. J.McManus, M.Zahniser, D.Nelson, L.Williams, C.Kolb, *Spectrochimica Acta*, A58, 2465-2479 (2002)
2. Nadezhdinskii A I, et al, *Quantum electronics*, **29**, (10) 916-920 (1999).
3. L.S. Rothman, et al, The HITRAN 2004 molecular spectroscopic database, *JQSRT*, vol. **96**, No.2, Dec. 1 (2005) in press.



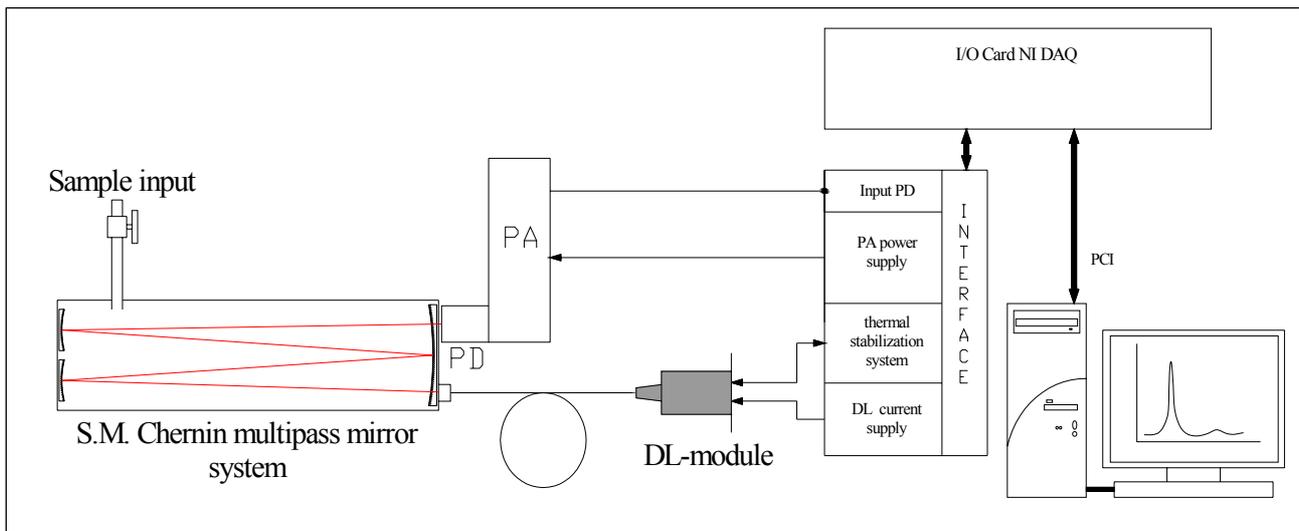
CO<sub>2</sub> cross section (cm<sup>-1</sup>/atm) [3] and spectral ranges used by different groups to measure carbon isotope ratio

4. G. Gagliardi, A. Castrillo, R. Iannone, E. R. Th. Kerstel, and L. Gianfrani, Applied Physics B, 77, 119-124 (2003).



Comparison between CO<sub>2</sub> absorption spectrum and photo-diode NEP (Noise Equivalent Power).

# Experimental Setup



## Experimental setup block-scheme.

**Diode module** incorporated an “Anritsu” DFB DL with fiber pigtail emitted at wavelength  $\lambda=1.6 \mu\text{m}$ , a thermistor and a Peltier thermo element. Chernin **multipass cell** with the 25 cm base length. The cell design permitted evacuation of the cell and filling it with the gas to be analyzed under low pressure.

**Photodetector** with a **preamplifier** installed on the cell provided for registration of the outgoing radiation.

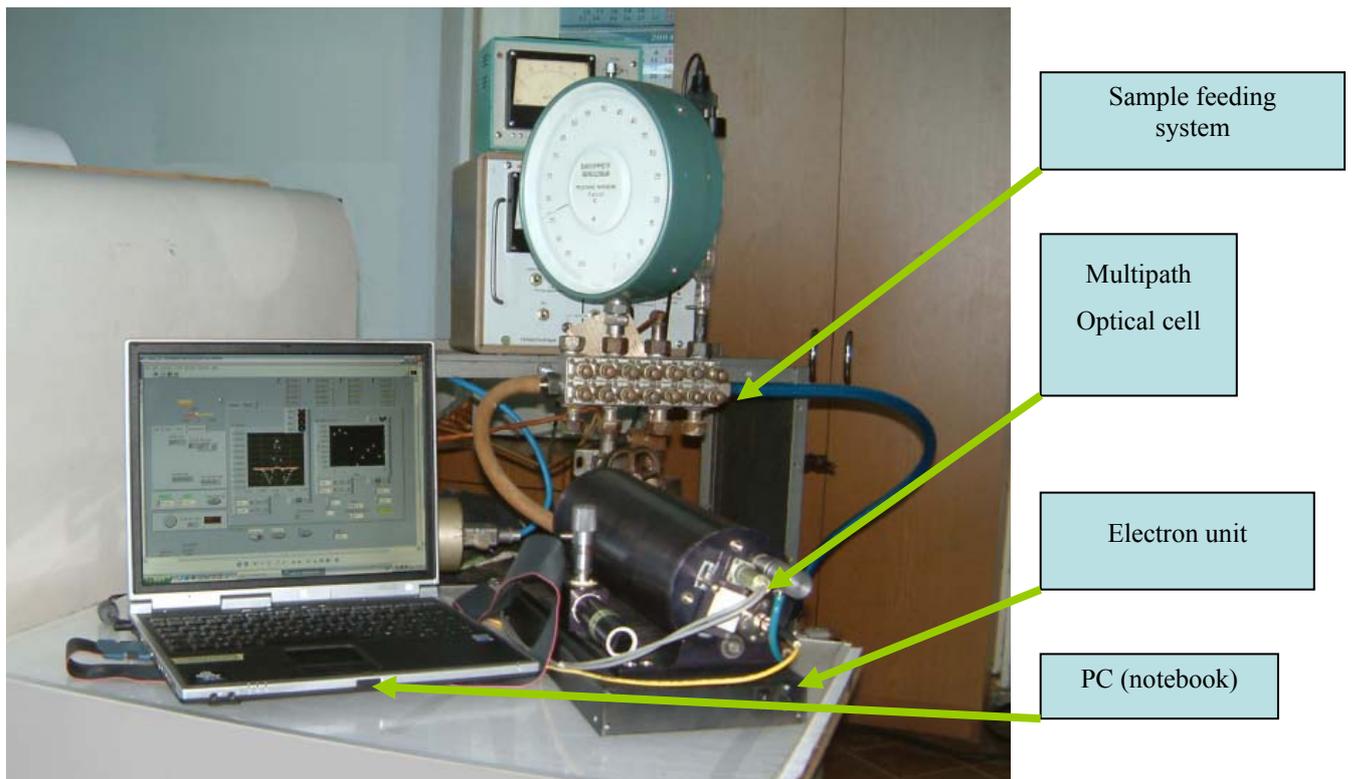
**Interface module** is intended for controlling the DL-module and the monitoring system. It incorporates a DL pumping current supply, a DL thermal stabilization system, and a PD preamplifier power supply.

