INSTRUMENT BASED ON VISIBLE DIODE LASER TO DETECT TRACE NO_2 CONCENTRATION WITH MINIMUM DETECTABLE CONCENTRATION AT PPT LEVEL

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Introduction

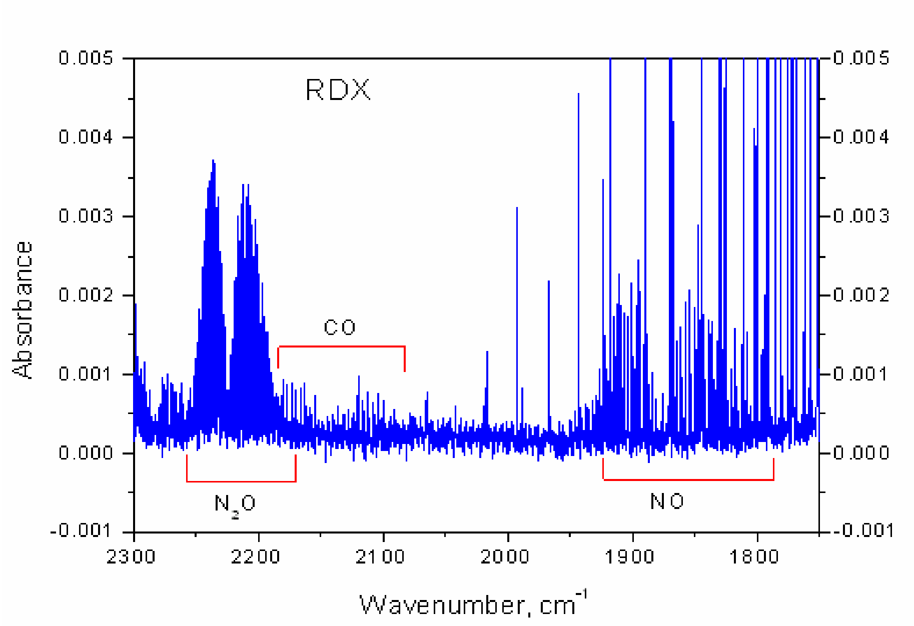
Detection of trace NO_x concentration is important for variety of applications. NO_2 molecule has intensive vibronic transition in near UV, visible, and near IR. In [1] near IR DL was used for its sensitive detection, ultrasensitive detection with visible DL was achieved in [2]. Research in this direction started in GPI several years ago and its preliminary results were presented in [3].

The instrument developed contains visible diode laser and two channels: analytical and reference ones. Analytical cannel includes "Chernin" multipass optical cell (0.5 m, 282 passes). The molecule under detection concentration was determined using signals in analytical and reference channels and cross-correlation algorithm [4, 5] proposed for complex spectra with overlapping lines. This algorithm provides optimal signal filtering and gives additional sensitivity improvement proportional to $\sqrt{\mathbf{N}}$ (N – number of spectral peculiarities in recorded spectrum).

Approaches developed recently (see separate posters) were incorporated in present instrument operation. Noise equivalent absorption achieved for this particular case was limited by diode laser intensity quantum noise and was equal to 10^{-7} for 1 sec averaging time.

Taking into account above mentioned parameters of experimental setup, instrument operation mode, and calibration procedure discussed minimum detectable absorption was found to be 2.7 ppt (atmosphere pressure – atmosphere broadened spectrum) and 0.75 ppt (for reduced pressure when broadening is close to Doppler one).

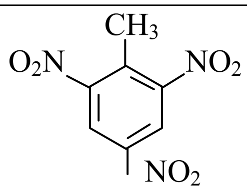
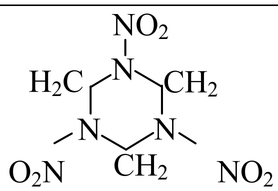
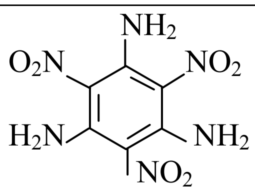
1. W.Lenth, M.Gehrtz, Appl.Phys.Lett., 1263-1265 (1985)
2. D.Sonnenfroh, M.Allen, Appl.Opt., 35, #21, 4053-4058 (1996).
3. A.Nadezhdinskii, Ya.Ponurovskii, M.Spiridonov, E.Kudryashov, in TDLS 2003, Abstracts of papers, Zermatt, 2003, p.87.
4. I.Zasavitskii, Yu.Kosichkin, A.Nadezhdinskii, E.Stepanov, A.Tishenko, A.Shotov, Kratkie soobsheniya po fizike, №9, 13-17 (1983) (in Russian).
5. A.Nadezhdinskii, I.Zasavitskii, in "Monitoring of gaseous pollutants by tunable diode lasers", R.Grisar, H.Preier, G.Schmidtke, G.Restelli (Ed.), Proc. Int. Symposium, Freiburg, FRG 1986, D.Reidel Publ.Com., Dordrecht, 1987, p.95-106.



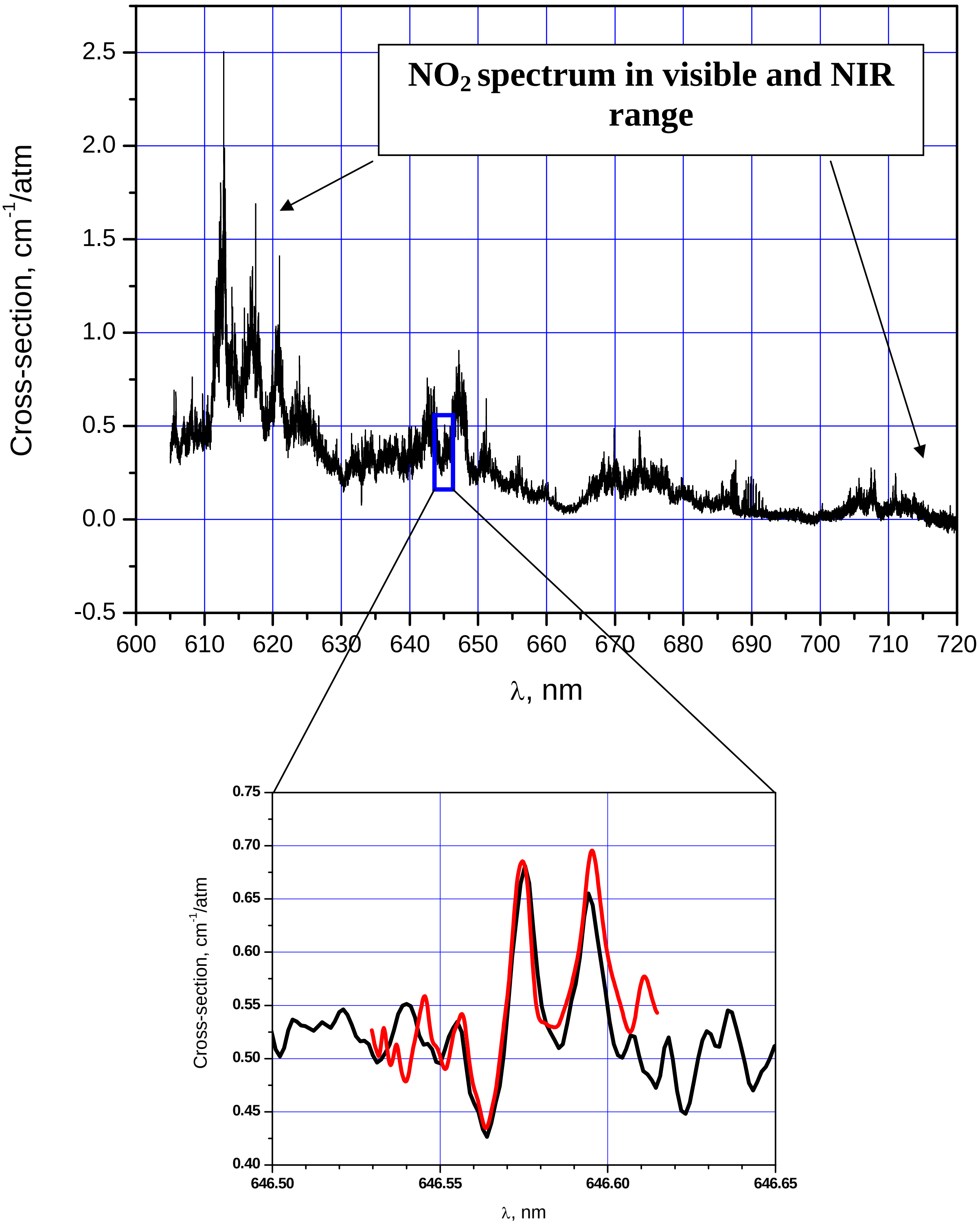
Absorption spectra (FTS Bruker 66-v) of explosives decomposition products have been investing-ated using FTS Bruker 66-v.

