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TDLS based complexes development for impurities detection in high-purity hydrides

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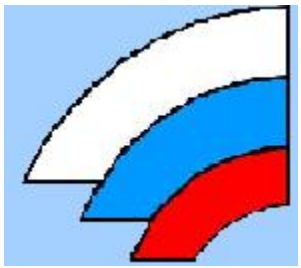
Scientific-Industrial Enterprise
SALUT



Introduction

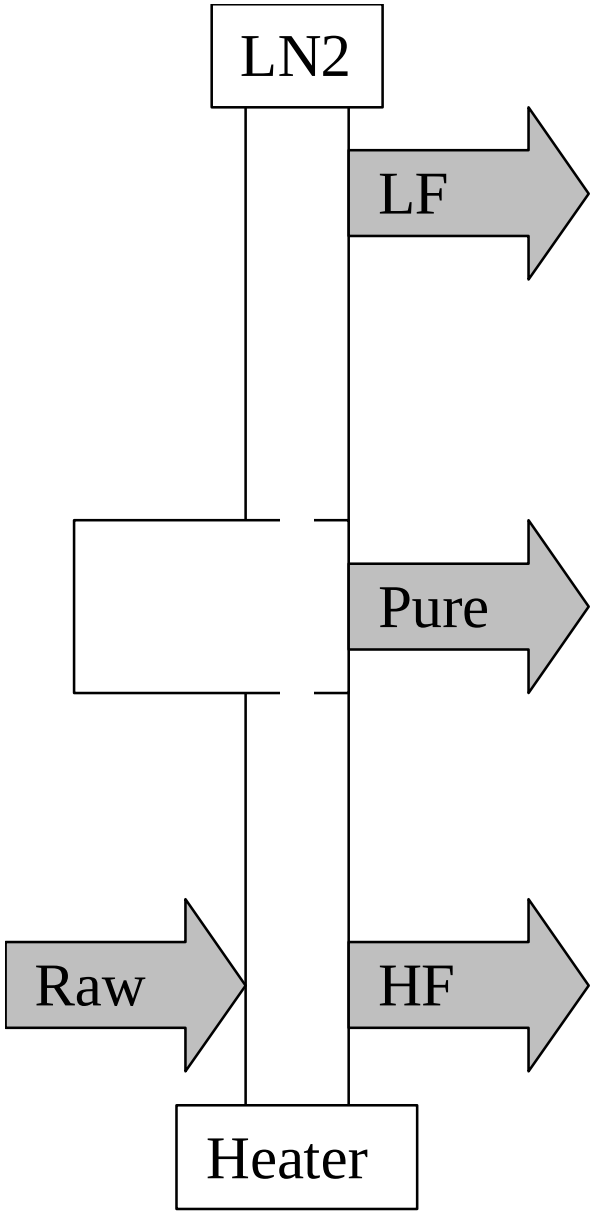
High-purity hydrides (AsH_3, PH_3, NH_3, GeH_3, SiH_4) are using for semiconductors production. Quality of semiconductors manufactured depends on impurities presence. There are many possible impurities in hydrides. H_2O, NH_3, H_2S, CO_2, and C_2H_4 are considered as most important.

Real time impurities concentration measurement during purification process is very important.

Requirements: One bottom operation, reliability, selectivity, quick response, concentration range 10^{-7} – 100 %.

Goal – to investigate hydrides spectra and to develop family of TDLS based complexes for continuous impurities control during hydrides purification.

Purification process



Block scheme (left) and view (right) of rectification column.

There are 4 gas flows of interest: raw material in, pure material out, and gas lines for light (LF) and heavy (HF) fractions

High purity hydride unloading from rectification column.

