Detection of water content in high-purity ammonia by means of diode-laser spectroscopy

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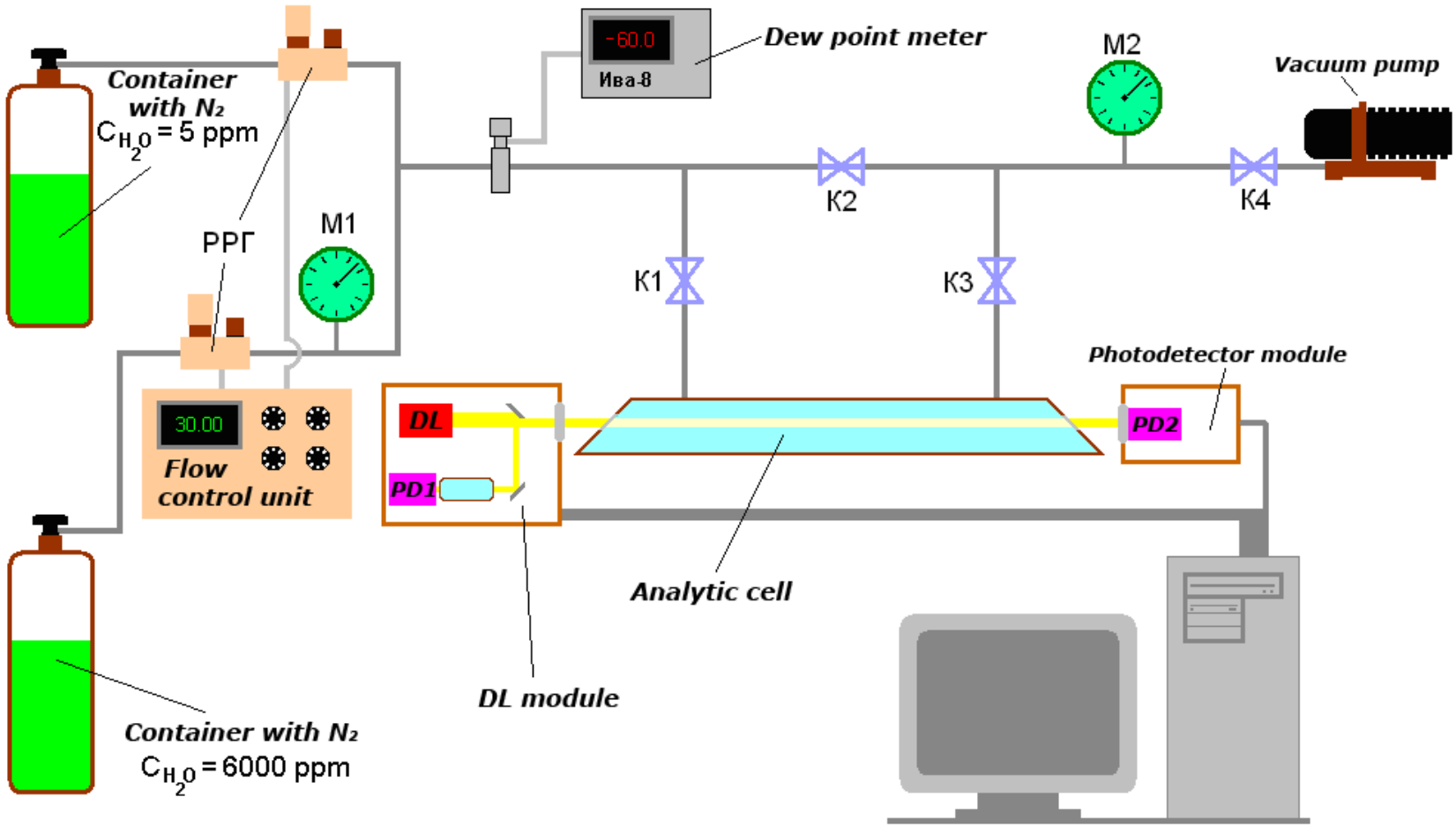
Abstract

The aim of this work was the development of an as-simple-as-possible instrument for trace water concentration measurements in high-purity ammonia. A near IR diode–laser based instrument has been applied for measuring of humidity in on-line detection of water in ammonia during a process of industrial rectification. The results of water concentration measurements were compared with alternative techniques (dew-point meter) and rather good agreement was achieved. A sensitivity of such simple diode-laser based instrument for direct measurement was estimated as 1 ppm. A method of measuring of integrated mass of water containing in heavy fraction extracted during rectification process gives even lower detection limit of less than 0.2 ppm depending on purity in initial ammonia.