RDX decomposition products absorption spectrum in Mid IR.

Table 1
Saturated vapor pressures of the several explosives (TNT, PETN, RDX, TATB).

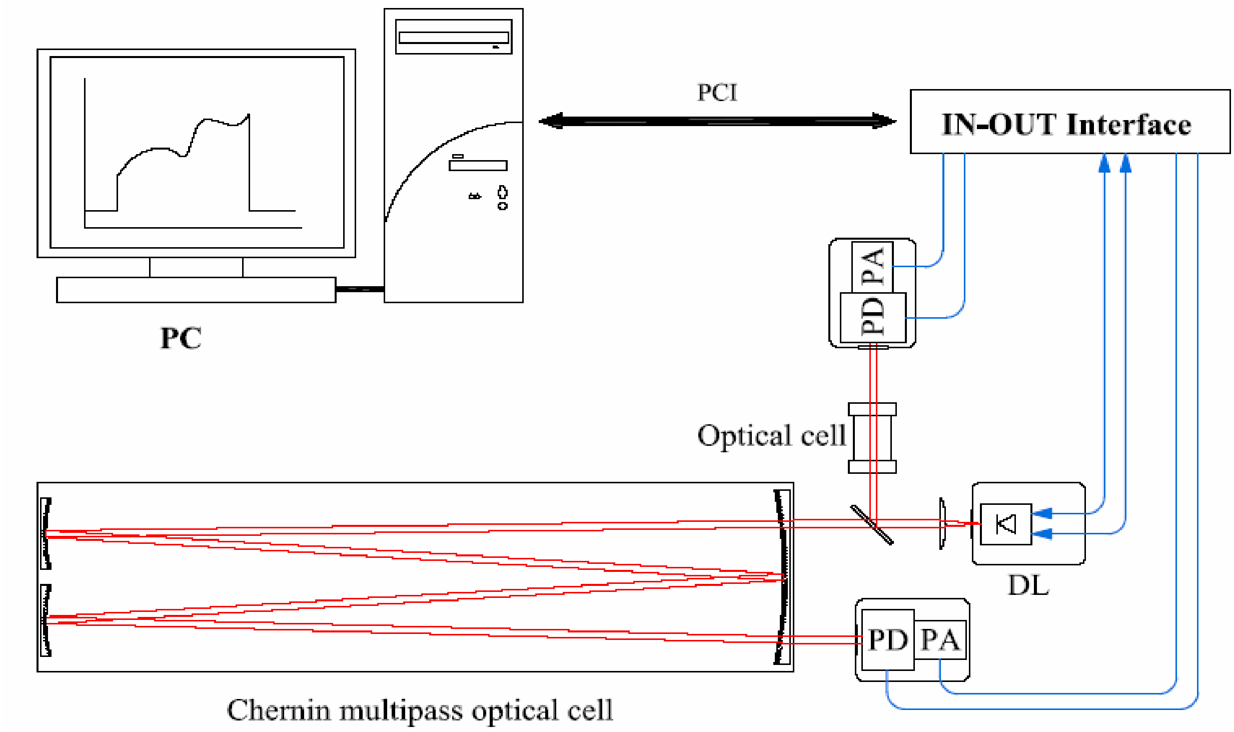
Substance	**Structural formula**	**Saturated vapor pressure (ppb)**	
		300K	**400K**
Trinitrotoluene (TNT)		13	4.7×10^5
Pentaerythritol tetranitrate (PETN)	CH_2ONO_2 | O_2NOCH_2-C-CH_2ONO_2 | CH_2ONO_2	0.0026	2.8×10^4
Hexagen (RDX)		0.0084	2.1×10^3
1,3,5-Triamino-2,4,6-trinitrobenzene (TATB)		3.6×10^{-9}	7.6×10^{-2}

An analysis has been performed of the physics and chemistry of drugs and explosives. While both drugs and explosives have very low saturated vapor pressure in standard environment they can be determined by detecting products of their decomposition.



