DETECTION OF TRACE AMOUNTS OF WATER IN AMMONIA BY MEANS OF TDLS TECHNIQUE

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Introduction

A presence of even trace amounts of water in industrial gases which serve as precursors in semiconductor industry can seriously influence a quality of final production.

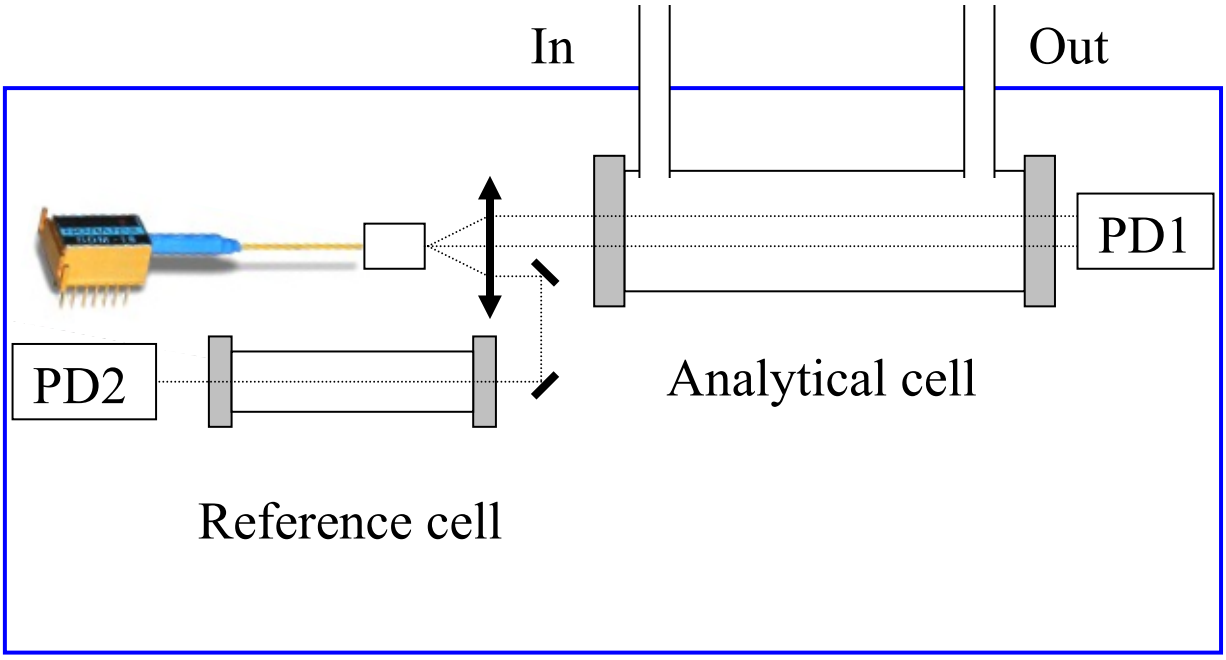
Usually the requirements for concentration of impurities are at ppm level or less. Such concentrations of water in ammonia could not be detected by dew point technique since ammonia dew point is only 33^{o}C and new technique should be invented. Near IR diode laser based systems were considered as effective tool for real time measurements (see for example [1]).

This work continues long-term collaboration between General Physics Institute (Moscow) and Institute of High Pure Materials Chemistry (Nizhniy Novgorod) [see 2]. Its goal was to develop and install in purification process diode laser based instrument. This instrument has to be simple, reliable, and be able to perform real time measurements.

1. D.Hovde, J.Hodges, G.Scace, J.Silver, Appl.Opt. 40, 829-839 (2001)

2. B.Andreev, G.Devyatykh, I.Zasavitskii, O.Lazukina, G.Maksimov, A.Nadezhdinskii, A.Prokhorov, V.Khorshev, C.Shyapin, Vysokochistye Veshestva, №4, 161-166 (1989)

Optical Block-Scheme



Fiber output laser radiation was collimated by a lens into nearly parallel beam. Small part of radiation (approximately 5 %) was sent to reference channel, passed sealed reference cell 36 mm long with 1.9 Torr of water vapor. Analytic channel incorporated 0.5 m long 40 mm diameter electropolished stainless steel tube with glass windows.

Whole detection system was installed in a box (blue box on picture) that was purged by dry nitrogen, so a part of optical path between laser, analytic cell, reference cell and detectors in both channels was almost free of atmospheric water. Low pressure was kept both in analytic and reference cells to distinguish absorption of environment water due to difference in line widths.

Diode laser module

Single mode fiber coupled Fabry-Perout diode laser (Nolatech, Moscow) operating at wavelength 1.396 μ was used in the instrument. This laser had practically single mode operation.