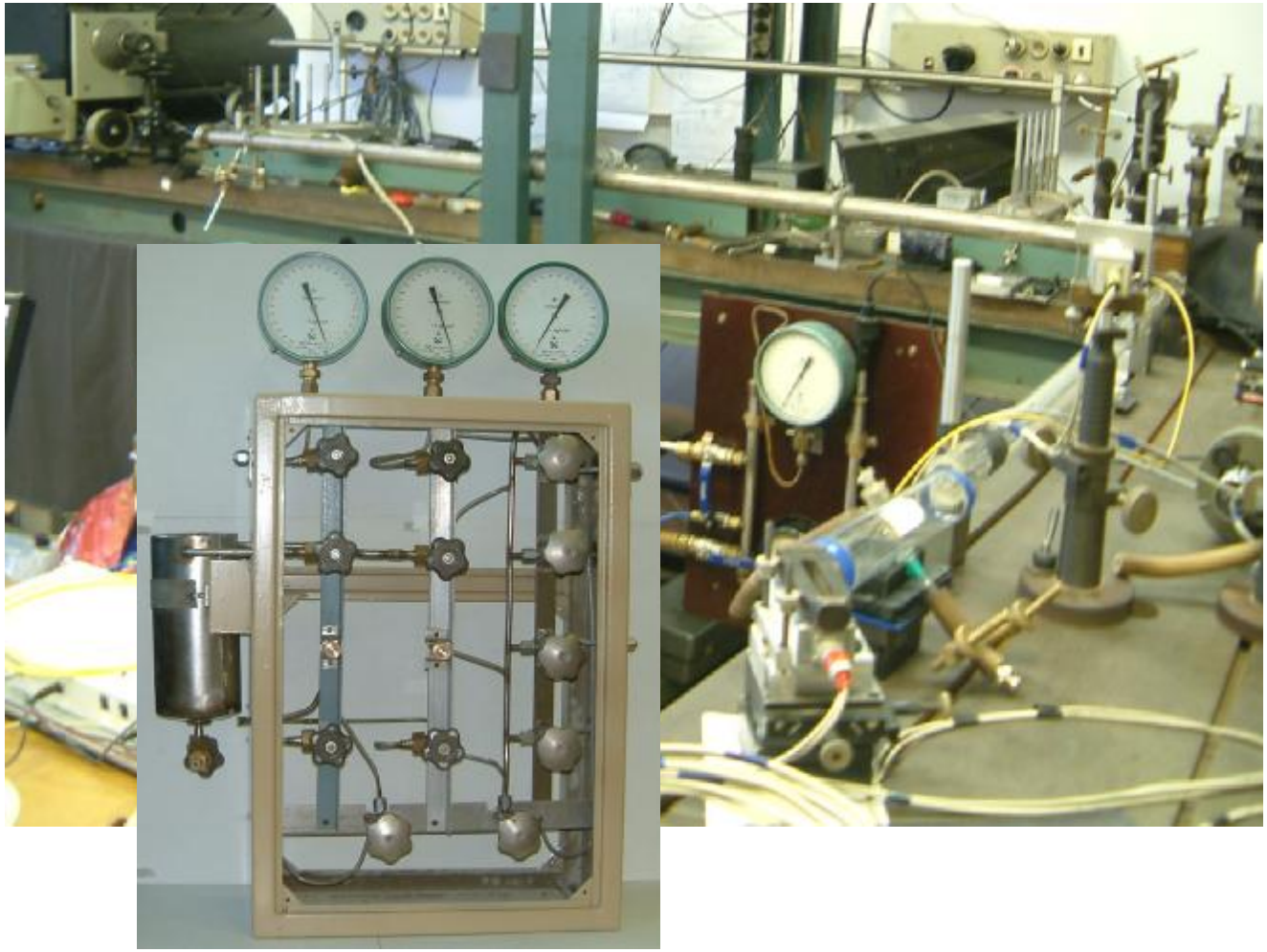
Family of TDLS complexes developed

Family of TDLS complexes was developed to measure impurities concentration in real time.