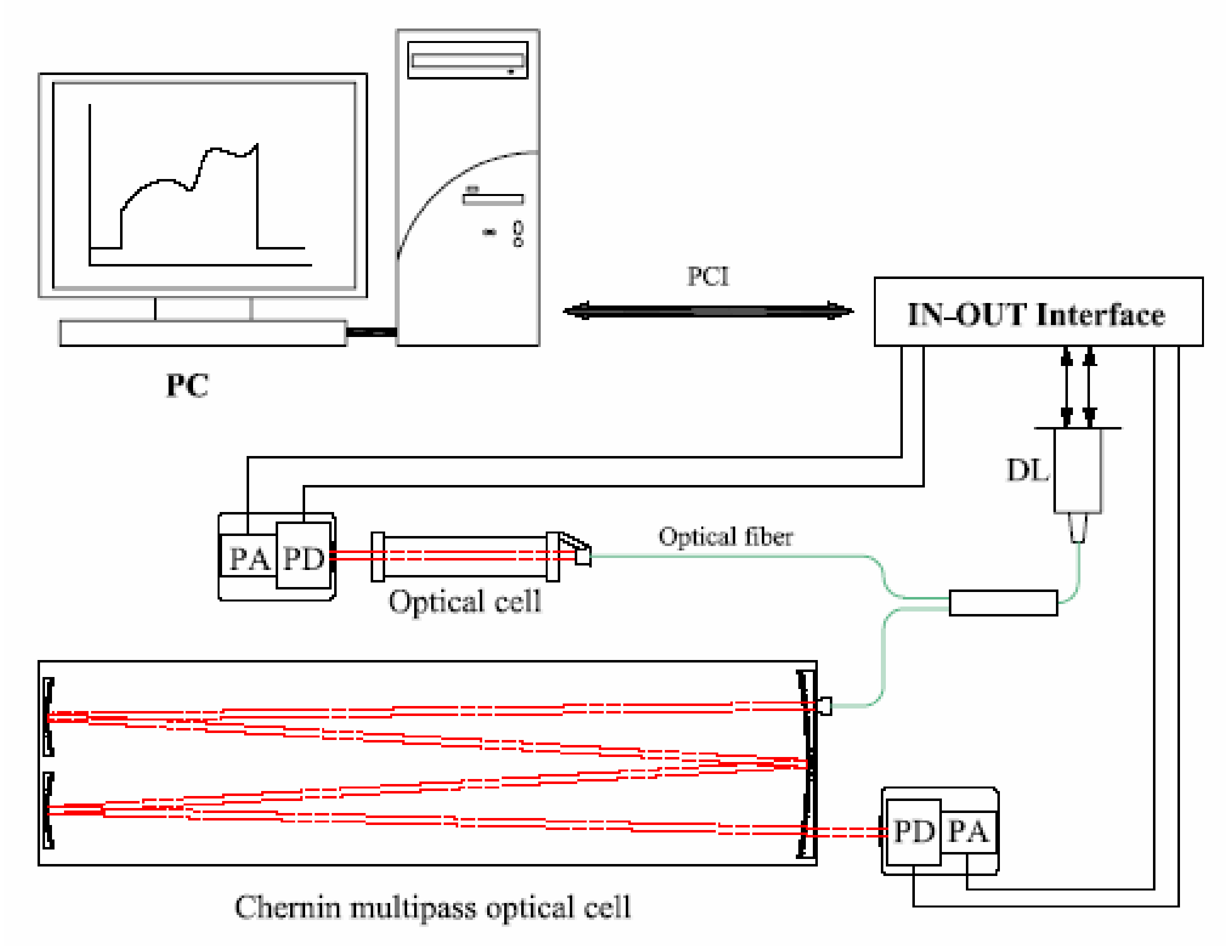
Identification of the Diode Laser and FT spectra near 646 nm. The Diode lasers that have been tested included about 70 visible (635-680-nm) diode lasers manufactured by Toshiba, Sanyo, Hitachi, Mitsubishi and Russian companies (Polus, Nolatech).