To **control** DL pumping and thermal stabilization systems, and to record signals with their subsequent processing in a gas analyzer, use was made of I/O Card NI DAQ PCI-6052E of “National Instruments”. The control of the measurement process was executed by software running under the NI LabView 7.0 environment.

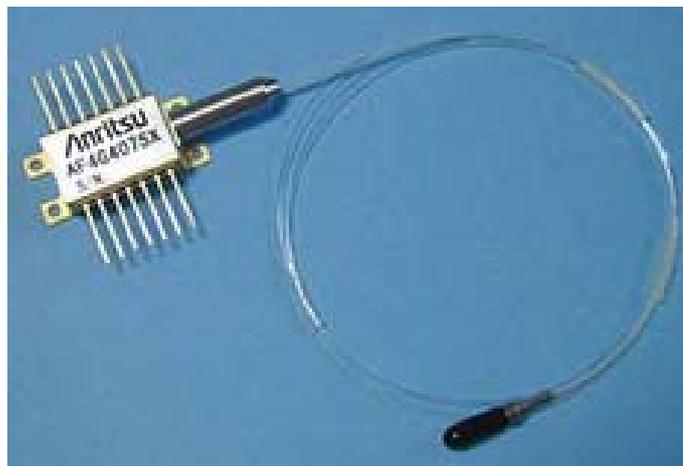
**The diode laser** was pumped with trapezoidal pulses. The current pulse magnitude,  $I_{\text{oper}} \sim 80 \text{ mA}$ , the pulse length was 0.4-1 ms, and the repetition rate was 5 kHz. DL frequency tuning ( $\Delta\nu \sim 2 \text{ cm}^{-1}$ ) took place because of changing of the refraction index of the laser active region during a pumping current pulse.

Scanning over the whole region of frequency tuning ( $\sim 60 \text{ cm}^{-1}$ ) was performed with the temperature stabilization system via smooth variation of the laser crystal temperature with a Peltier thermo element.