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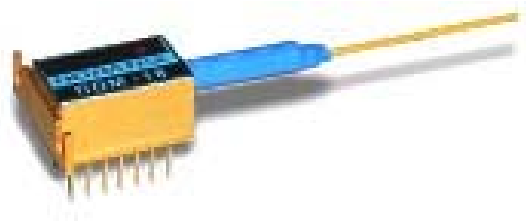
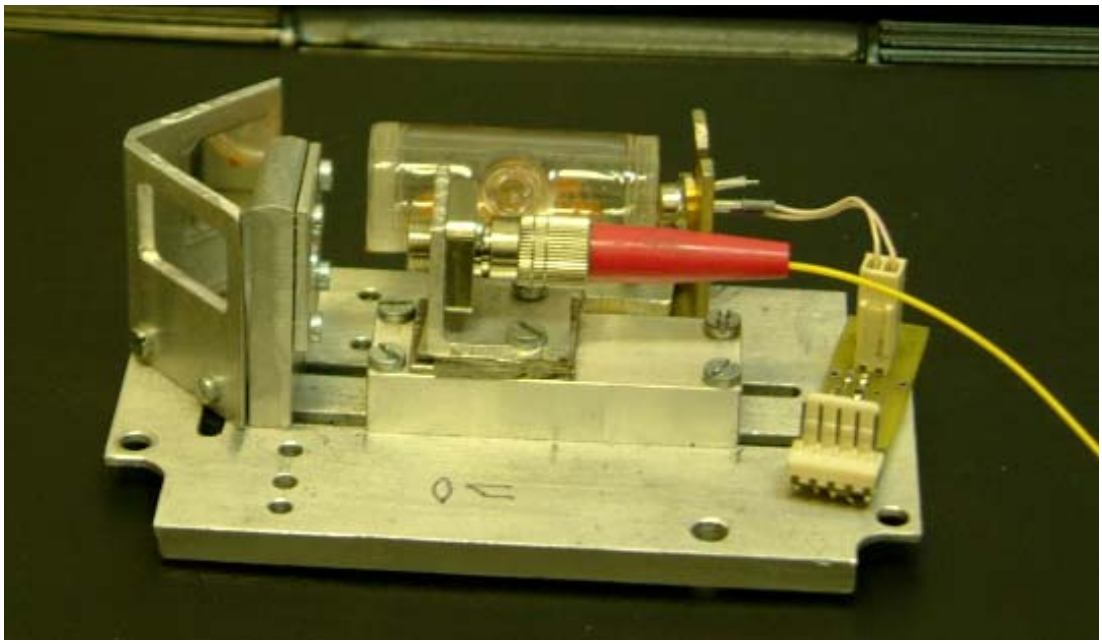


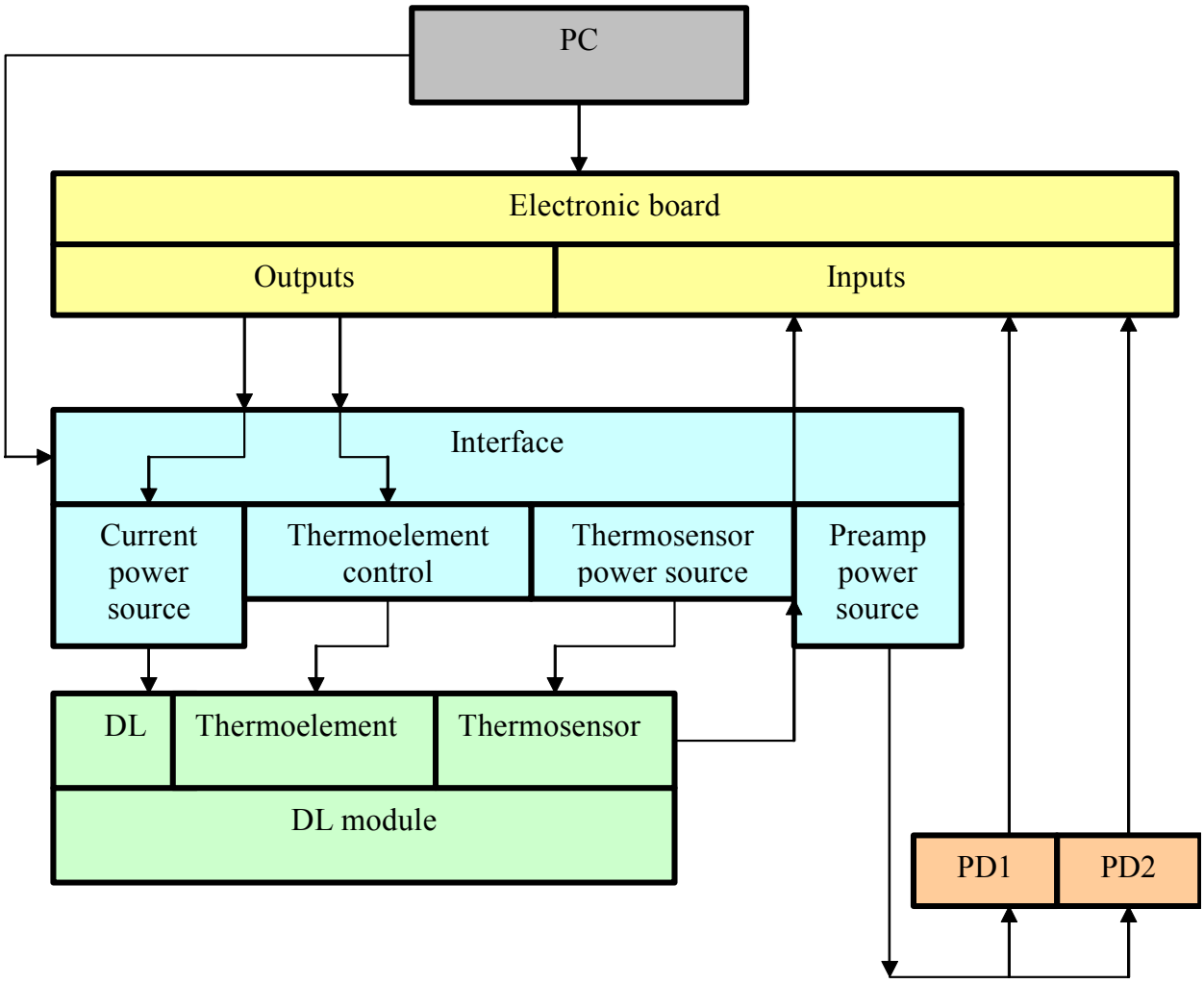
DL module parameters

ID	H_2O
Manufacture	Nolatech, Moscow
Operator	AGB
Date	7.05.04
Power, mWt	1
Molecule	H20
Line identification	2-0
Wavelength, nm	1396
TE specifications	
Rt, kOm	14.62
T0, ^{o}C	3750
TE limits U, V	-10, +5
Thermal RC, s	11
Delay time, s	0.2