1. H_2O in NH_3
2. H_2O in PH_3
3. NH_3 in PH_3
4. NH_3 in AsH_3 in “raw”, “pure”, and “LF” channels
5. CO_2 and H_2S in AsH_3 in “raw”, “pure”, and “HF” channels
6. C_2H_4 in AsH_3 in “raw”, “pure”, and “HF” channels

Spectroscopy

For majority of molecules under consideration spectral information in near IR are unavailable. Spectra were recorded using 3 channels DL based spectrometer developed and Bruker IFS 66v (spectral resolution 0.01 cm^{-1}).

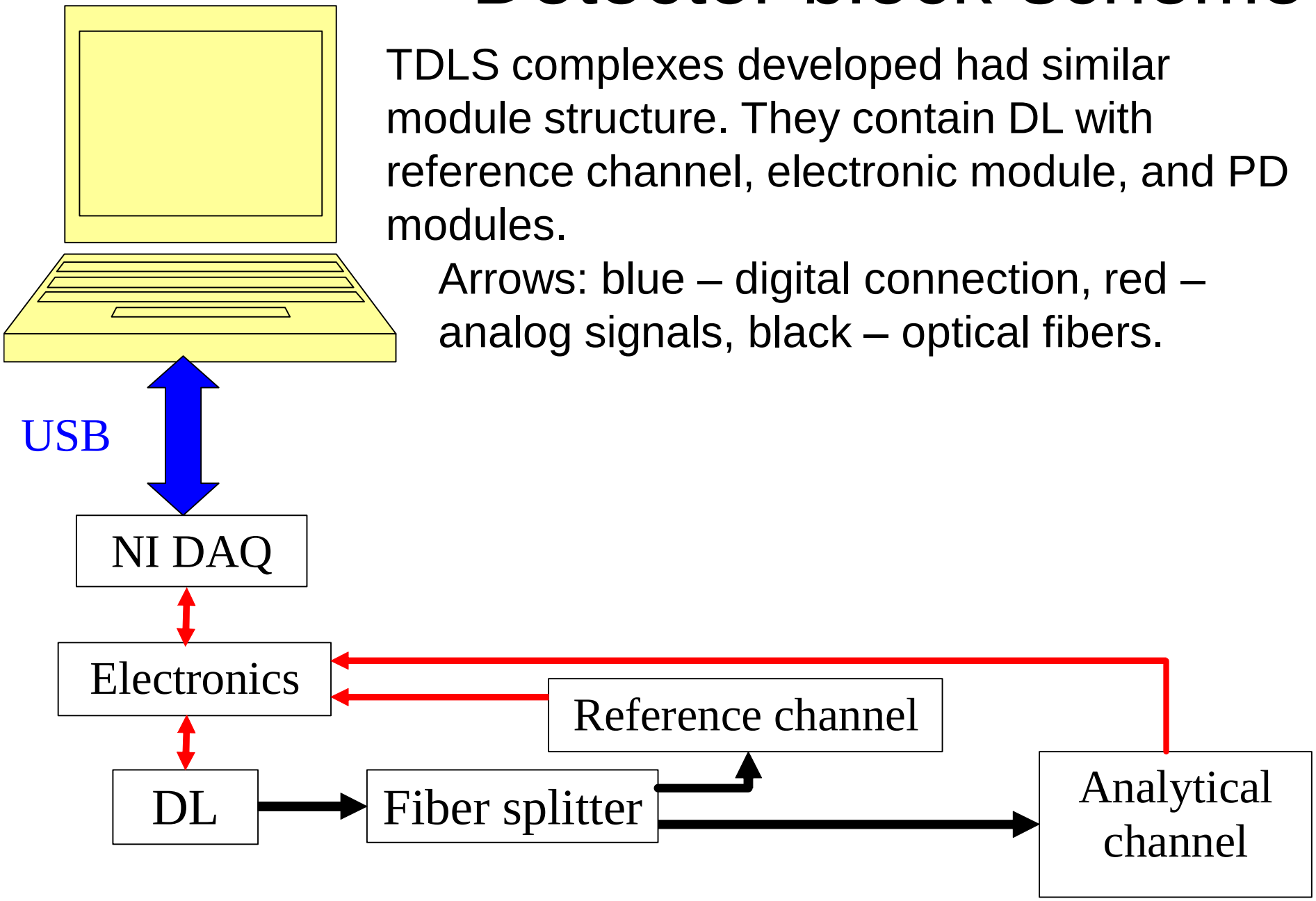


View of 3 channels DL based spectrometer developed with gas distribution system to deal with hazard objects.