# Instrument View

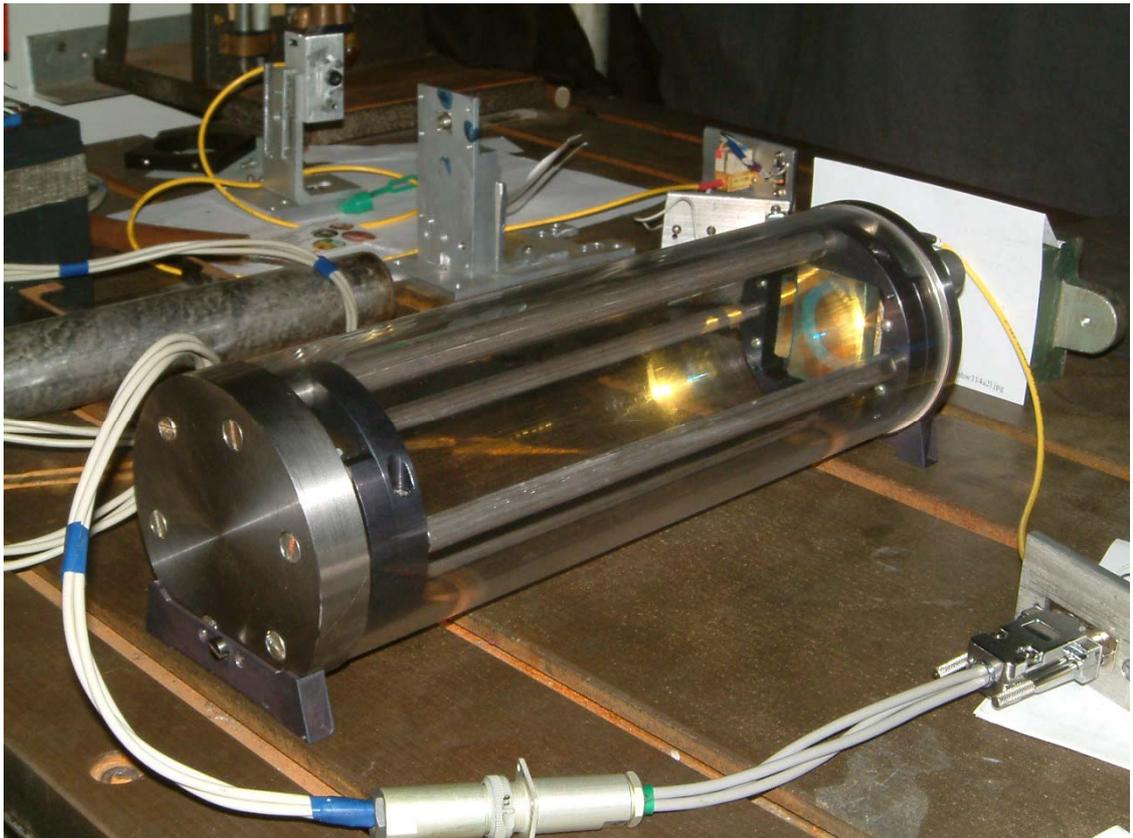
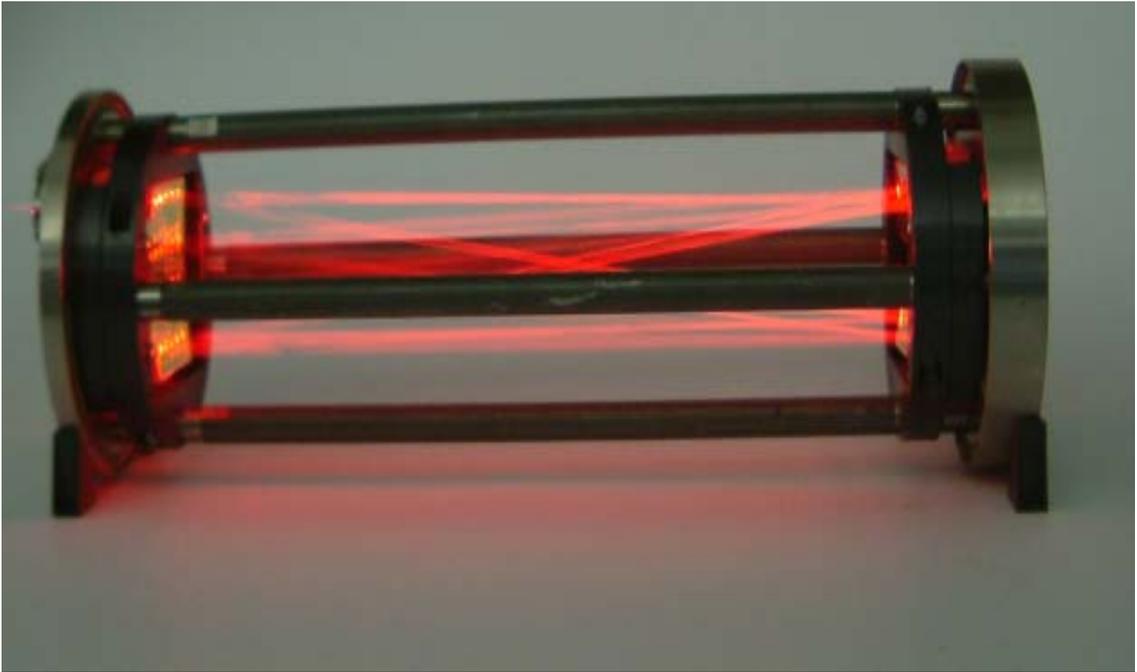


General view of the  $^{13}\text{CO}_2/^{12}\text{CO}_2$  measuring setup



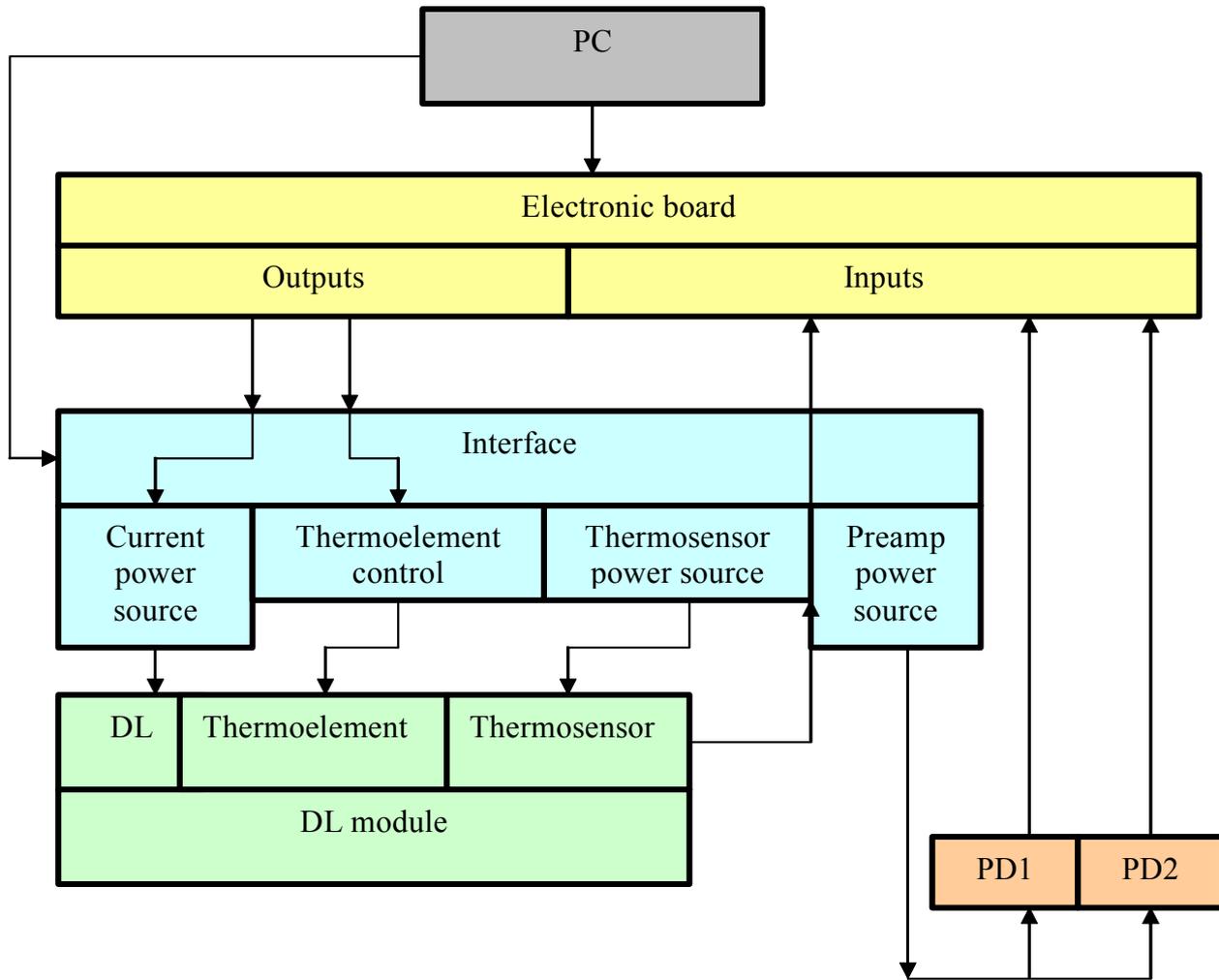
Anritsu DFB DL with fiber pigtail  $\lambda=1.6\ \mu\text{m}$