Possible methods of detection

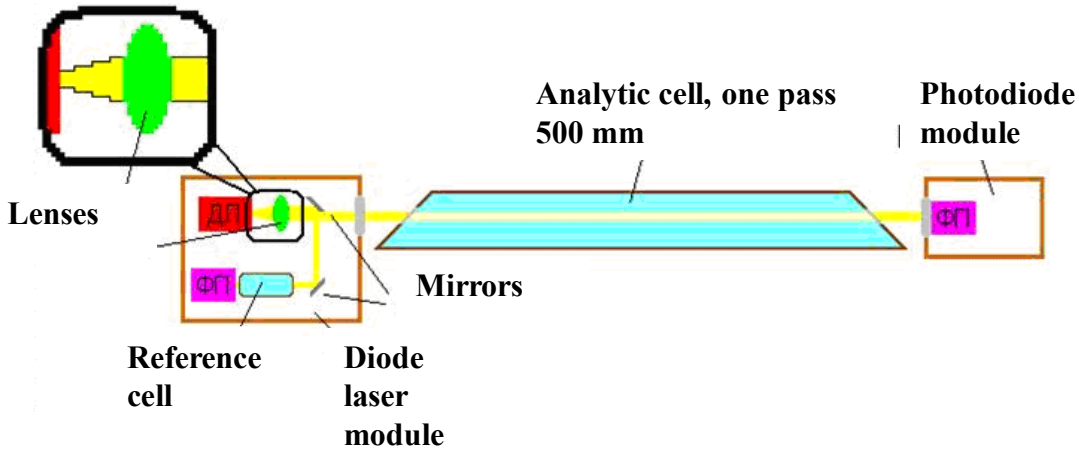
- So far (in Russia) the following methods have been used for monitoring water in ammonia:
- a method of "dew point" with the detection limit of about 300 ppm;
- a method of gas chromatography with heat conduction detector, the detection limit is of an order of 50 ppm;
- a method of reaction gas chromatography with ionization flame detector, the detection limit is of few ppm;
- a method of sub-millimeter gas radio-spectroscopy, the detection limit is 0.1 ppm.

Experimental set-up1: comparison of two methods



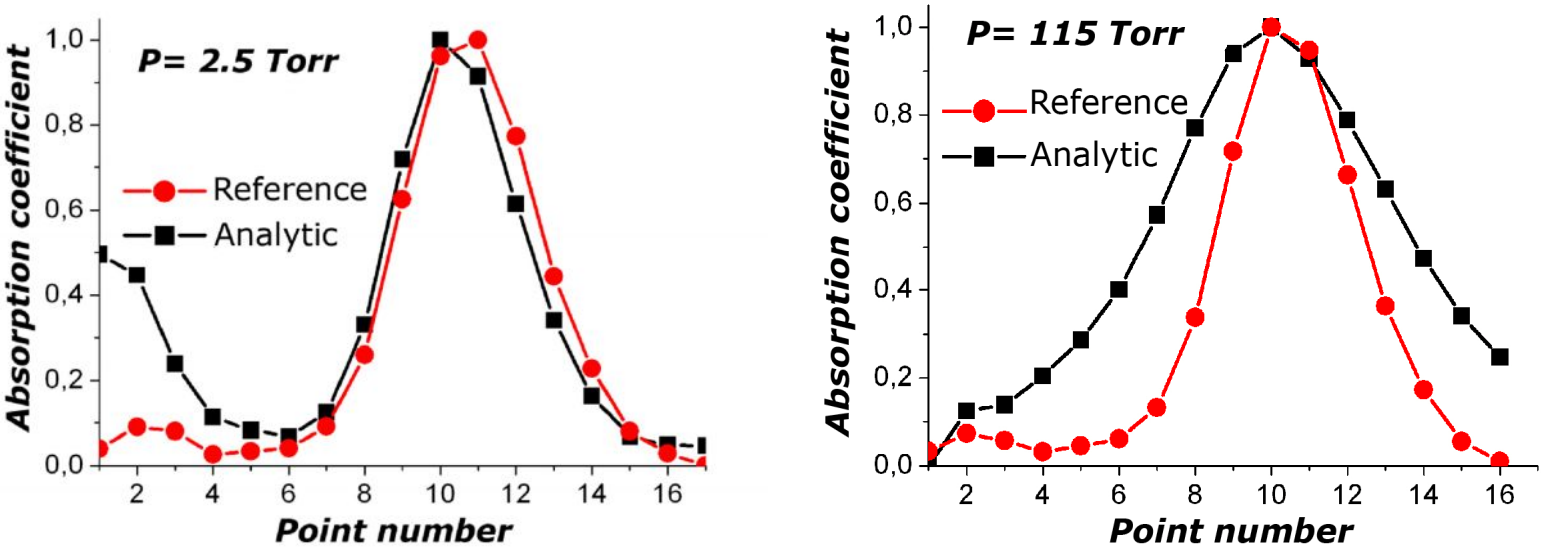
Method of diode laser spectroscopy and “dew point” method were compared. Dry nitrogen with different content of water was used as probe material. K1 – K4 – valves, РРГ – electronically controlled valves, M1, M2 – manometers, PD - photodetector