Block-Scheme

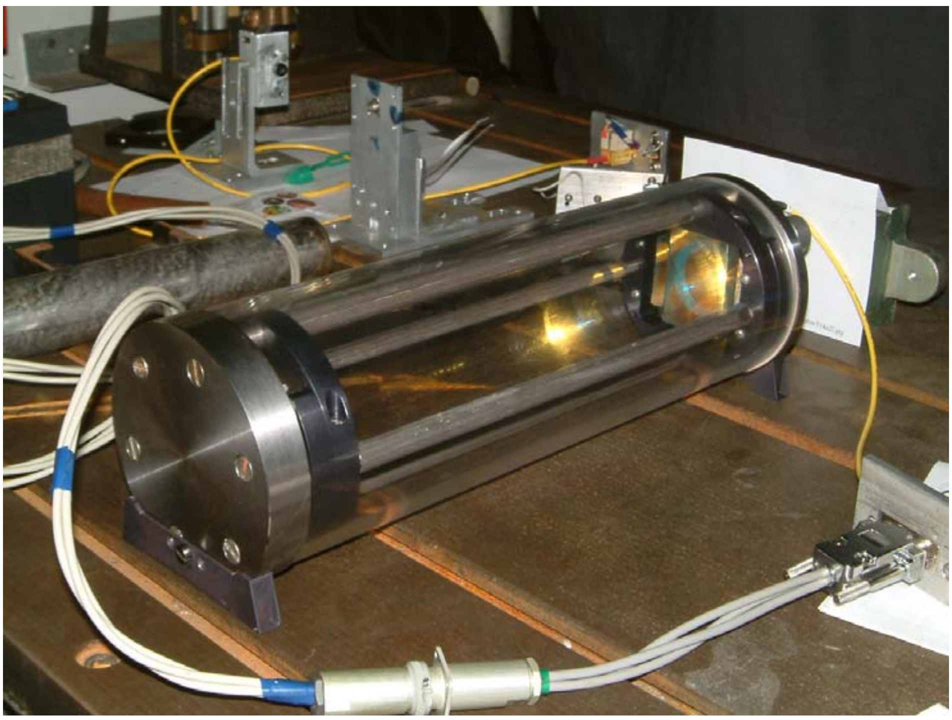


Instrument View

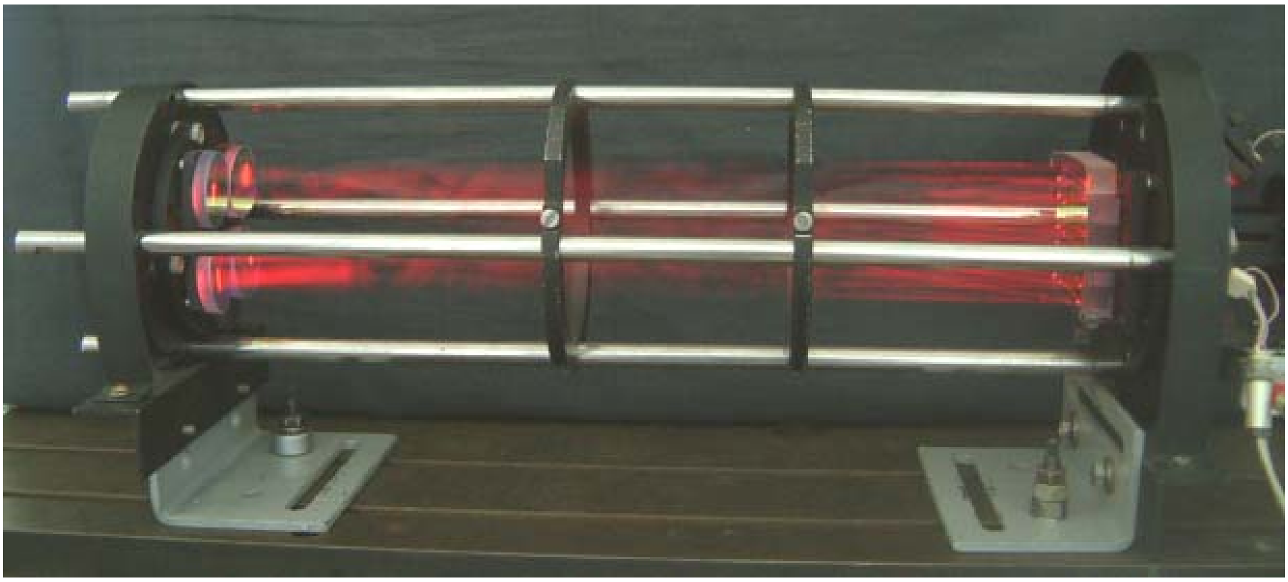
Block-Scheme for fiber coupled DL

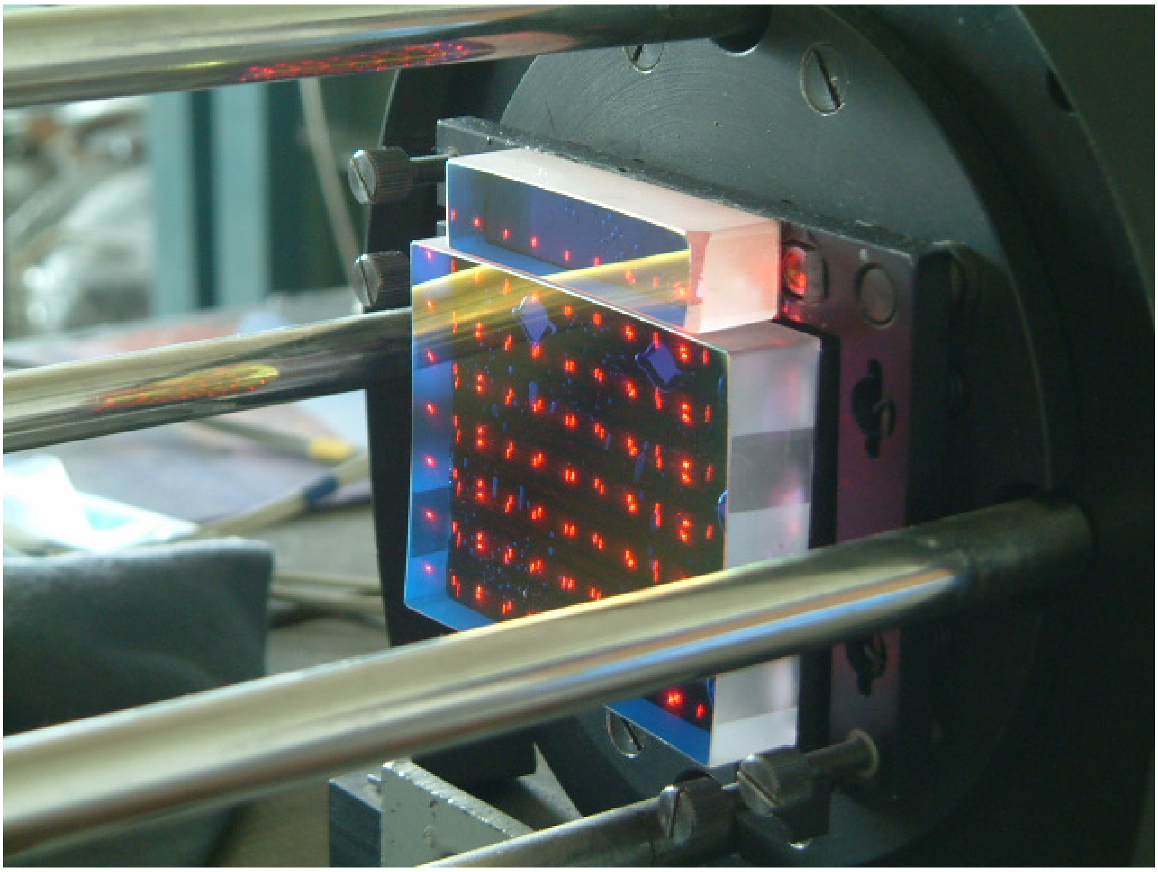


Instrument View



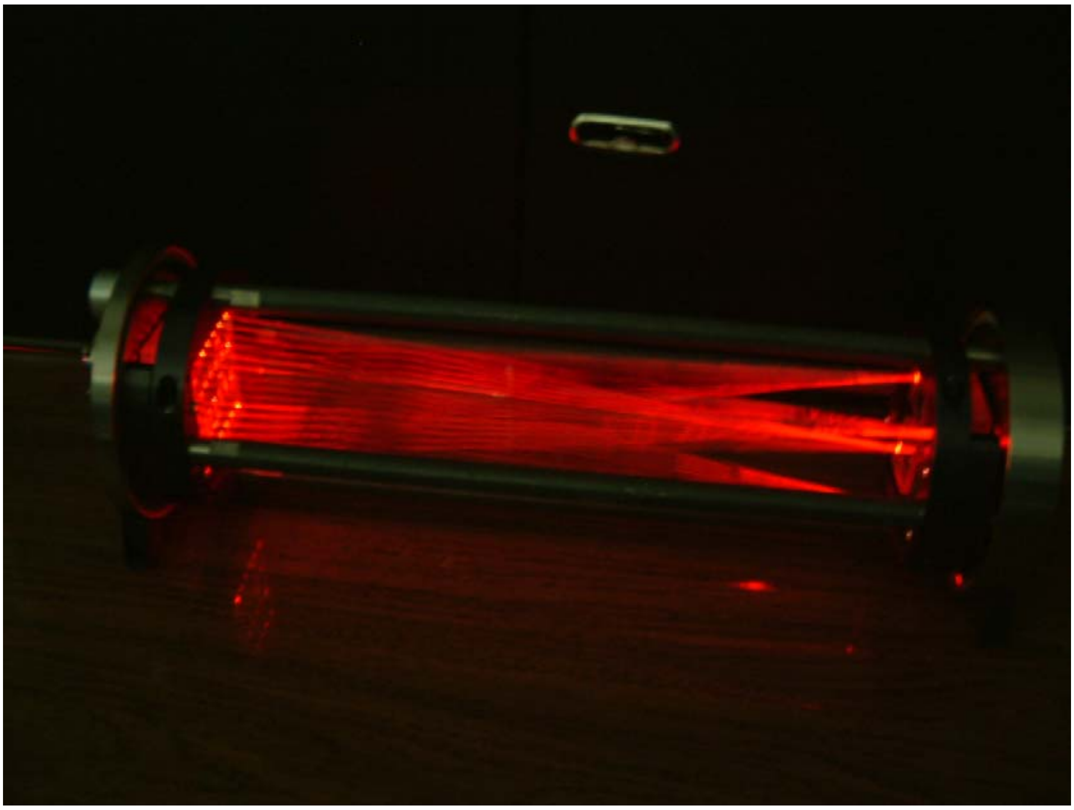
Chernin Multipass Cell

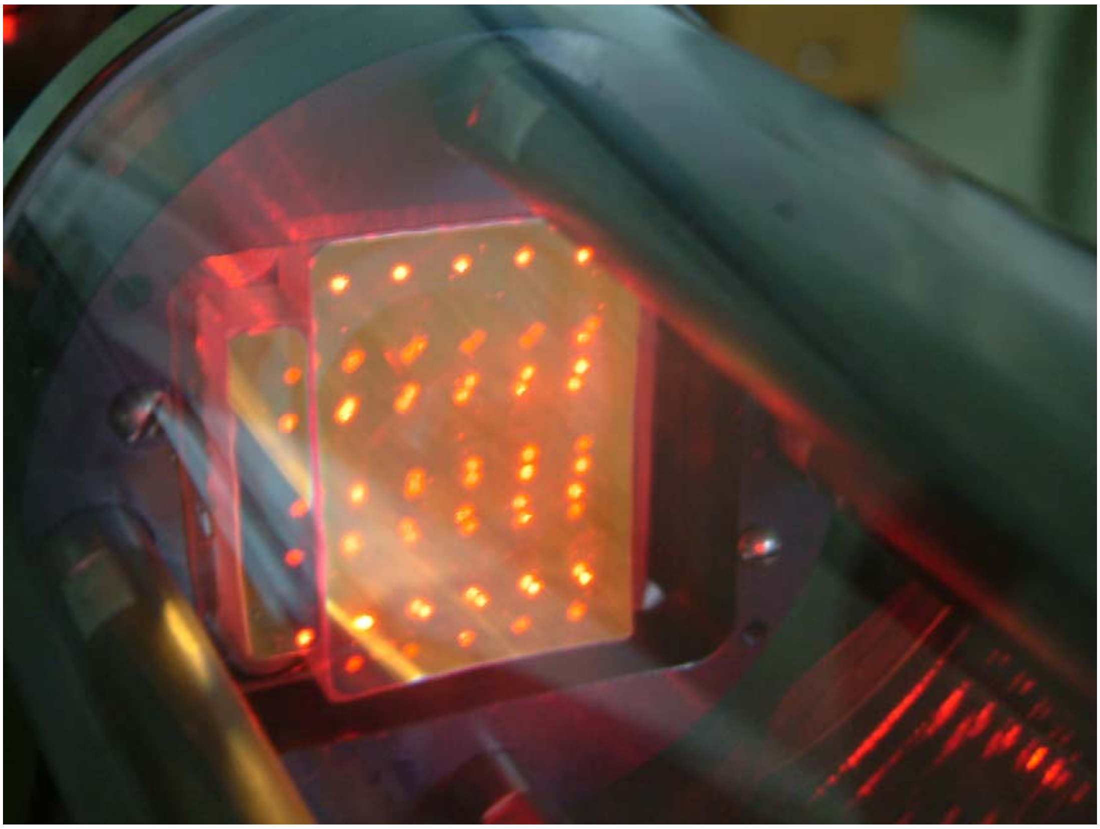