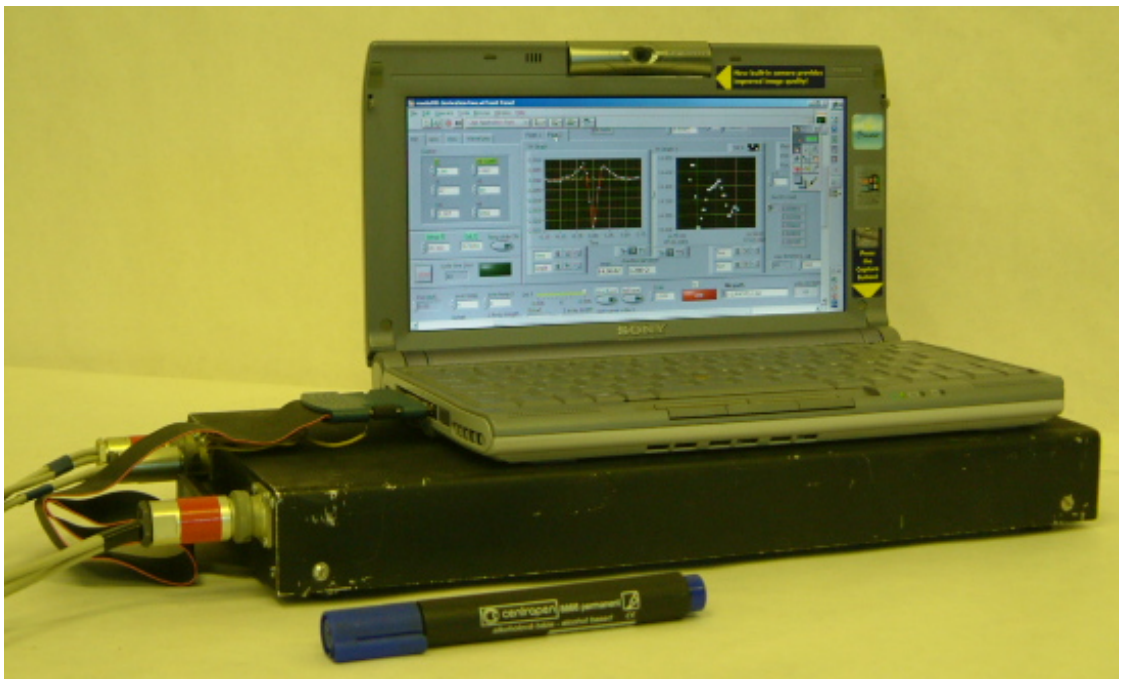


View of optical elements with reference cell

Electrical Block-Scheme



View of interface module

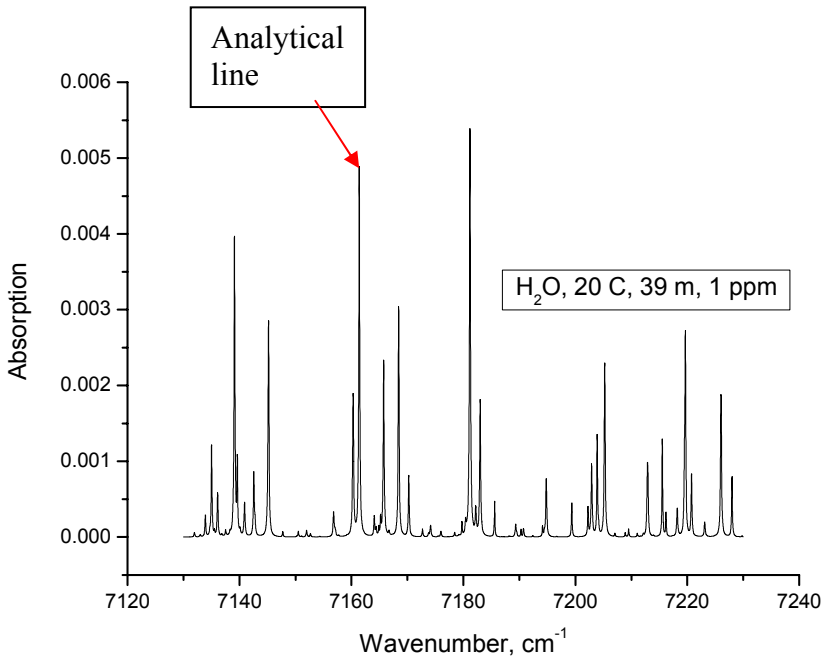


View of interface connected to data acquisition board (12 bit NI DAQ) installed in notebook.

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

H_2O Absorption in Near IR Spectral Range

DL was tuned on wavelength 7162 cm^{-1} (1396 nm), corresponding to one of the strongest absorption lines in near IR.

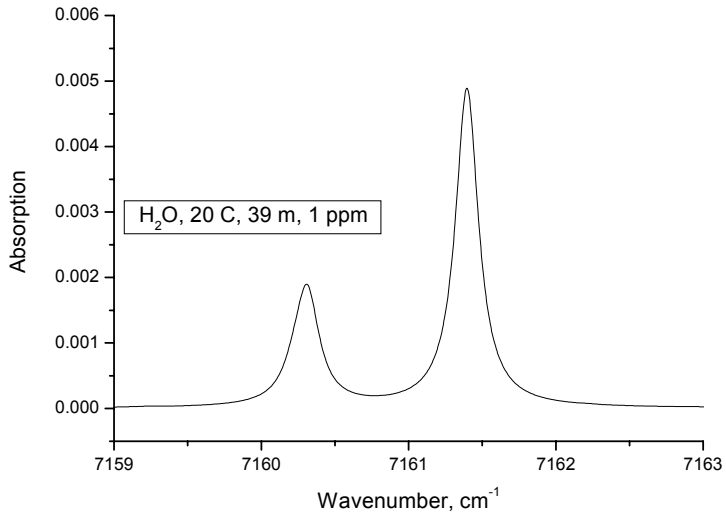


The photo-detector signal can be represented as

$$I = I_0 \exp\left[-\sigma(\nu) P_0 C L\right] = I_0 \exp\left[-K(\nu)\right]$$

where I_0 – intensity of DL radiation, K(ν) – absorption spectrum, σ - cross-section, P_0 - pressure, C – water concentration, L – optical path.