Optical scheme



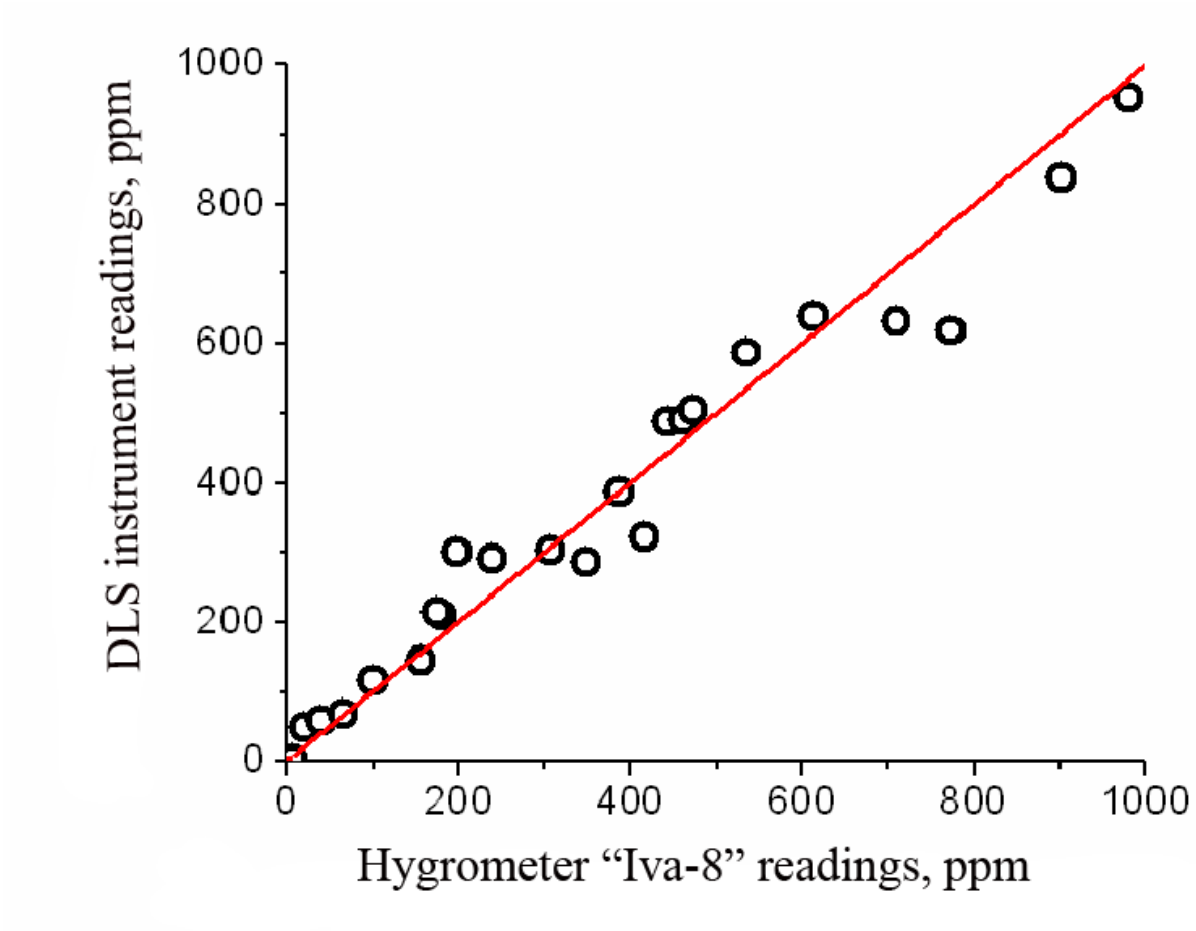
Diode laser radiation was collimated through analytic cell (500 mm long tube) to analytic photodetector; a small part of radiation was directed to reference photodector through reference cell with water vapor at low pressure (1.85 Torr).