Multipass cell: baselength - O.5 m, dielectric mirrows with 99.9 % reflectivity; 282 passes, 141 m.

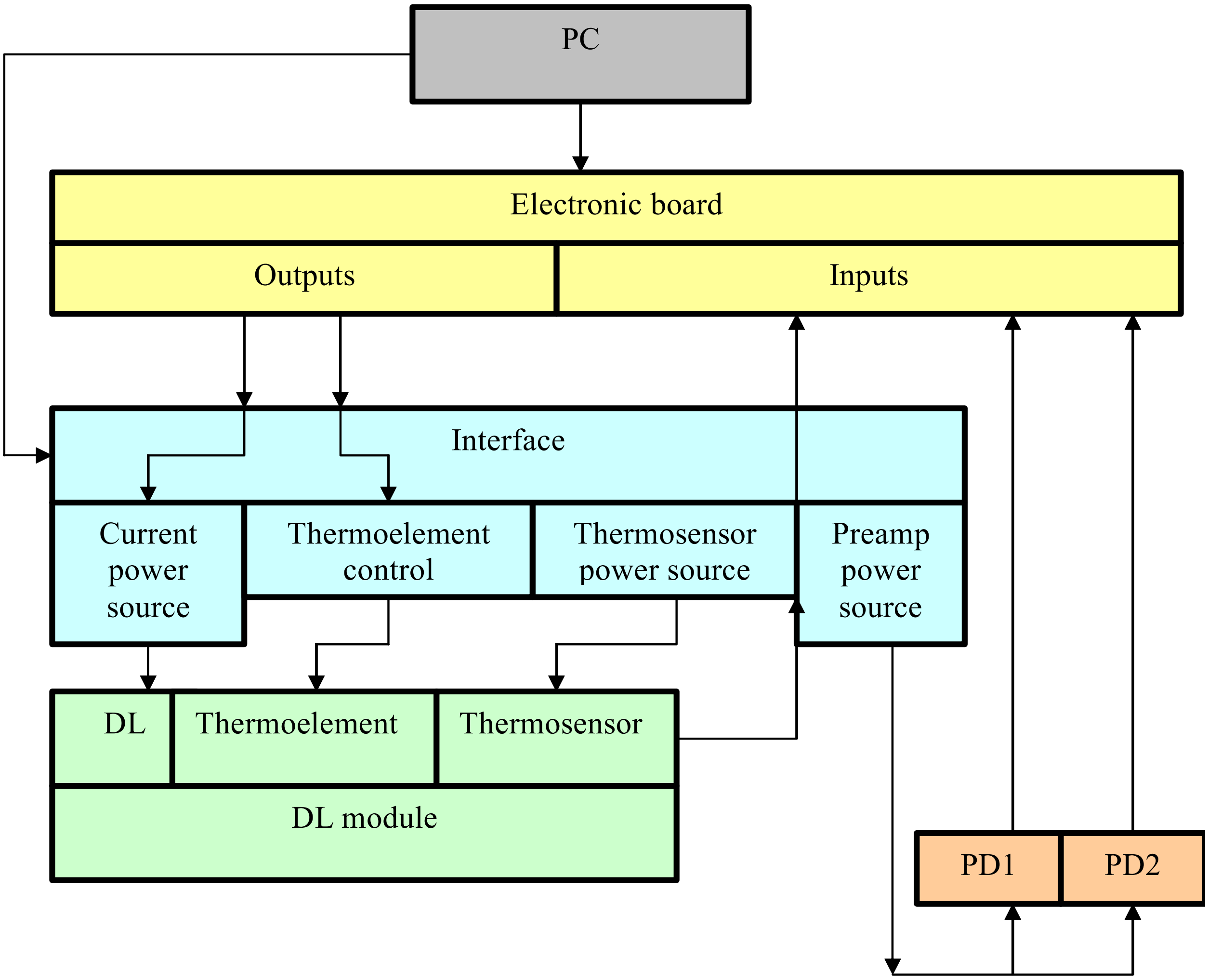
Chernin Multipass Cell



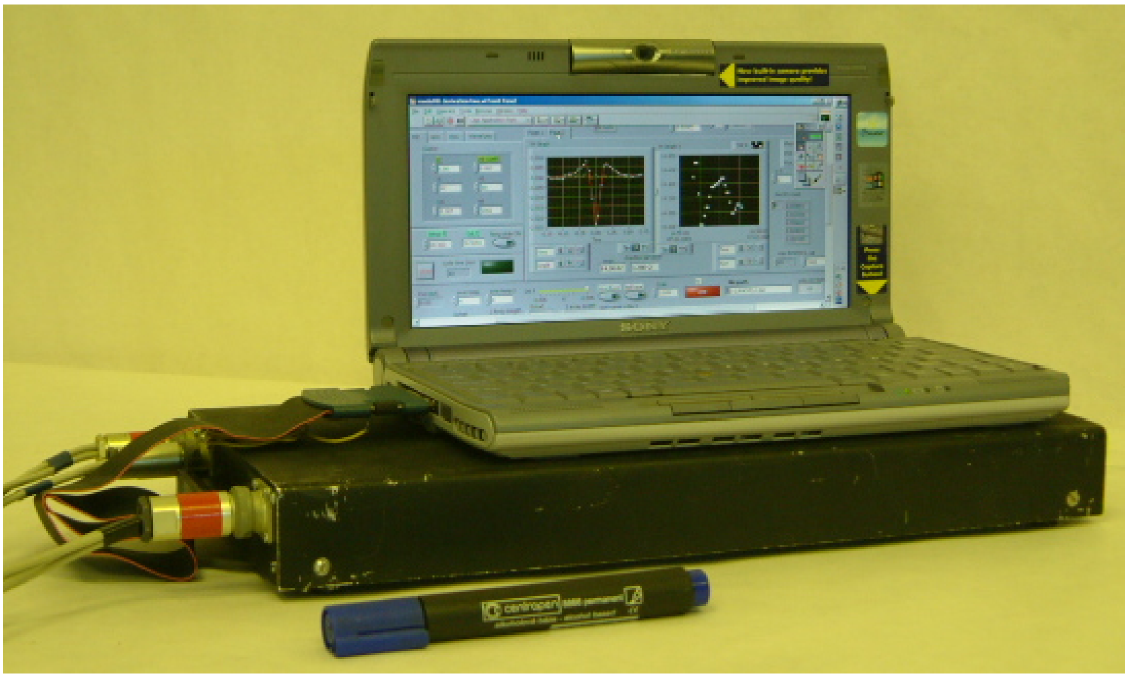


Multipass cell: baselength - 25 cm, dielectric mirrows with 99.5 % reflectivity; 132 passes, 33 m.