Instrument Operation



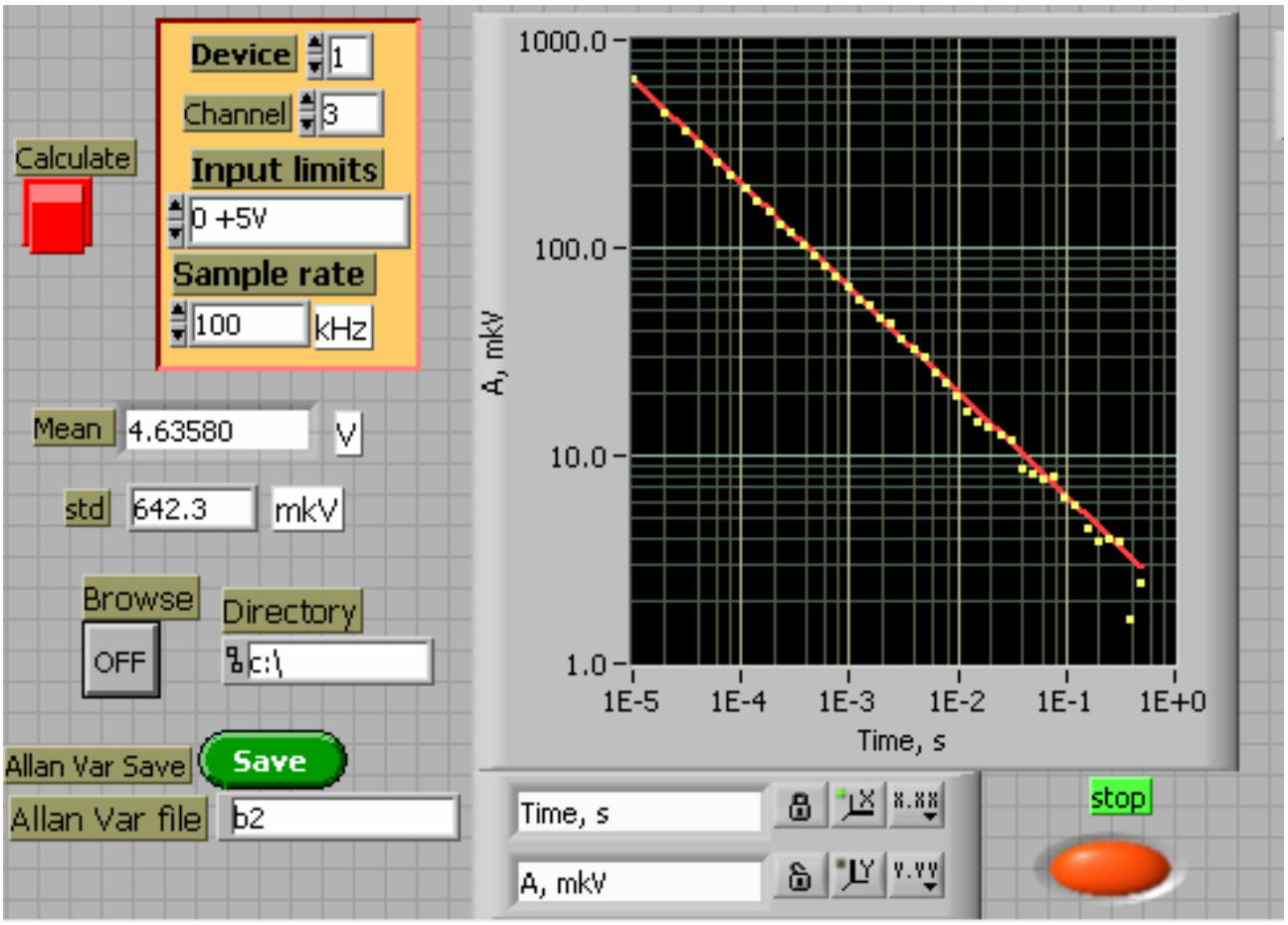
Water vapor absorption near analytical line

Having the same pressures in analytic and reference cells, the concentration of water in analytic cell C_1 could be calculated as