Waveforms of absorption lines

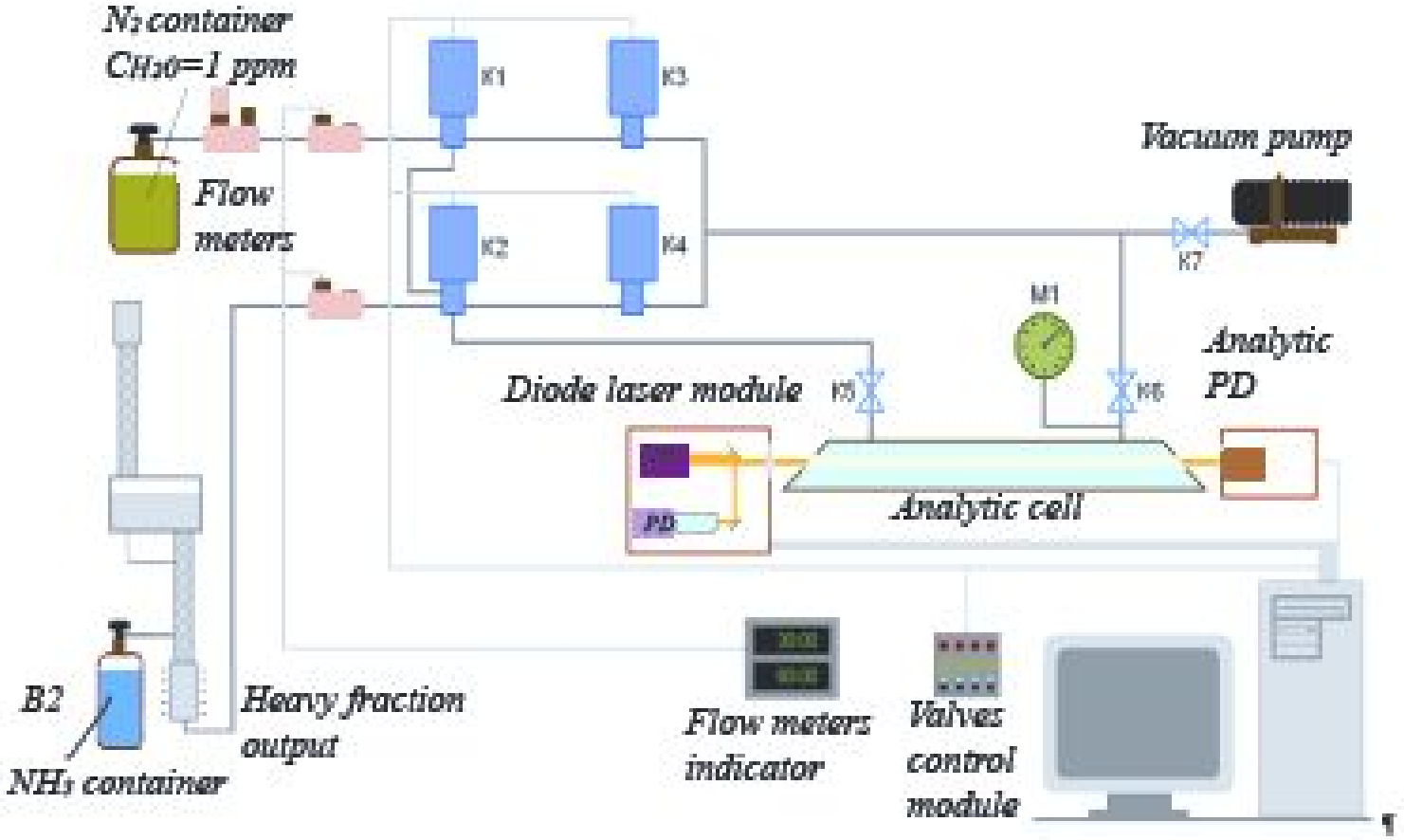


Waveforms of water absorption line in analytical channel at different total pressure of "nitrogen – water vapors" model mixture.
The water vapor pressure in reference cell (35 mm long, red curves) was 1.85 Torr. Concentration of water in analytic cell was calculated as
Ca = (Cr× K(ν)a× Pr ×Lr) / (K(ν)r×Pa×La), here r –reference, a – analytic, K(ν) – absorption in corresponding channel, P – pressure, L – optical path.

Comparison of two methods (DLS and dew point)