Detector block-scheme

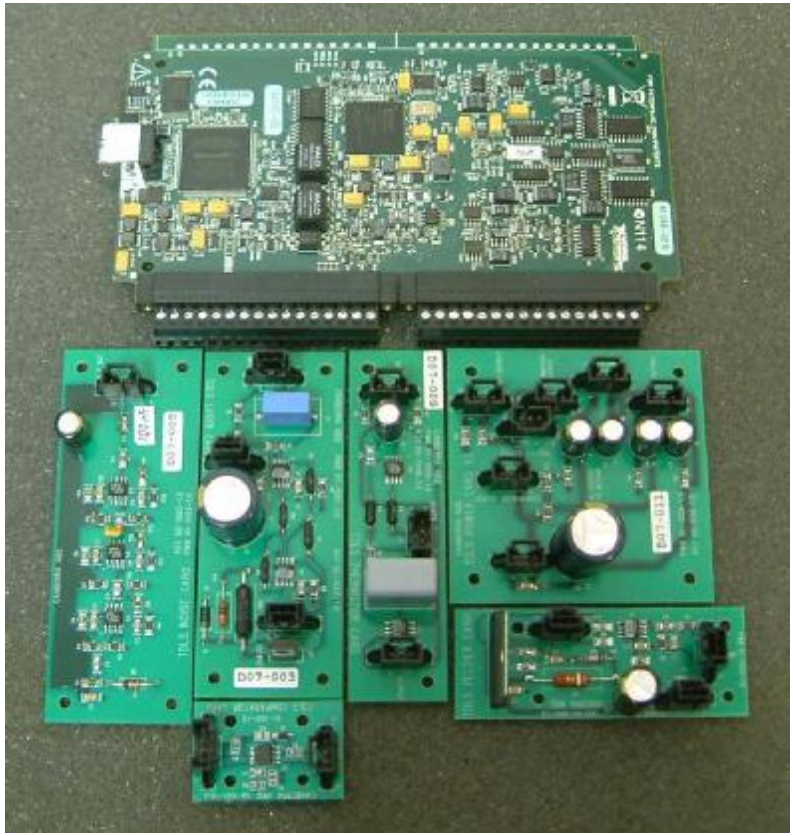
TDLS complexes developed had similar module structure. They contain DL with reference channel, electronic module, and PD modules.

Arrows: blue – digital connection, red – analog signals, black – optical fibers.



Electronics

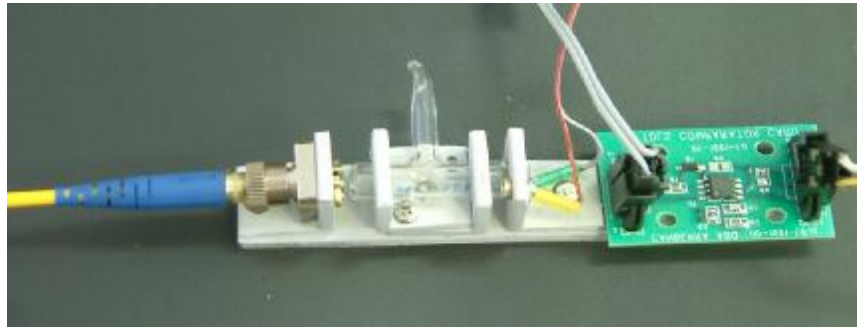
All TDLS complexes contain the same set of electronics