$$C_1 = \frac{K_1 L_0 C_0}{K_0 L_1}$$

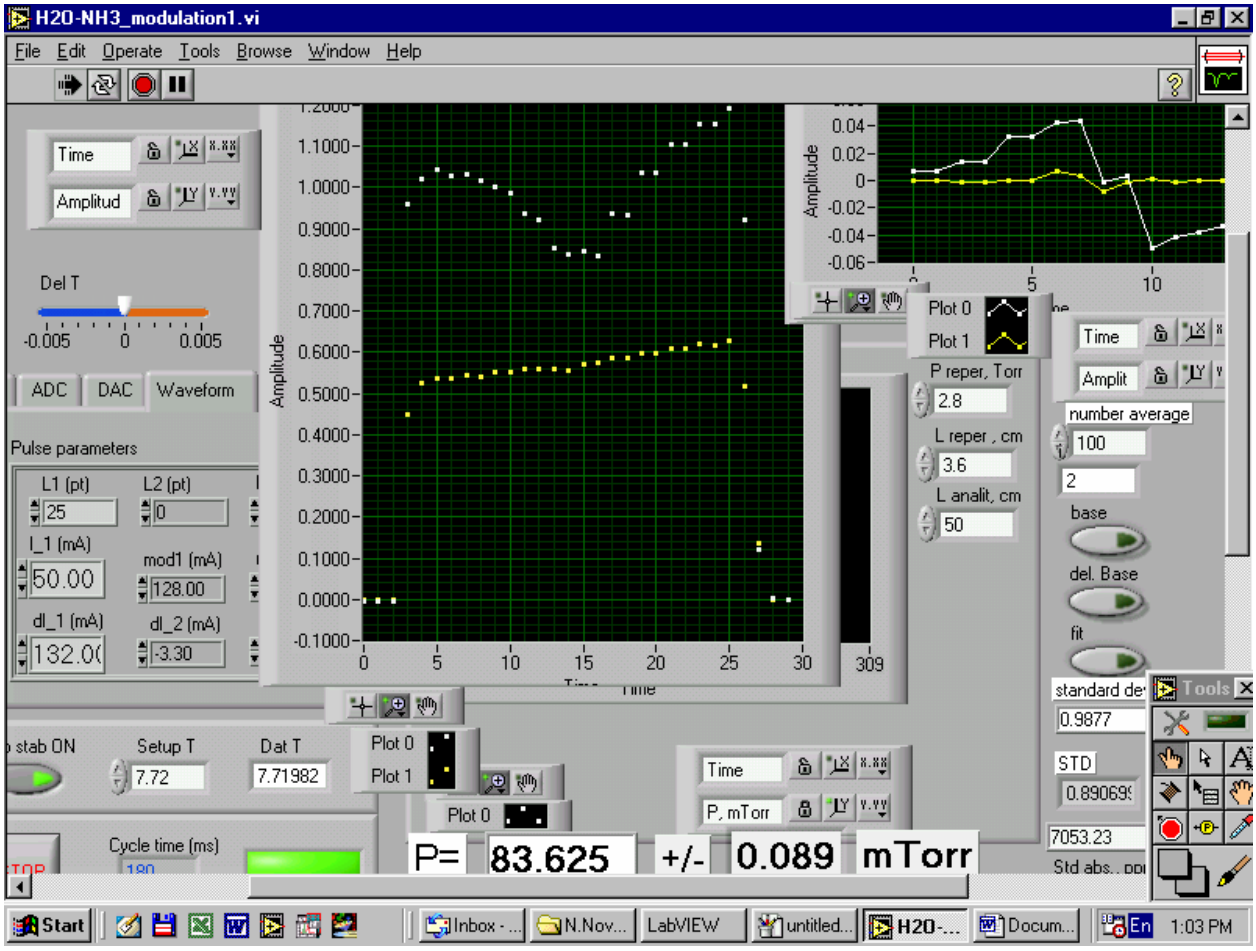
K_1 and K_2 – absorption coefficients in analytic and reference channels, respectively, C_0 – water concentration in reference channel. Actually, for better accuracy, concentration was calculated in more complicated way using correlation functions approach (see separate poster). This method allowed better suppression of noises since correlation function served as optimal filter.

Allan Deviation of Analytical Signal



Allan deviation of signal in analytic channel. In present case minimum detectable absorption was determined by resolution of 12 bit NI data acquisition board and corresponds to 10^{-6} for 0.1 sec averaging time.