# Chernin Multipass Cell



Chernin multipass cell: baselength - 25 cm, dielectric mirrors with 99.5 % reflectivity; 182 passes, 45.5 m.

# Electrical Block-Scheme



View of interface module

# $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ absorption spectra. Procedure of determining the isotope composition

Fig.a shows a model  $\text{CO}_2$  transmission spectra in the vicinity of  $1.6\ \mu\text{m}$  (according to the HITRAN). Red curves represent the contribution of  $^{13}\text{CO}_2$  absorption for the natural isotope abundance. Analytical spectral lines have been chosen so that the gas temperature in the cell produced practically no effect on the measurement results. Therefore, lines with equal temperature dependence of absorption cross-section (see Fig.b) have been chosen. The bottom of Fig. a shows the chosen spectral region and analytical spectral lines of two isotopes of carbon dioxide. Analytical lines were R4 for  $^{12}\text{CO}_2$  and P12 for  $^{13}\text{CO}_2$ .

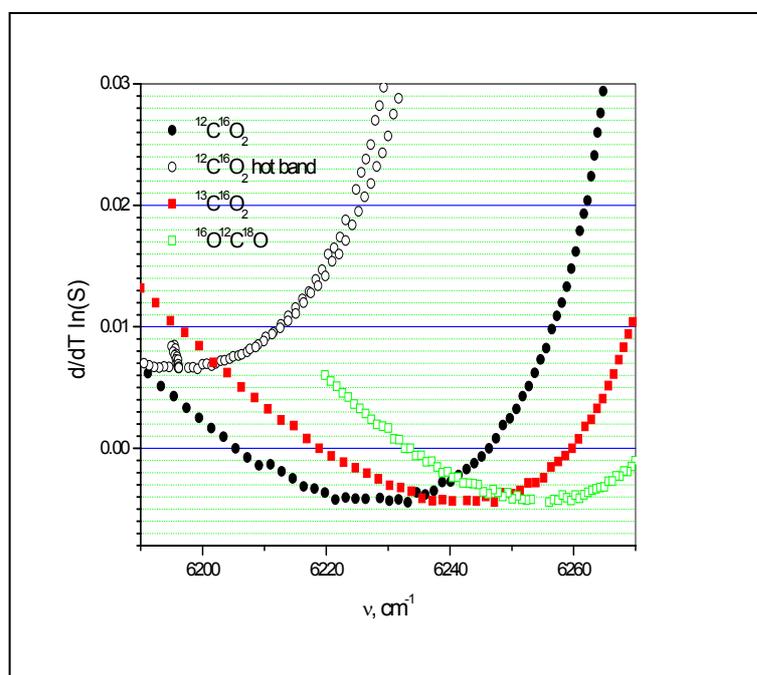
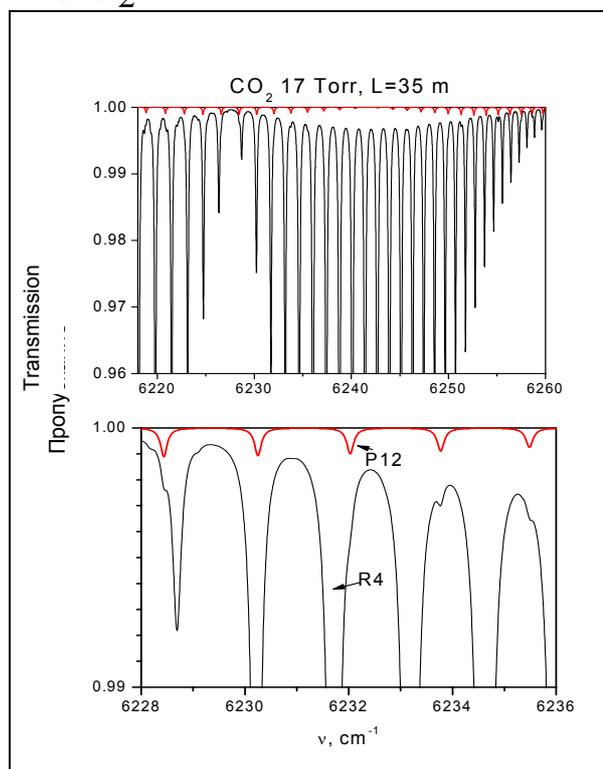
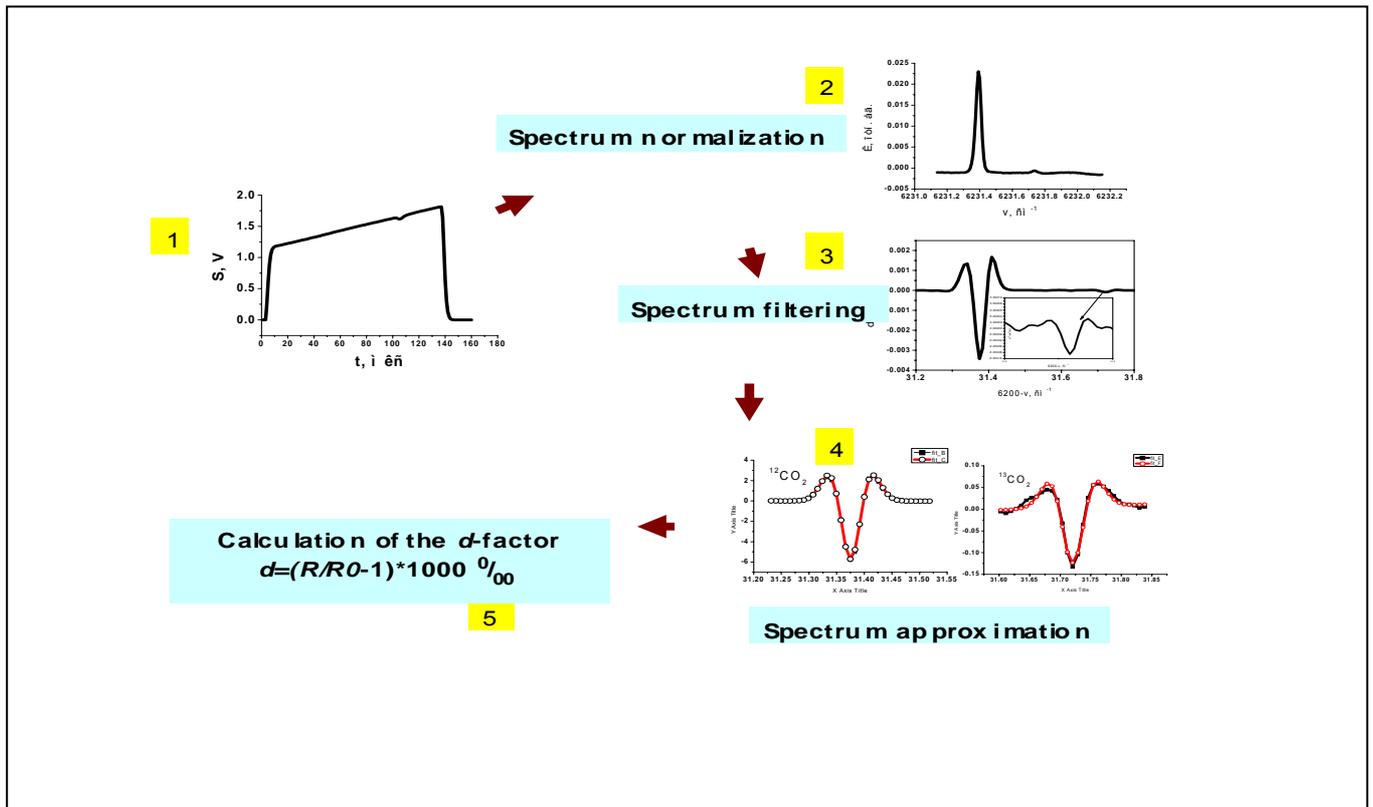


Fig.a  $^{13}\text{CO}_2$  and  $^{12}\text{CO}_2$  transmission spectra [1]