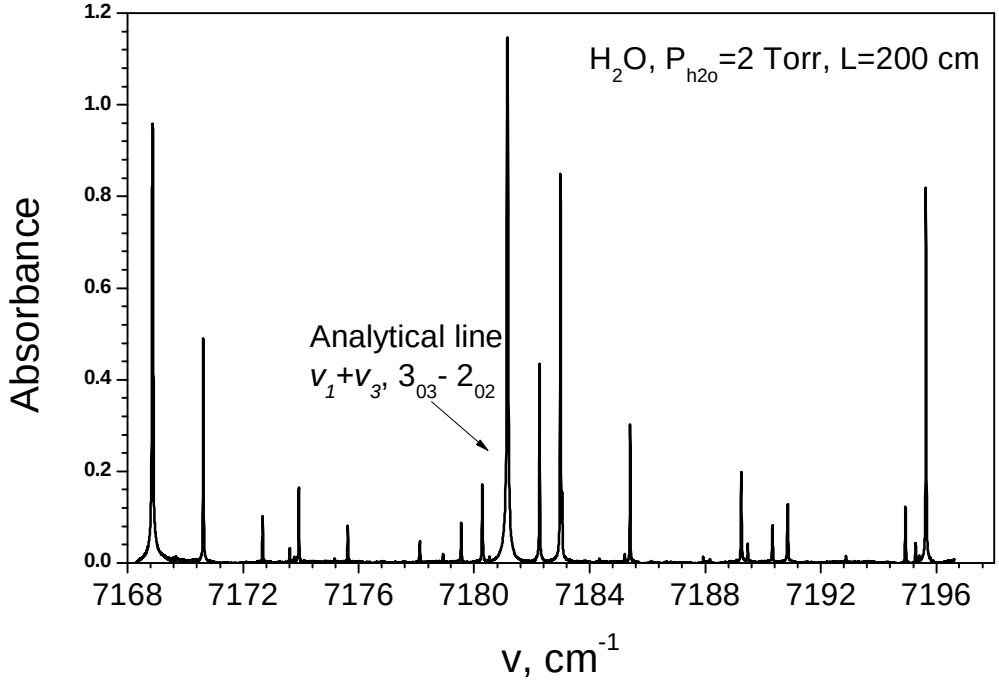
National Instrument USB DAQ

Electronics developed by GPI and Canberra Albuquerque and manufactured by Canberra Albuquerque