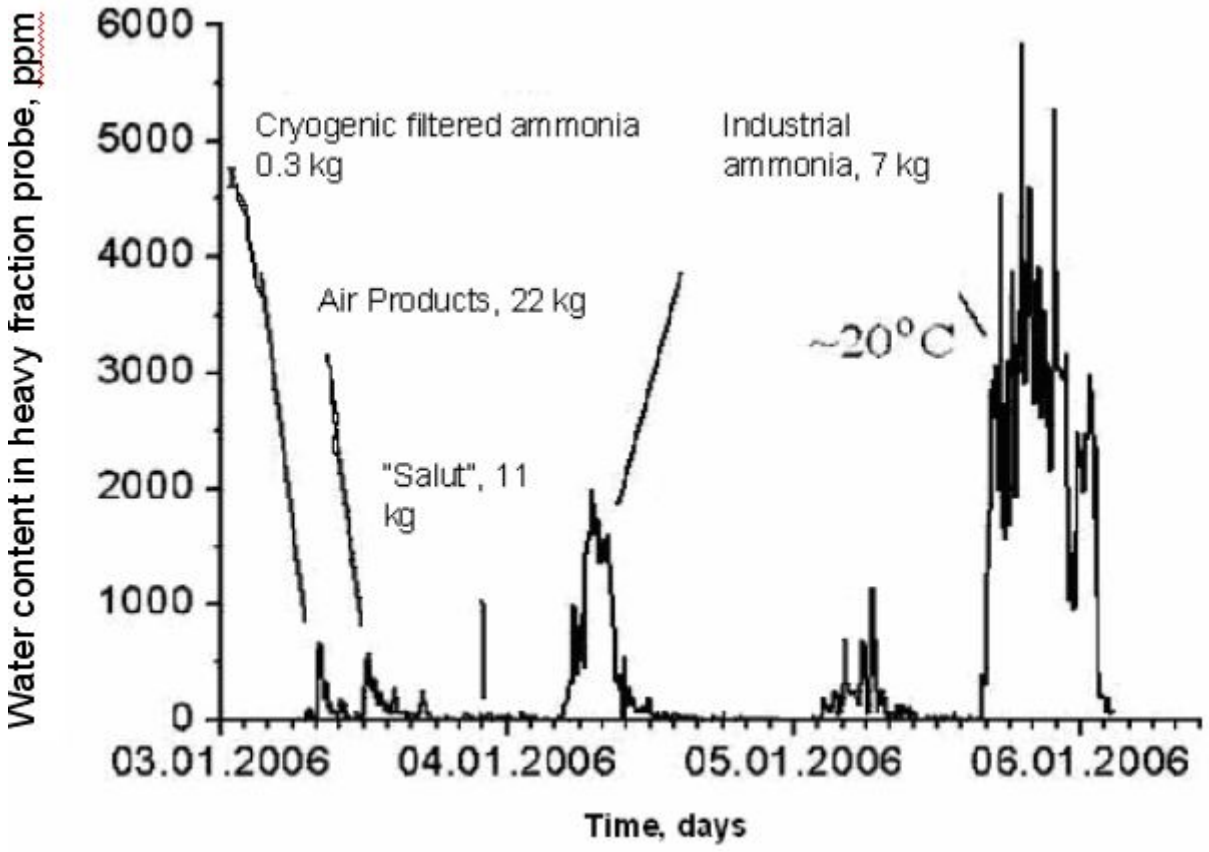


Experimental set-up2: detection of water in ammonia



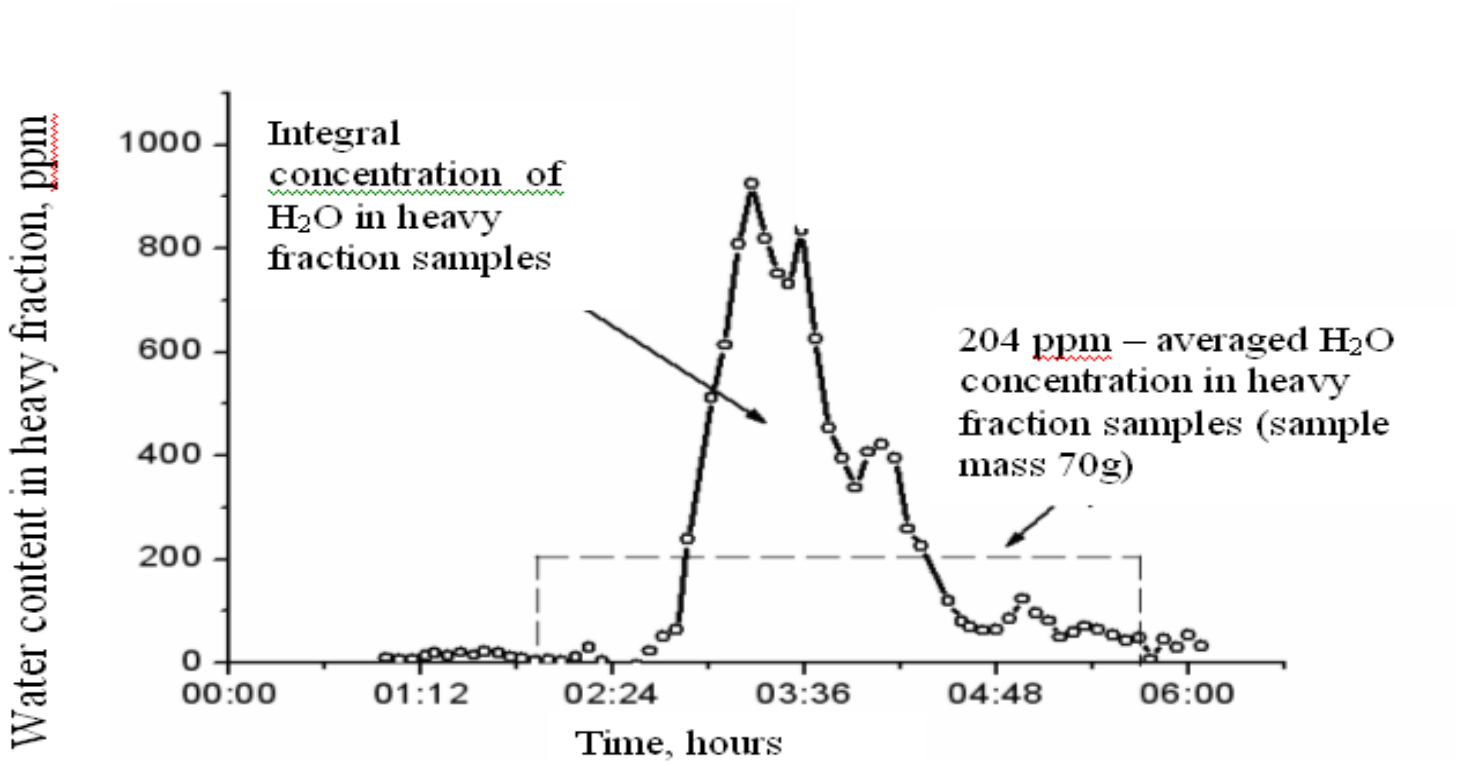
K1 – K7 – valves, M1 – manometer, PD –photodetector. NH_3 container with initial ammonia was connected to lower part of rectification column