Electrical Block-Scheme



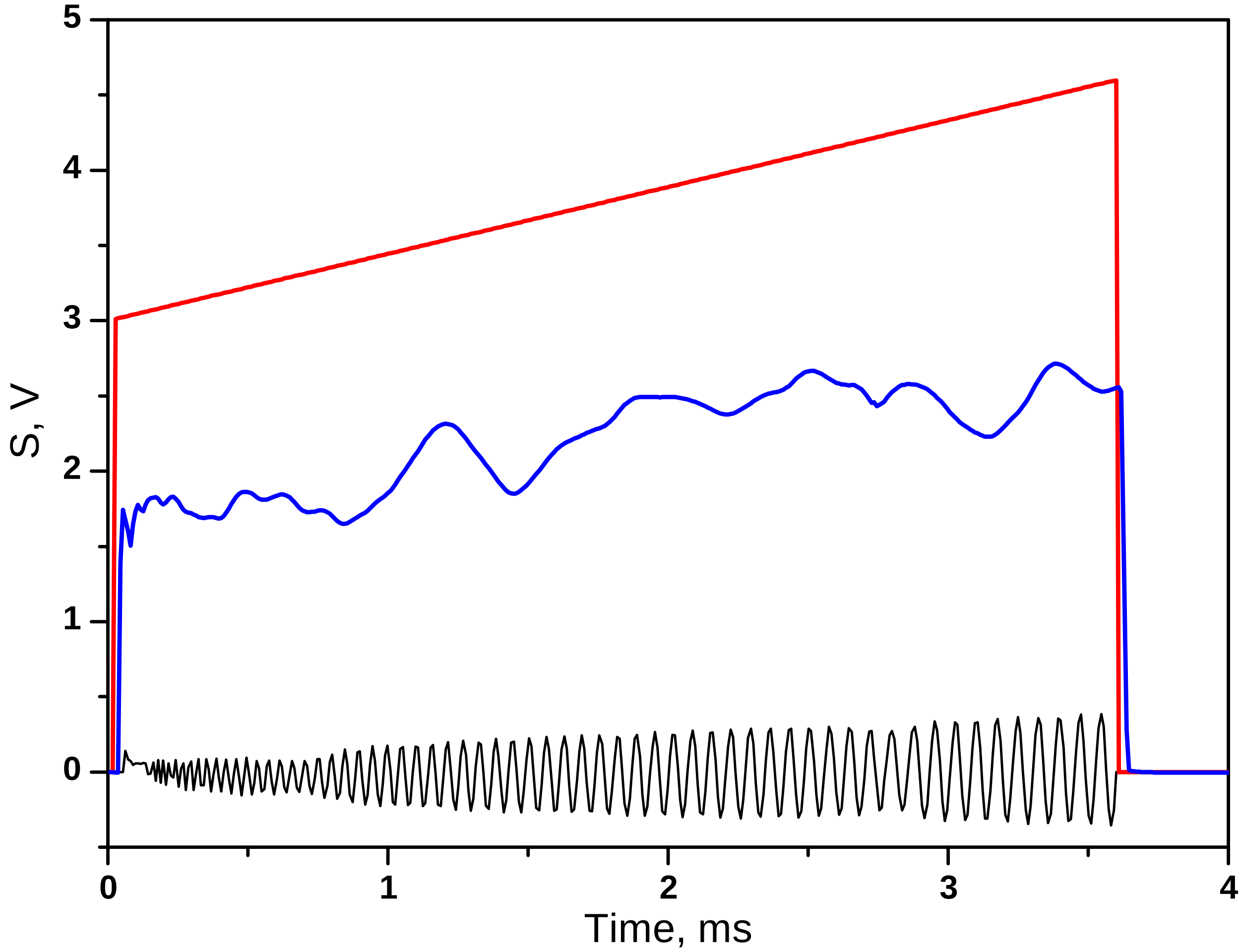
View of interface module



View of interface connected to data acquisition board (12 bit NI DAQ) installed in notebook.

View of interface connected to data acquisition board (16 bit NI DAQ) installed in industrial computer.