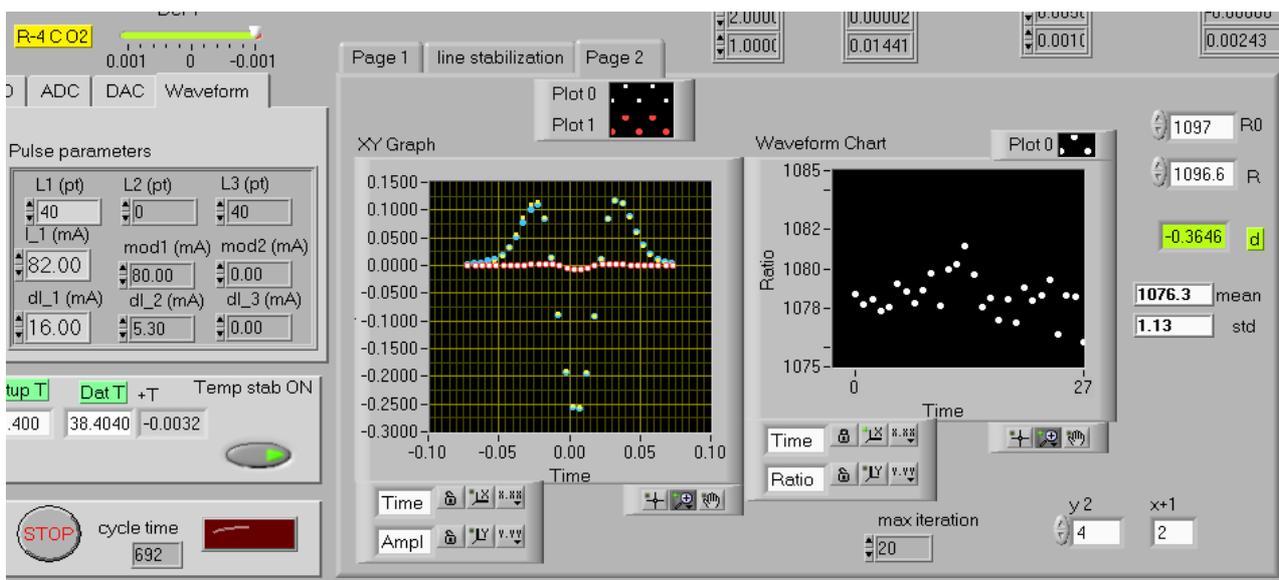
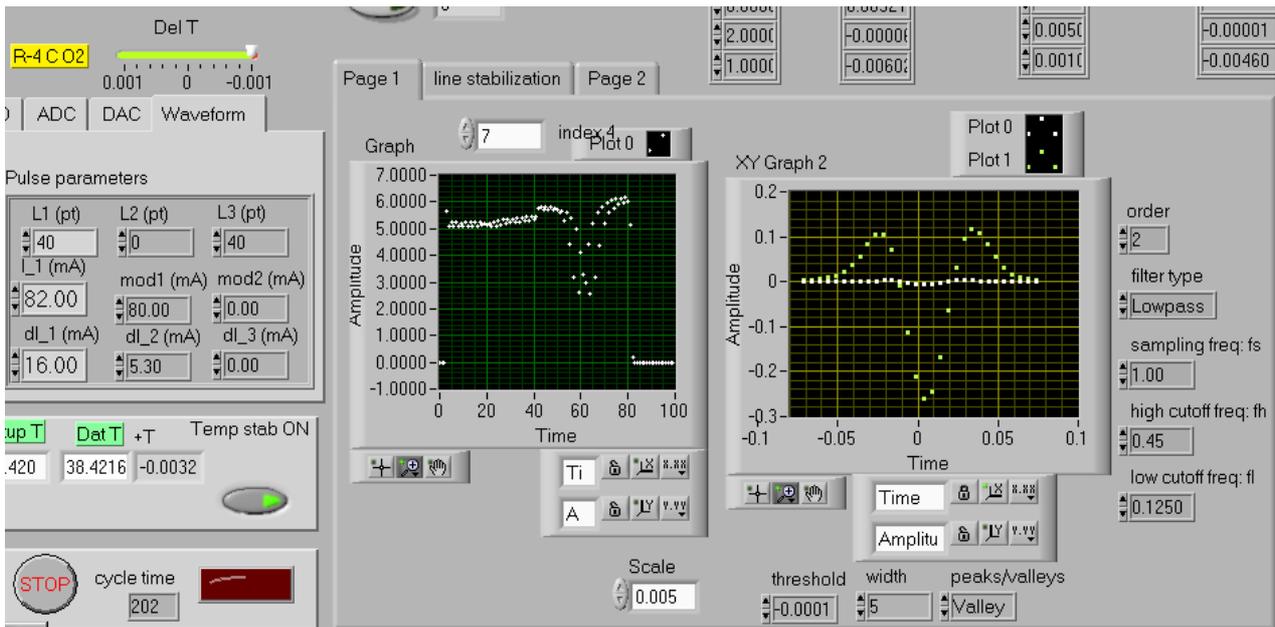
Fig.b. Relative temperature dependence coefficient for absorption cross-section of spectral lines.

# Data Processing



1. Signal recording.
2. Spectrum normalization and frequency scale linearization. Absorption coefficient determination.
3. Spectrum filtering. Absorption spectral line second derivative is used as filter giving second derivative auto-correlation function of the line.
4. Spectrum approximation. It was made with the second derivative of the Doppler profile.
5. Calculation of the  $d$ -factor. The ratio of  $R$  integral absorption coefficients of <sup>13</sup>CO<sub>2</sub>/<sup>12</sup>CO<sub>2</sub> is found and then magnitude  $d = (R/R_0 - 1) * 1000 \%$  is calculated.  $R_0$  was obtained from [3].