Water concentration in different probes



Water concentration in heavy fraction was measured continuously for four days during rectification of different ammonia probes

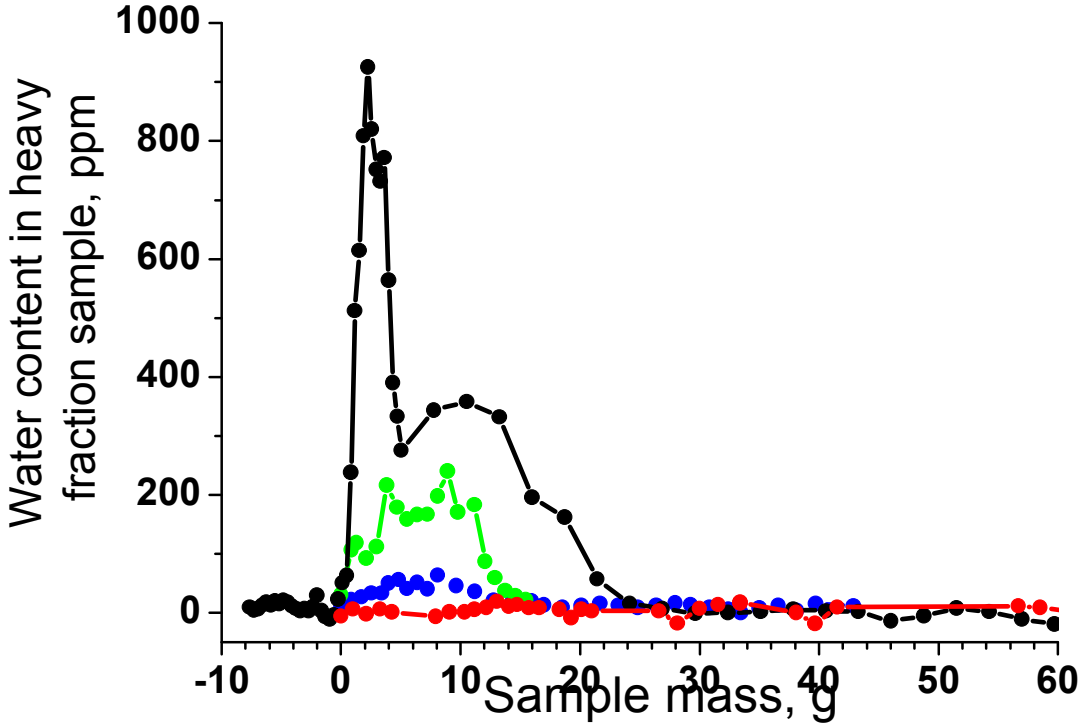
Determination of water content in heavy fraction



Water content in initial ammonia (Miskh, 2200 g) was calculated knowing integral amount of water in heavy fraction:

204 ppm*70g/2200g=6.5 ppm

Examples of water detection in initial probes by measuring water in heavy fraction