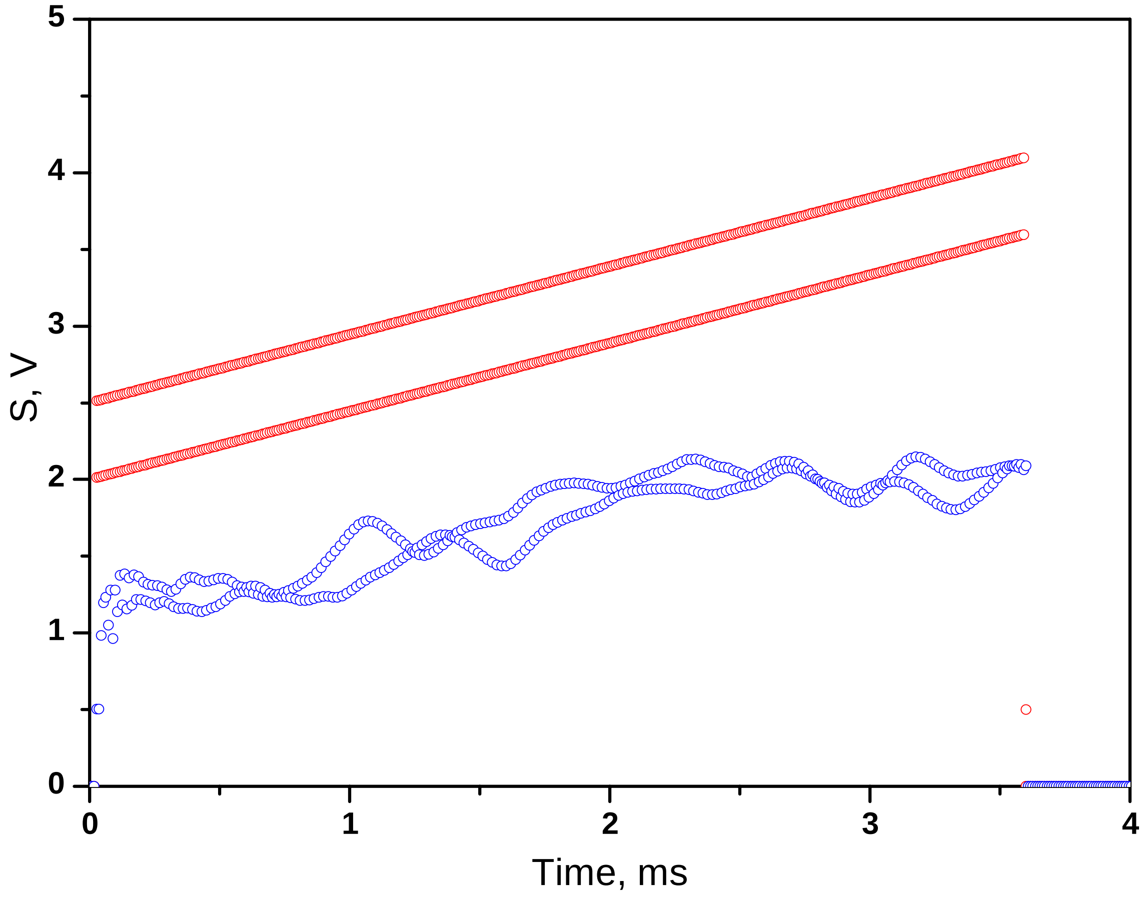
Operation Mode



Recorded signals in analytical (red) and reference (blue) channels when laser was excited by trapezoidal periodical current pulses. Black line shows FP etalon fringes for frequency scale calibration (0.05 cm^{-1} free spectral range). For convenience long pulse is presented. In experiment pulse duration was 0.12-0.4 ms.

Analytical channel contained Chernin multipass cell with 141 m optical length. In reference channel 5 cm cell with 30 Torr NO_2 was installed.

Operation Mode

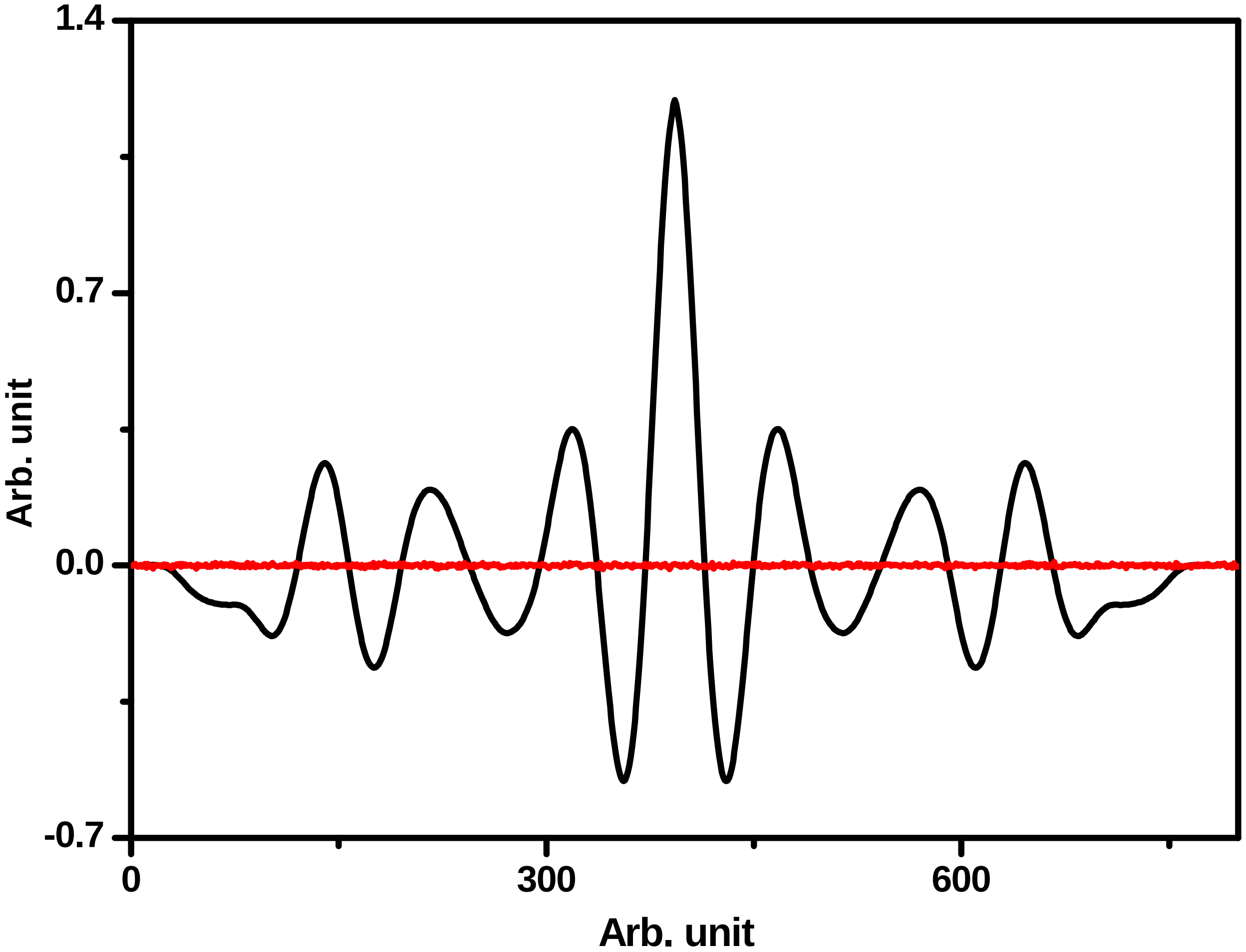


Recorded signals in analytical (red) and reference (blue) channels when modulation was added to excitation current. It looks like two frequency laser operation with tuning (see separate poster). Then difference signal between two branches can be calculated. For convenience long pulse is presented. In experiment pulse duration was 0.12-0.4 ms.

Analytical channel contained Chernin multipass cell with 141 m optical length. In reference channel 5 cm cell with 30 Torr NO_2 was installed.