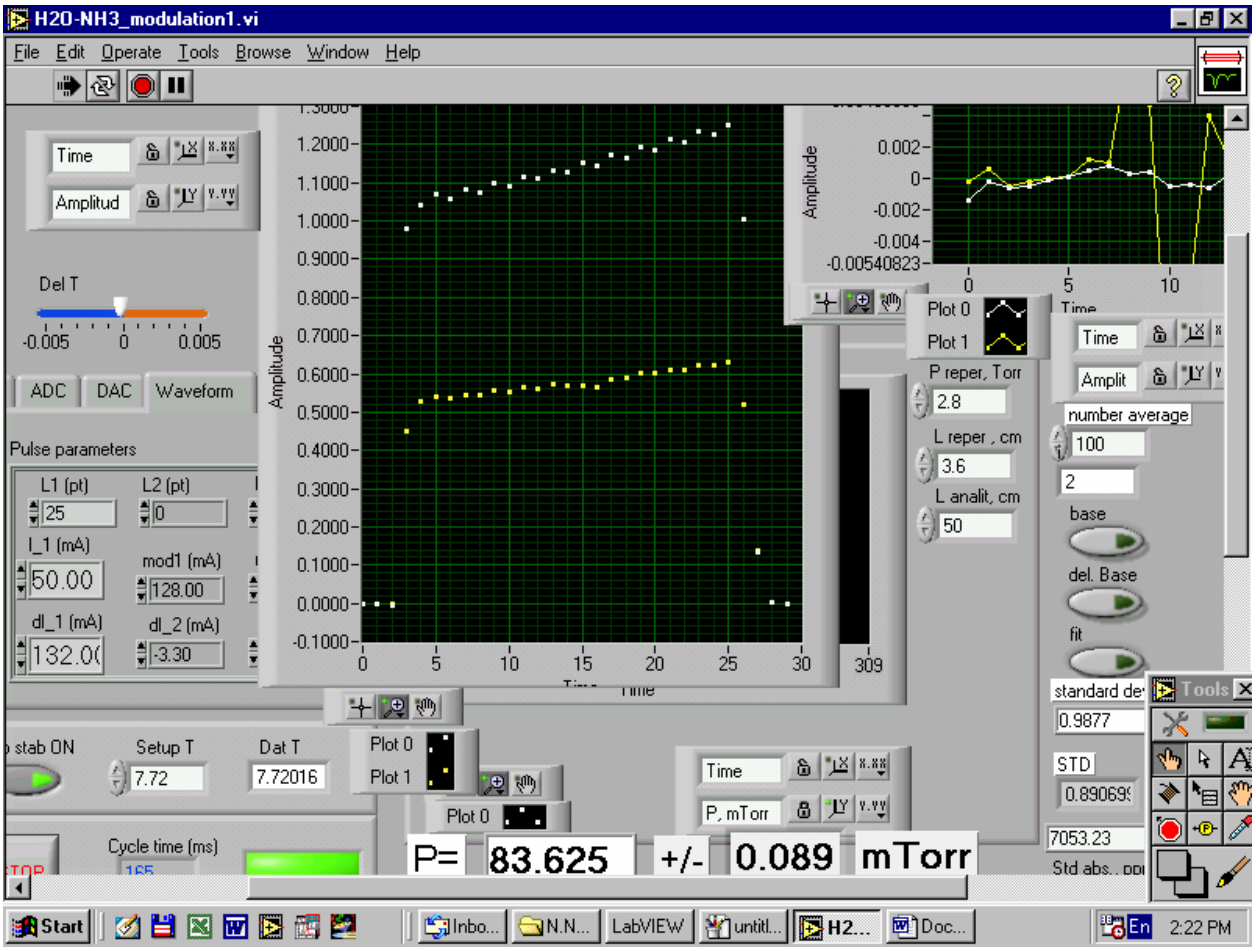
Influence of Atmospheric Water



A view of software control panel.

The data were obtained without dry nitrogen purging. Graphs on the center screen represent averaged signals in analytical (white points) and reference (yellow points) channels. Graphs in upper right screen represent correlation functions for analytic and reference signals, colors are the same as for central screen.

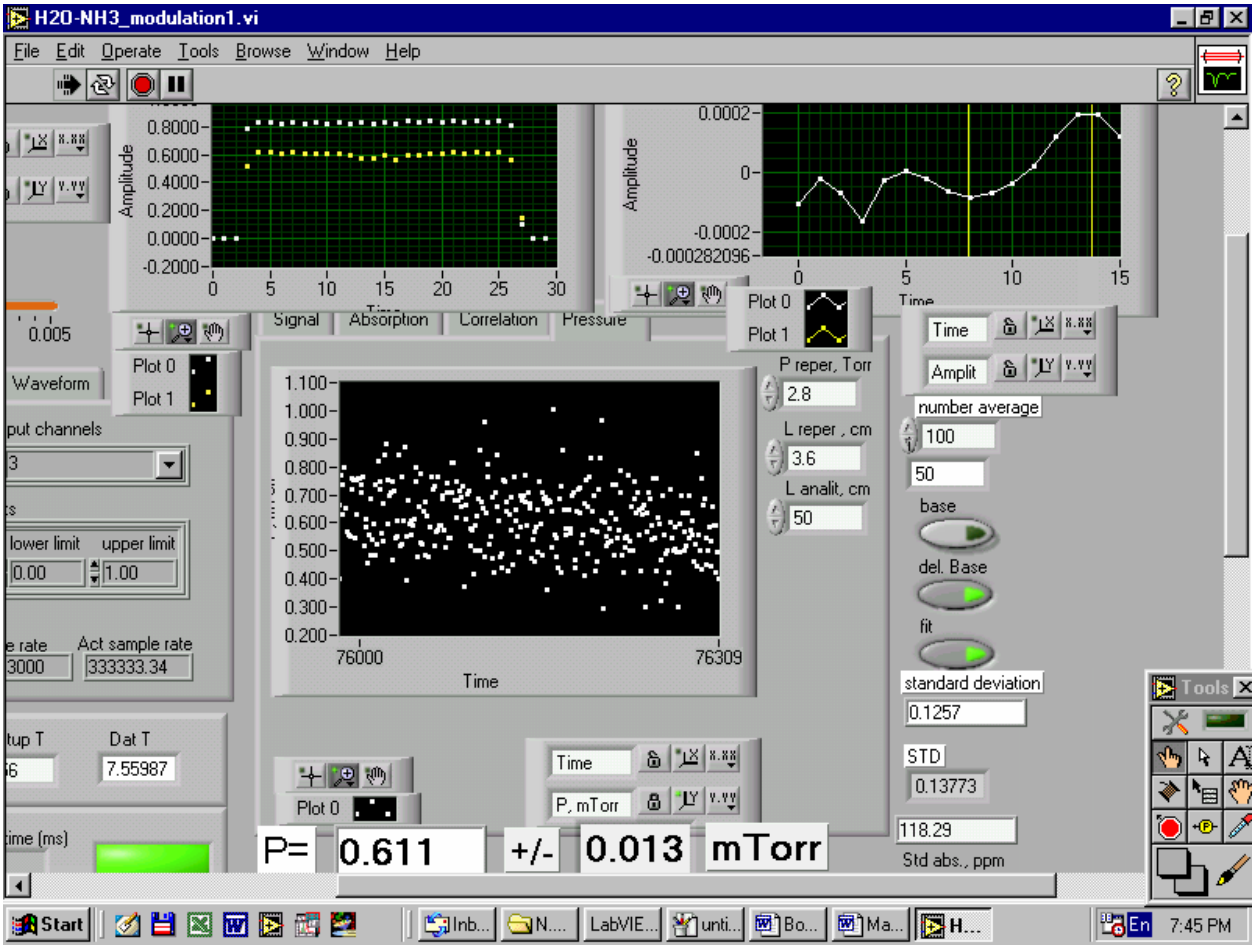
Water Detection with Dry Nitrogen Purging