Water concentration was measured continuously during rectification process for four different probes

Calculation of water content in initial probes

M_{probe}, mass of initial probe, g	M_{sample} Sample mass (heavy fraction), g	Water concentration, ppm	
		$C_{average}$ (measured in heavy fraction)	C_{H2O} (calculated for initial probe)
2200	**70**	**205**	**6,52**
1480	**15,4**	**115**	**1,20**
1500	**42,9**	**24,1**	**0,69**
3300	**104**	**6,3**	**0,20**

Assuming that almost all the water in initial ammonia would be concentrated in heavy fraction, concentration in initial probe could be calculated:

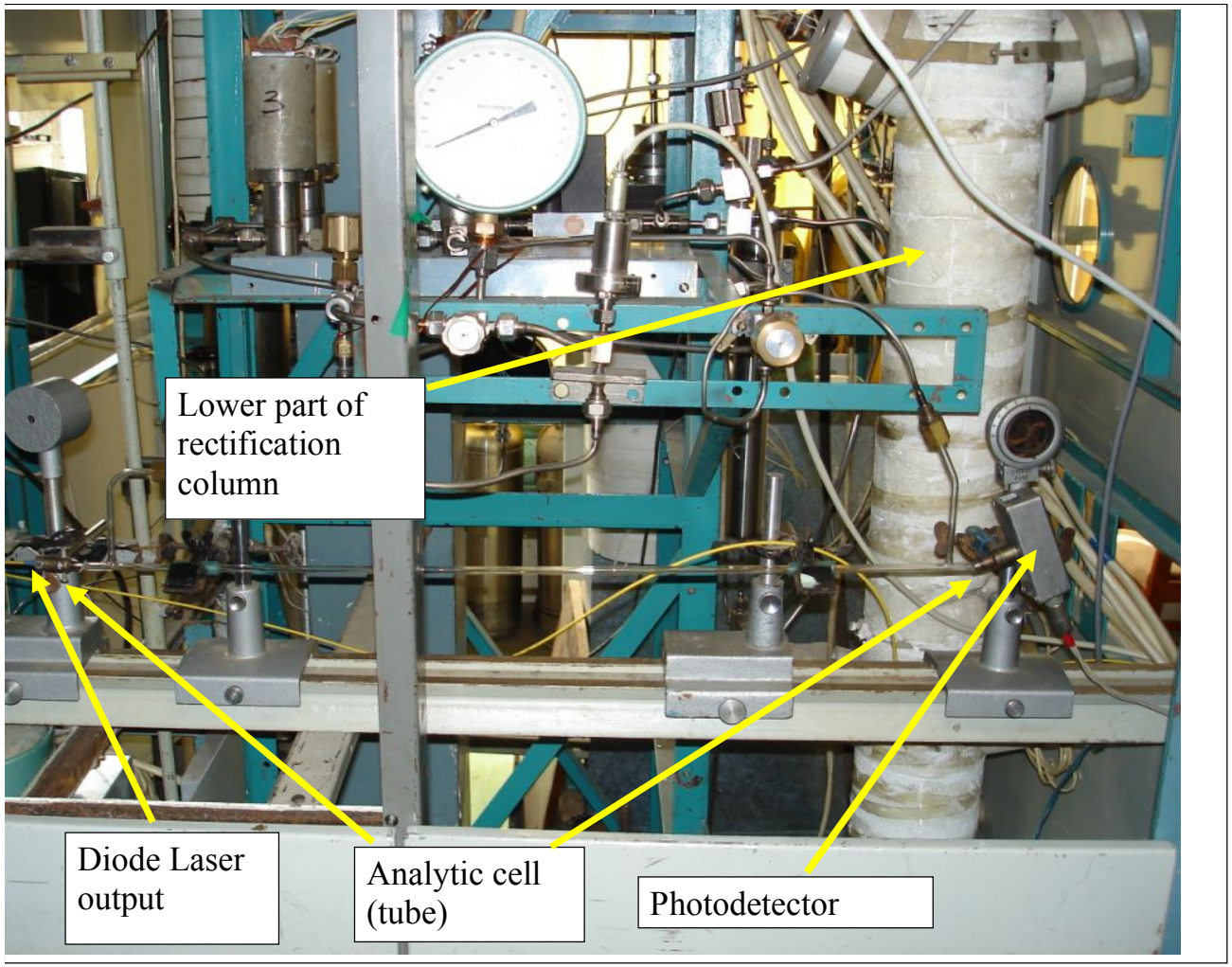
$$\mathbf{C_{H2O}\ (ppm) = (M_{sample}/M_{probe}) \times C_{average}}$$