Data Processing

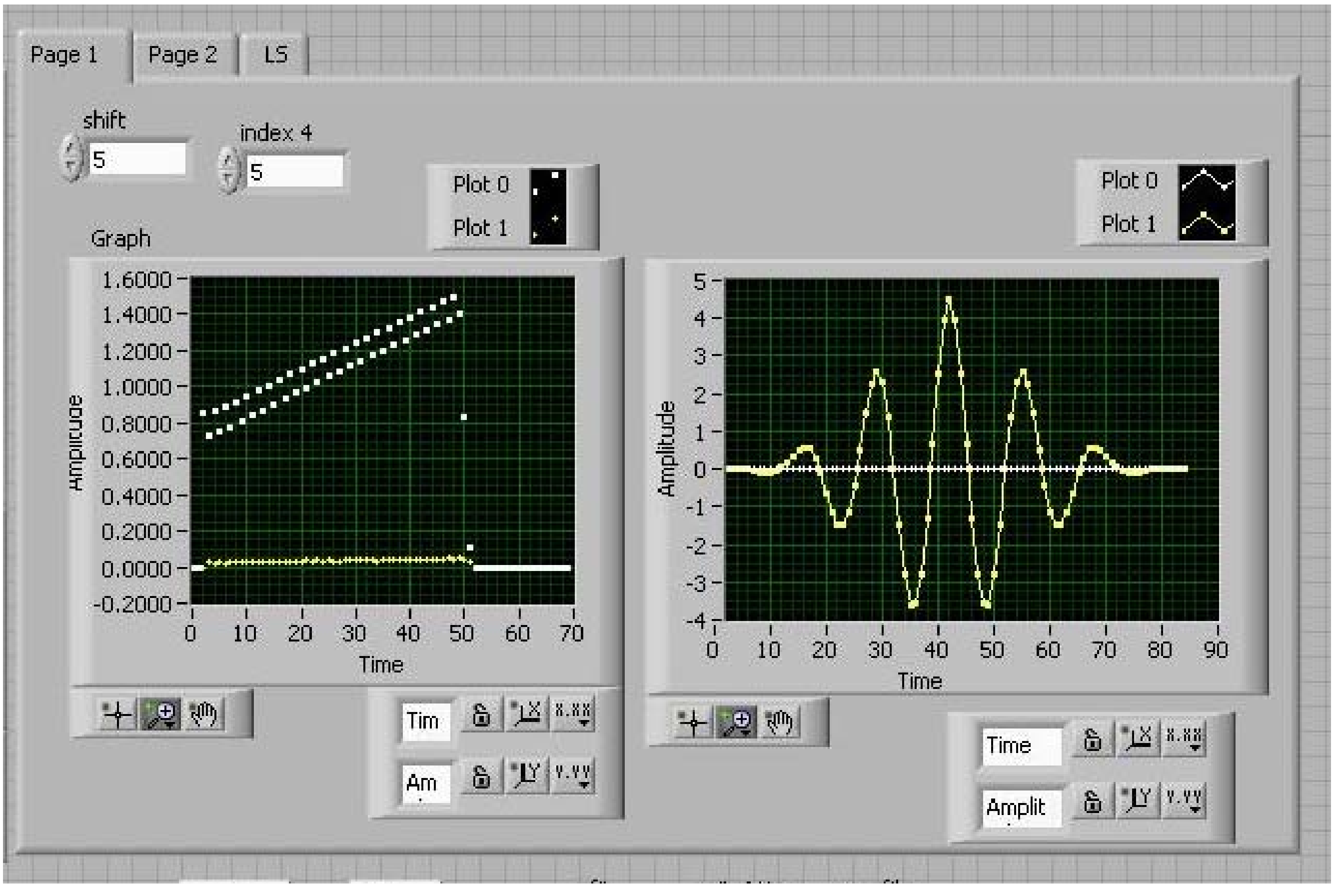
The molecule under detection concentration was determined using difference signals in analytical and reference channels and cross-correlation algorithm [4, 5] proposed for complex spectra with overlapping lines. This algorithm provides optimal signal filtering and gives additional sensitivity improvement proportional to $\sqrt{\mathbf{N}}$ (N – number of spectral peculiarities in recorded spectrum).



Autocorrelation function of reference signal (black) and cross-correlation function of analytical and reference signals (red).

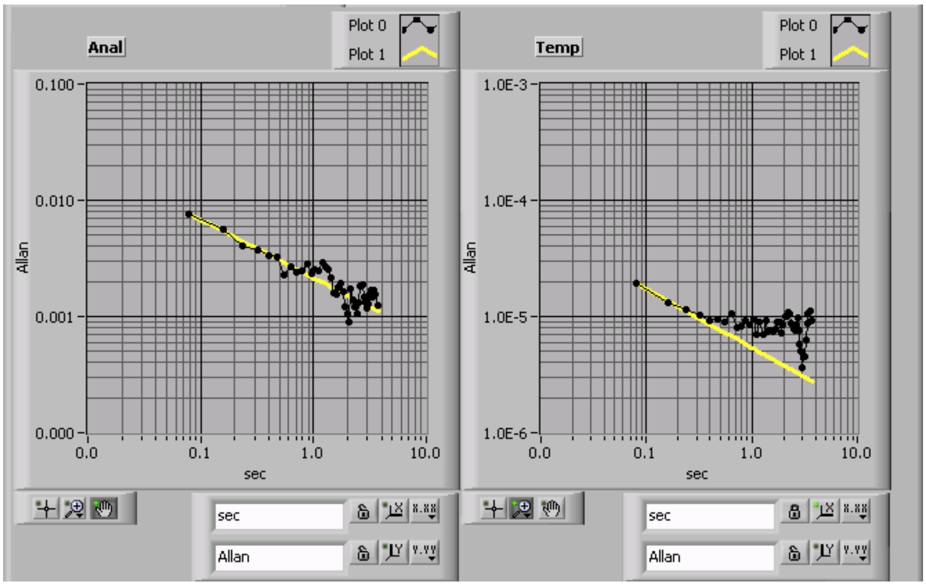
Software

The control of the measurement process and subsequent processing of the result was executed by software running under the **LabView 7.1** environment and **NI DAQ** drivers.

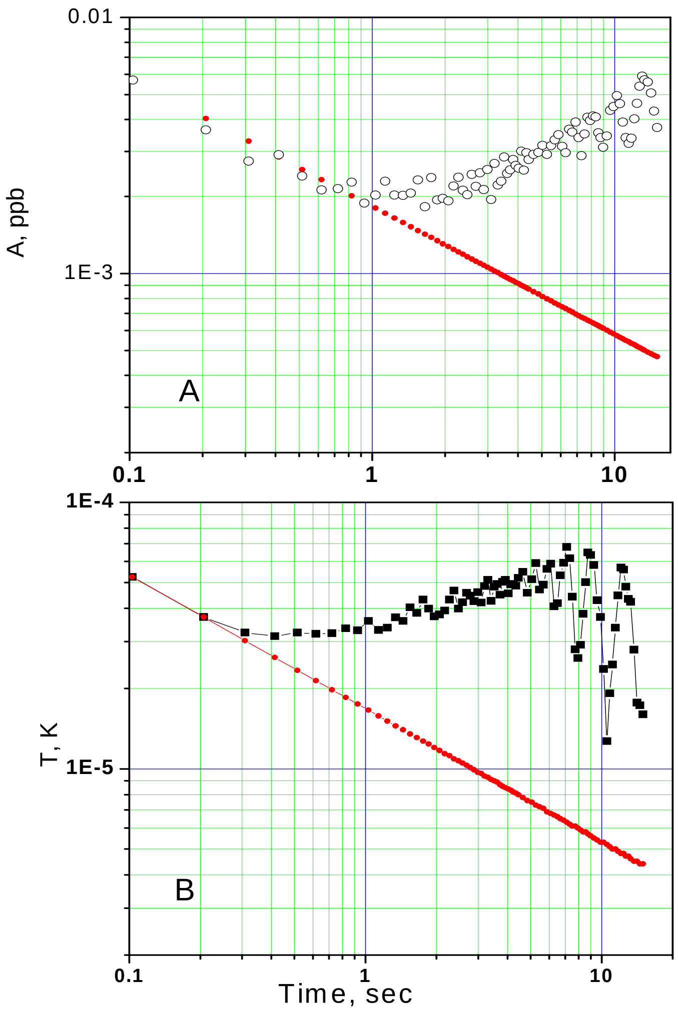


Software developed control panel. Left picture – analytical (white) and reference (yellow) signals. Right picture – correlation functions of analytical (white) and reference (yellow) difference signals (see above).

Sensitivity



Software control panel to measure Allan deviation in two independent channels (in present case analytical signal and temperature).



Allan deviation of minimum detectable NO_2 concentration (A) and temperature (B). Concentration was measured at atmosphere pressure and minimum detectable absorption was found to be 2.7 ppt (atmosphere pressure broadened spectrum) and 0.75 ppt for reduced pressure (broadening is close to Doppler one).

NO_2 Leakage Detection