A view of software control panel

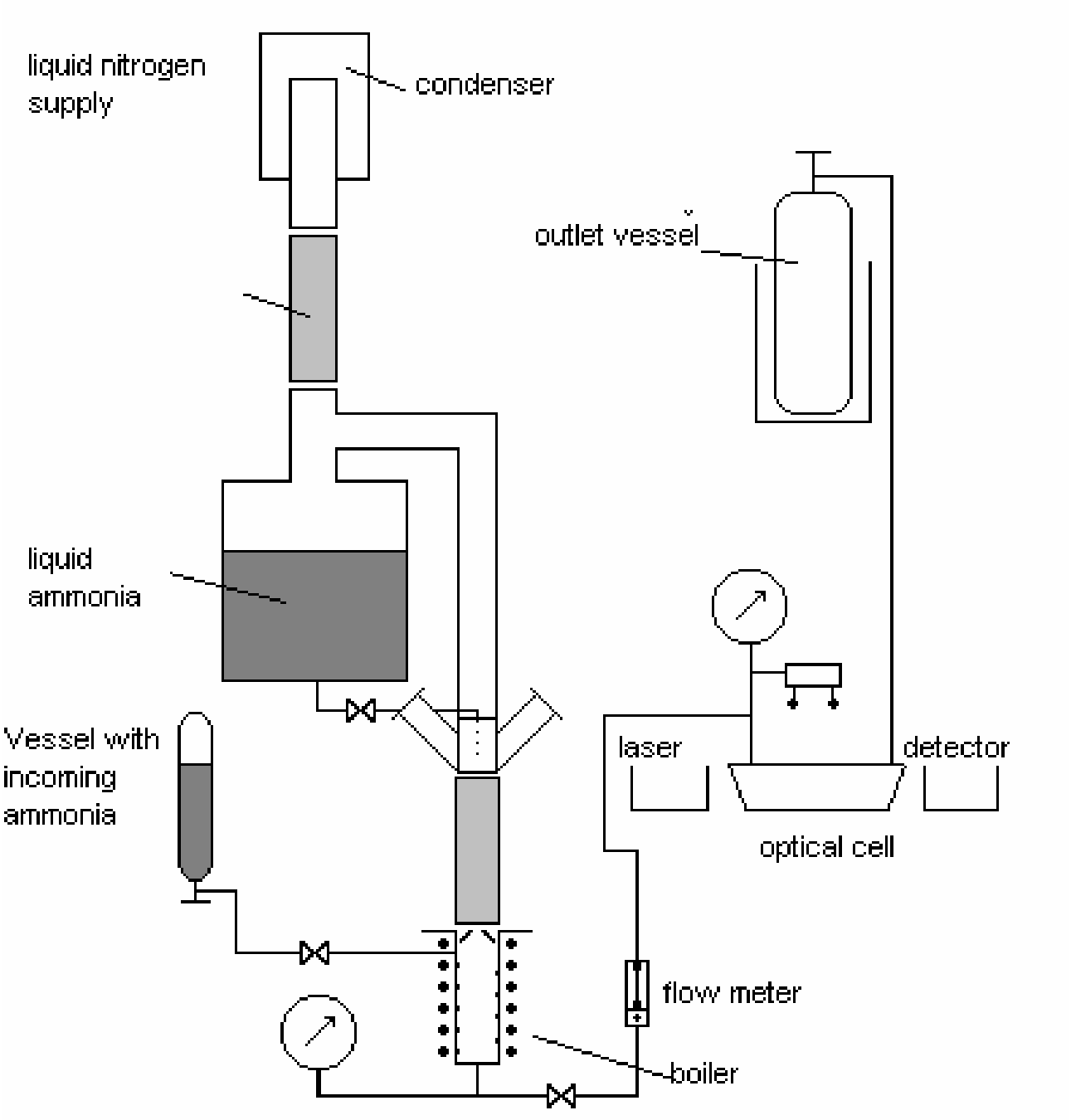
The data were obtained with dry nitrogen purging for 90 minutes. Graphs on the center screen represent averaged signals in analytic channel (white points) and reference channel (yellow points). Graphs in upper right screen represent correlation functions for analytic and reference signals, colors are the same as for central screen.

Water Detection Sensitivity



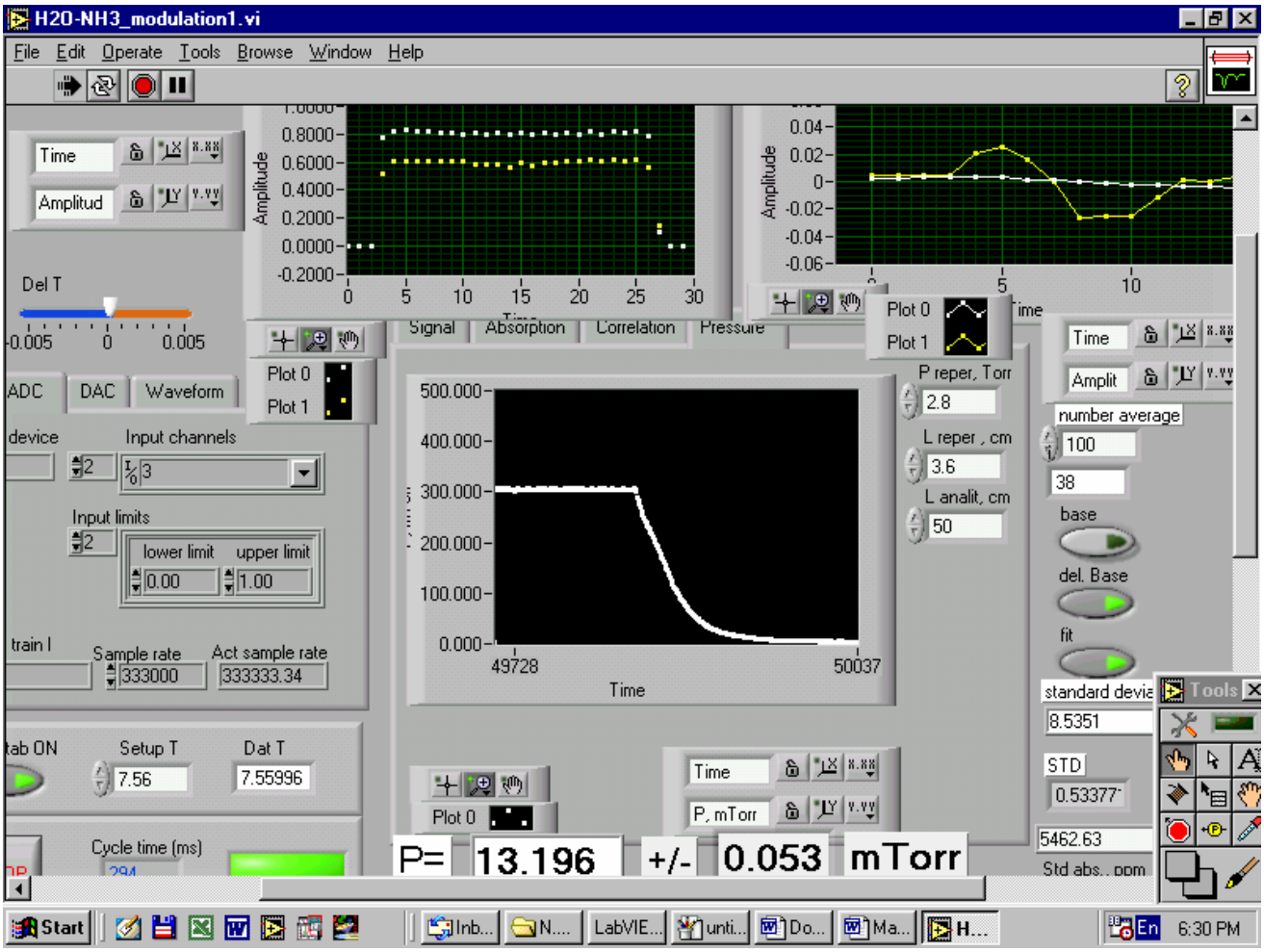
Central screen shows water concentration in ammonia in mTorr (partial water vapor pressure). Ammonia pressure in this experiment was 21 Torr. Standard deviation of 0,013 mTorr corresponds to 2.5 ppm for 0.3 sec averaging time.