Colors of numbers correspond to colors of lines on previous slide

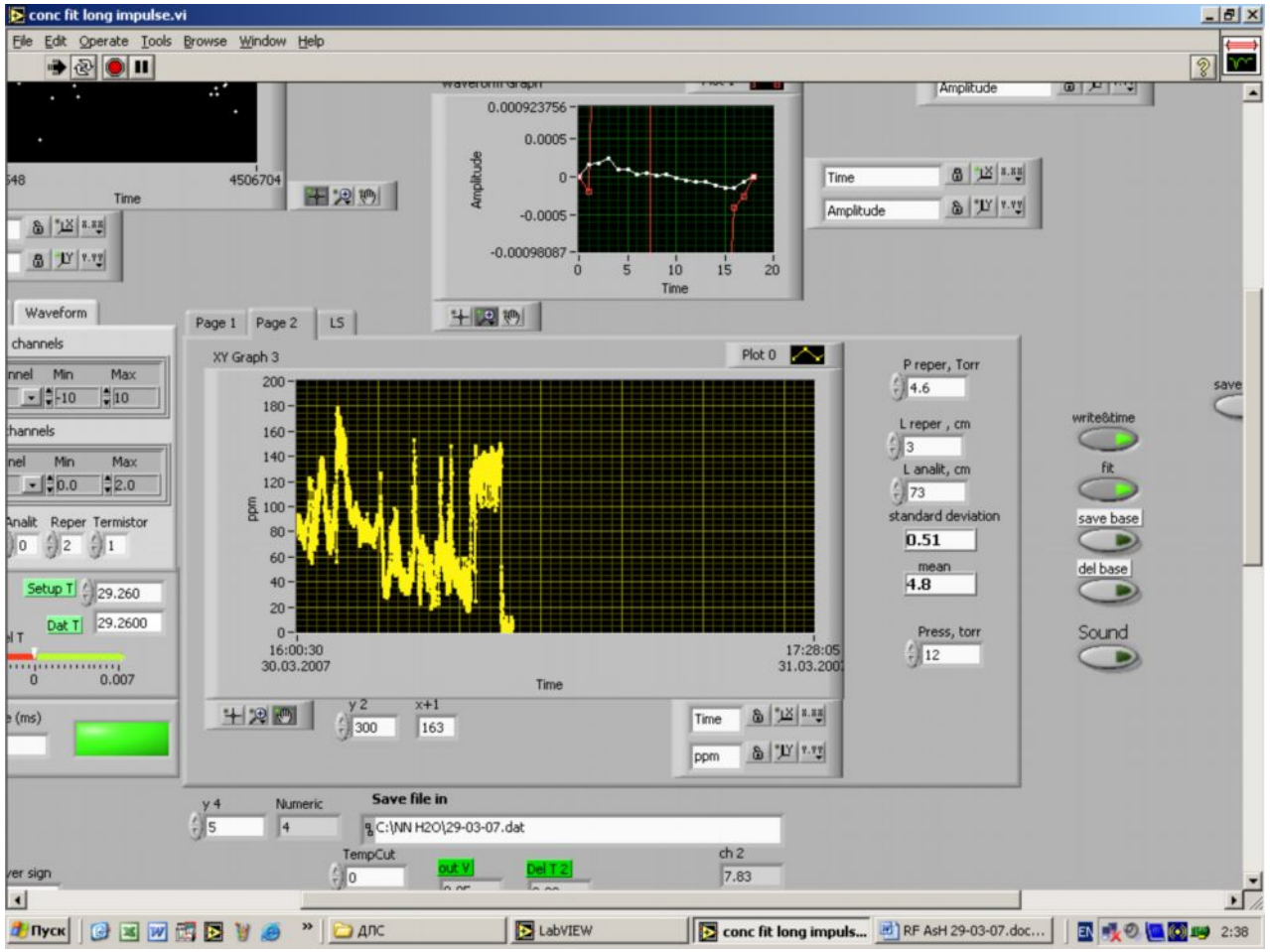
A simple near-IR-diode-laser-based instrument was developed for trace water concentration measurements in high-purity ammonia. This instrument was applied for measuring of humidity in on-line detection of water in ammonia during a process of industrial rectification. The results of water concentration measurements were compared with alternative techniques (dew point meter) and rather good agreement was achieved. A sensitivity of such simple diode-laser based instrument for direct measurement was estimated as 1 ppm. A method of measuring of integrated mass of water containing in heavy fraction extracted during rectification process gives even lower detection limit of less than 0.2 ppm depending on purity in initial ammonia.

Technical ammonia brand A	**200 ppm**
Cryogenic dried ammonia	**53 ppm**
Recrification column dried ammonia	**0.1 ppm**

General view of experimental set-up



Example of system operation



Central graph shows time dependence of water concentration in ammonia during rectification process