# Software

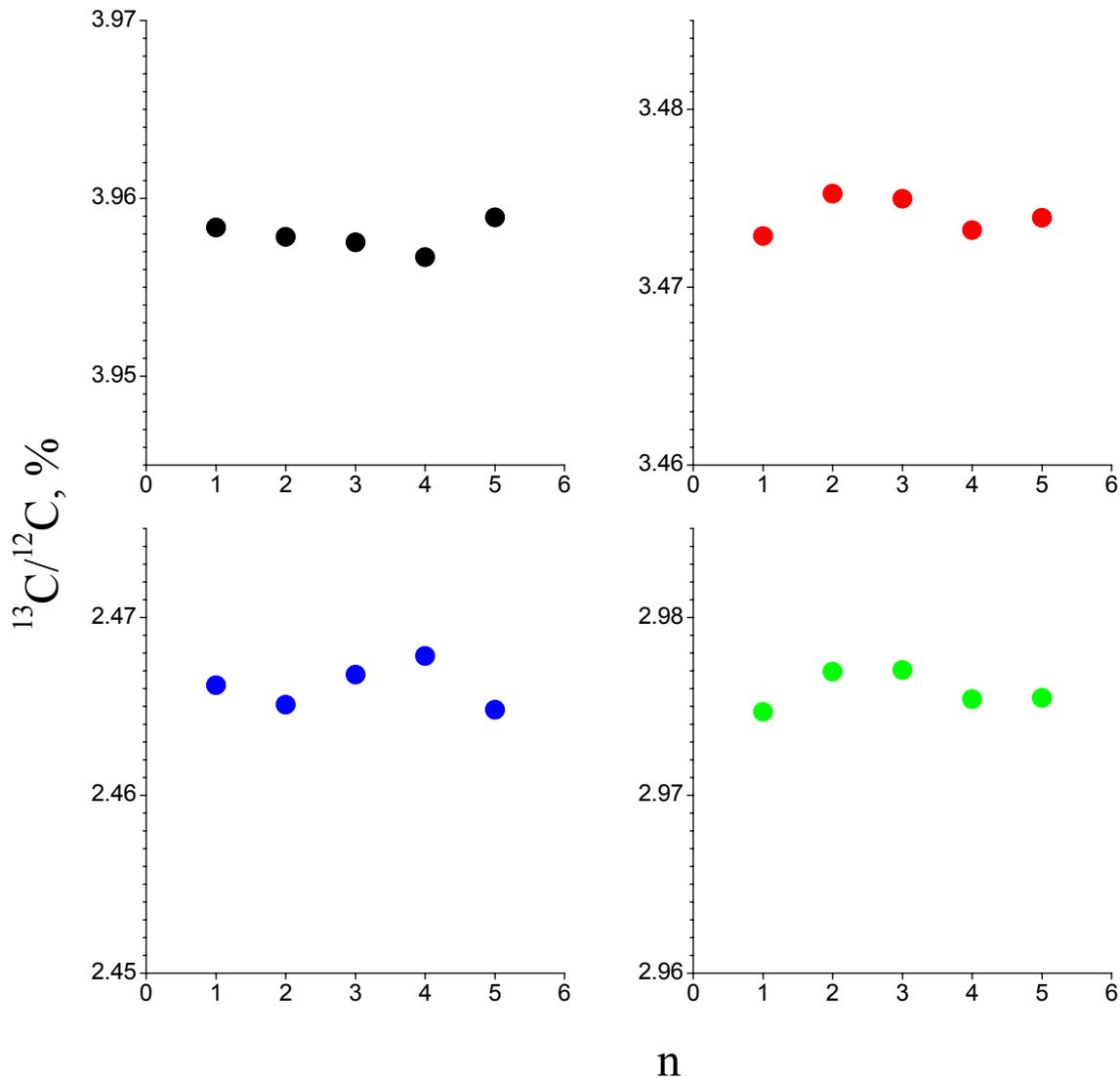


Software control panel view.

Software running under the LabVIEW graphical programming environment permits real-time control of the measurement and data processing. Full time of 100 pulses accumulation, averaging and data processing took 0.2 s.

# Device Calibration

Intercalibration campaign was performed with the Institute of Molecular Physics of RRC “Kurchatov Institute”. Five calibrated carbon dioxide gas samples of various isotope composition were prepared. Isotopes ratio in these samples was measured with a mass-spectrometer and TDLS.



Results obtained using instrument developed.

Multipass cell was filled with five probes of each gas sample, and isotopes ratio was measured (five points on each picture).

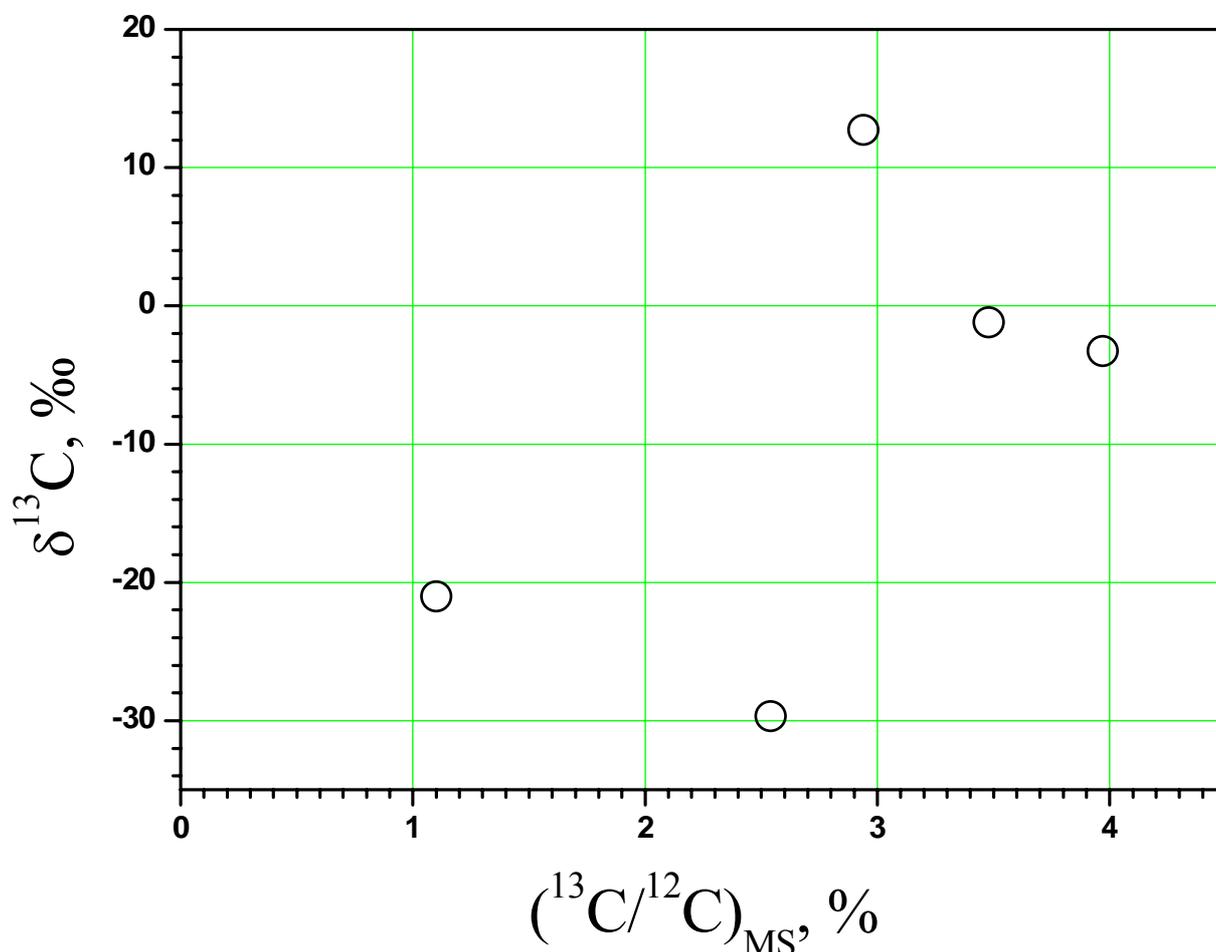
Precision achieved - 0.13 ‰ was limited by DL intensity quantum noise. This precision corresponds to minimum detectable absorption at level of  $1.3 \cdot 10^{-7}$ .