Ammonia Purification Column



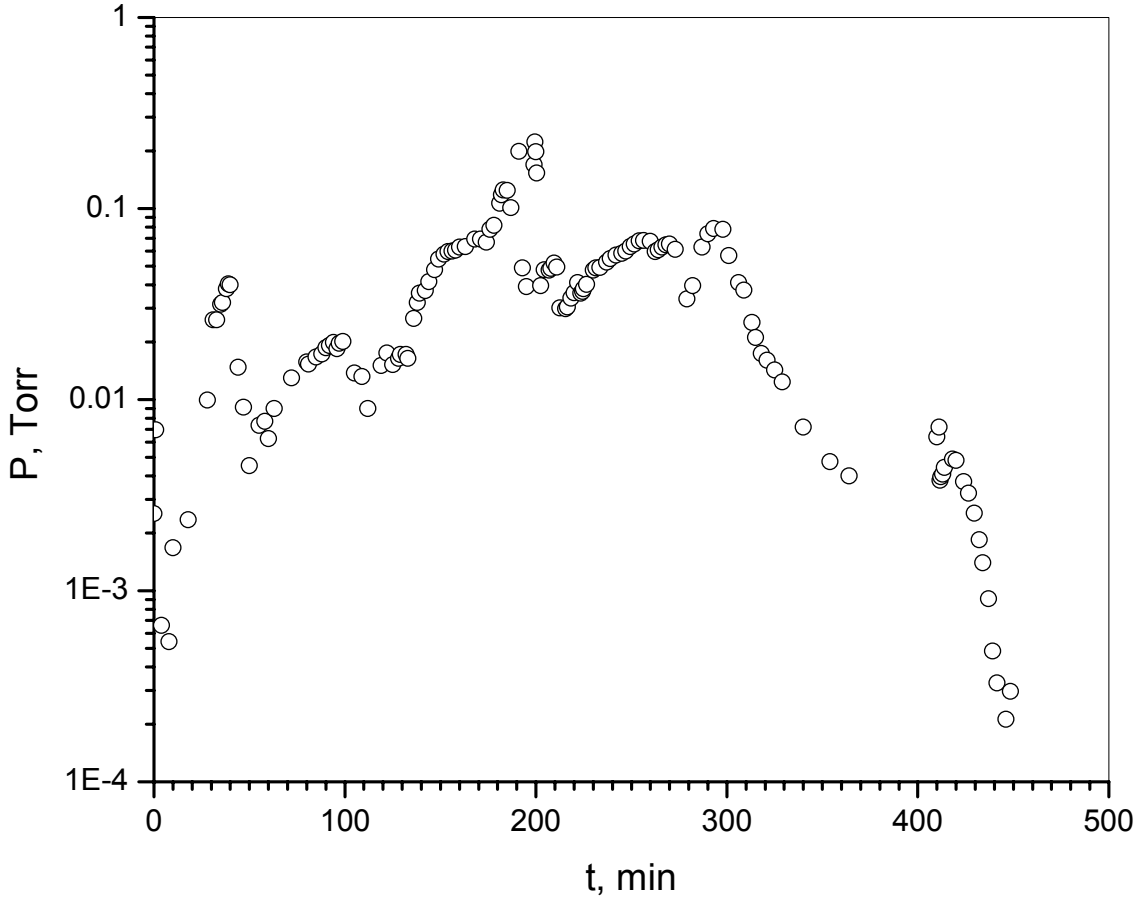
Block scheme of purification column and the instrument installation

Real Time Ammonia Purification Control



A view of software control panel during purification process. Central screen shows a decrease of water.

Optimization of Purification Process



Example of water continuous monitoring during the process of ammonia purification. The lower outlet of column, having the excess of water was investigated. During the process under consideration its parameters were optimized based on data obtained (details will be published elsewhere). Results presented on Fig. shows that optimized purification process can be finished after 450 min. This time is significantly less than it was considered traditionally.