# MS and TDLS Inter-Comparison

Results of intercalibration campaign are presented in Table 1.

**Table 1**

Sample No	15	5	25	3	1
$(^{13}\text{C}/^{12}\text{C})_{\text{DLS}}, \%$	3.97	3.47	2.46	2.97	1.08
$(^{13}\text{C}/^{12}\text{C})_{\text{MS}}, \%$	3.97	3.48	2.54	2.94	1.10



Inter-comparison of isotopes abundance measurements by MS and TDLS. Difference between MS and TDLS results is due to MS memory with respect to previously measured samples.

Analysis shows that precision achieved - 0.13 ‰ can be considered as accuracy if HITRAN data are accurate enough.

# Breath Test

“Breath test” is well-known non invasive medical technique to detect *Helicobacter pylori* responsible for different diseases. Presence of *H. pylori* in this test is followed by changing of  $^{13}\text{C}/^{12}\text{C}$  ratio in infected patient breath.

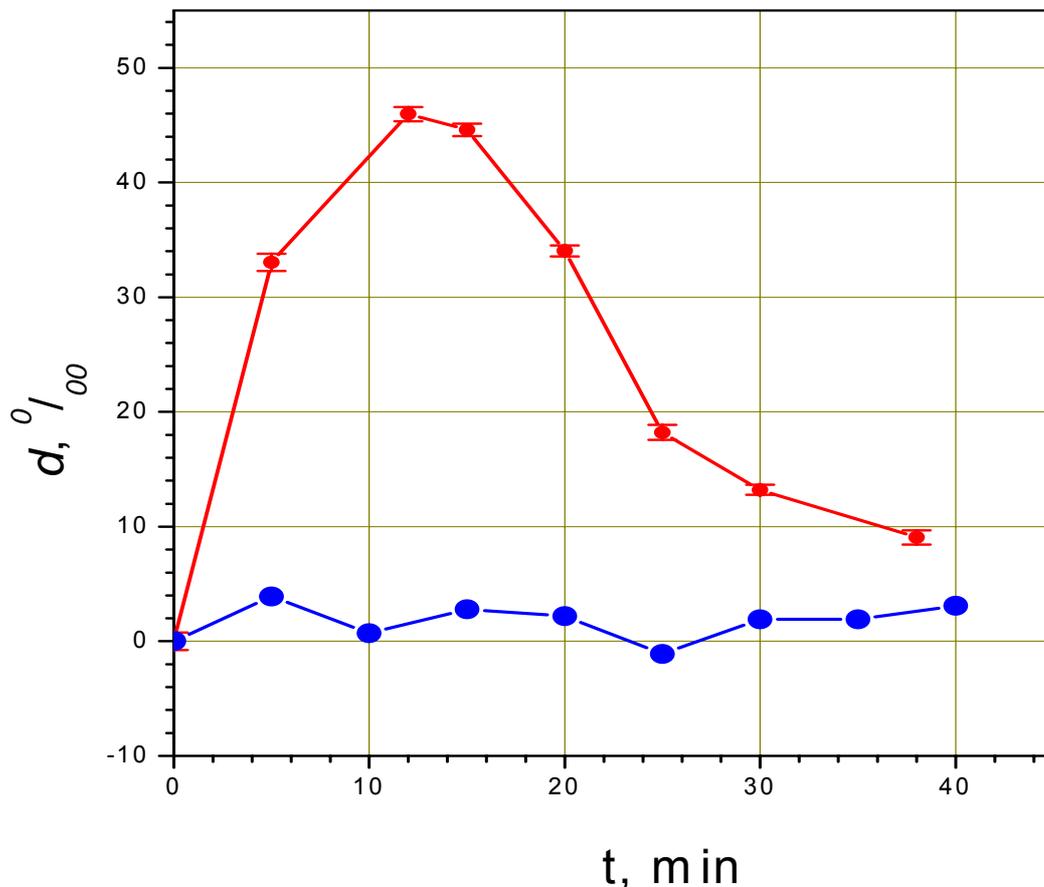


## “Breath test” instruction and accessories

Usually MS instruments are using in this diagnostics to measure isotopes ratio in breath samples.

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Example of real time clinical “breath test” results obtained using instrument developed for infected (red) and non-infected (blue) patients.

Results of clinical tests using TDLS technique and instrument developed showed that they are quite acceptable for clinical practice.

# Conclusion

The paper reports on the development of equipment and software for rapid measurements of  $^{13}\text{CO}_2$  concentration from the  $\text{CO}_2$  absorption spectrum in the near-infrared range. The relative error of the  $d$ -factor definition in the breath-test on 100-fold accumulation of single measurements was within  $0.7 \text{ ‰}$ . With the aim to determine the absolute error of isotopic ratio measurements, we took independent calibrating measurements of 5  $\text{CO}_2$  samples with different isotope composition using both DLS equipment and mass-spectrometers.

Precision achieved for present measurement is equal to  $0.013 \%$  and is caused by DL quantum noise. Analysis shows that this value can be considered as accuracy if HITRAN data are accurate enough. Achieved precision corresponds to minimum detectable absorption at level of  $1.3 \cdot 10^{-7}$ .

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