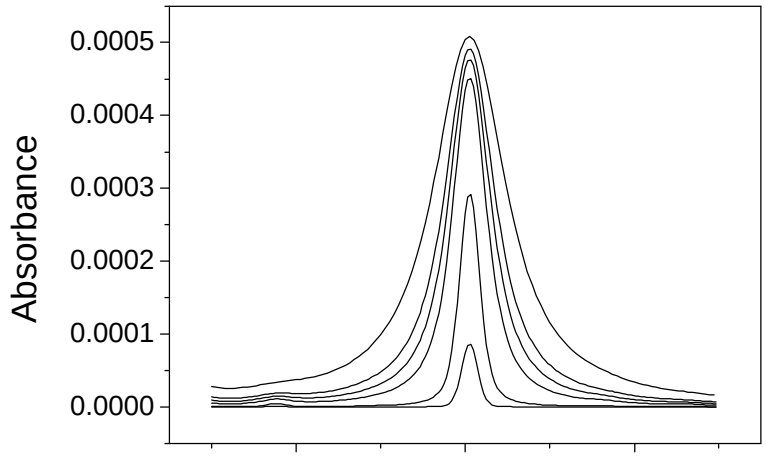
View of reference channel



Analytical line for H_2O in NH_3

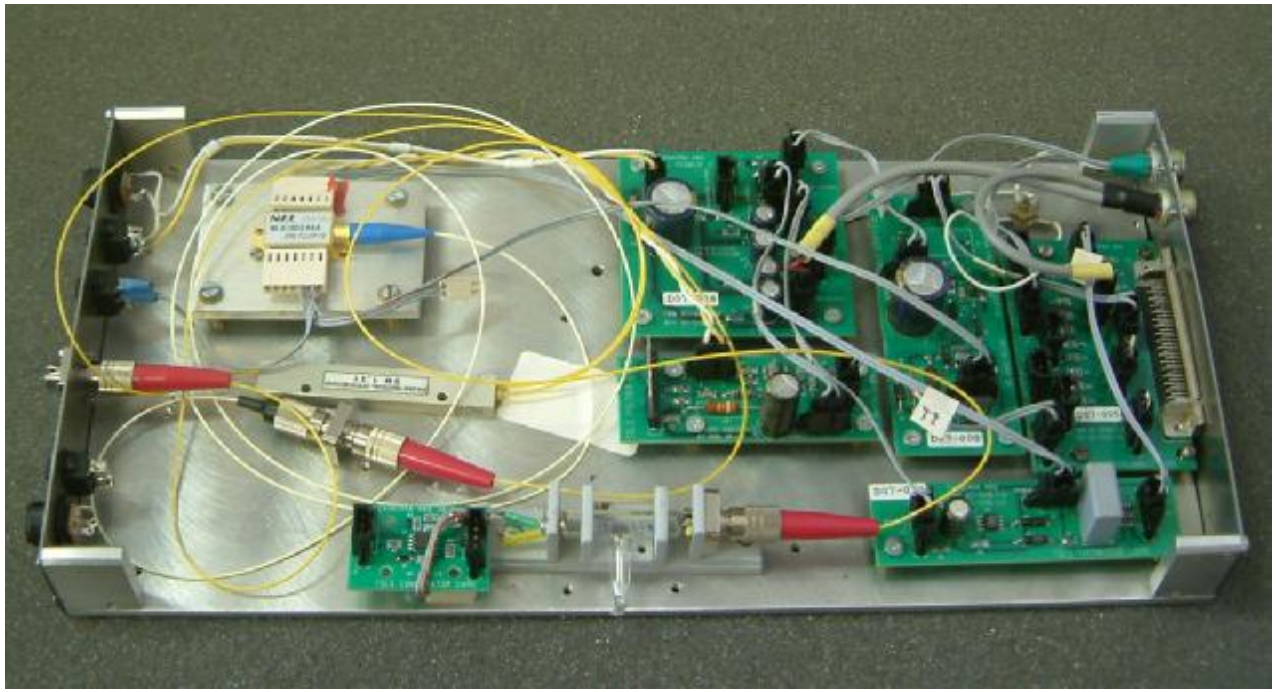


Selection of analytical line to measure water vapor in ammonia.



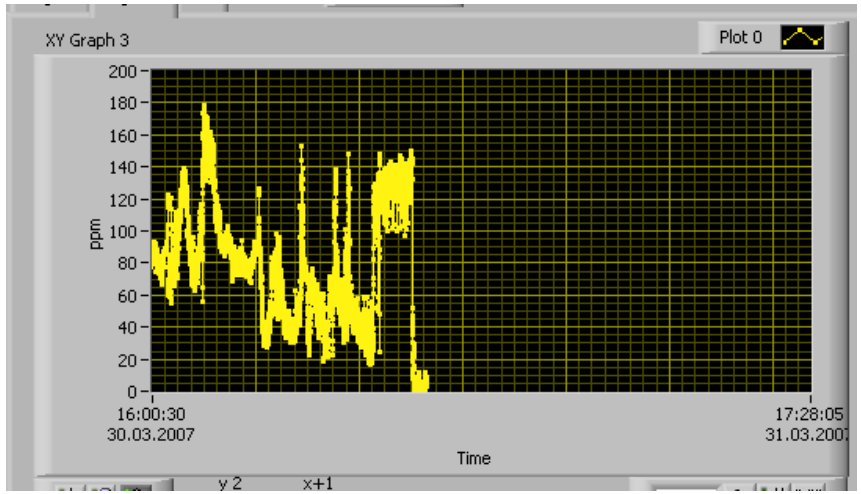
Analytical H_2O spectral line shapes for different NH_3 pressures: 760, 500, 400, 300, 100, 20 Topp.

H_2O in NH_3

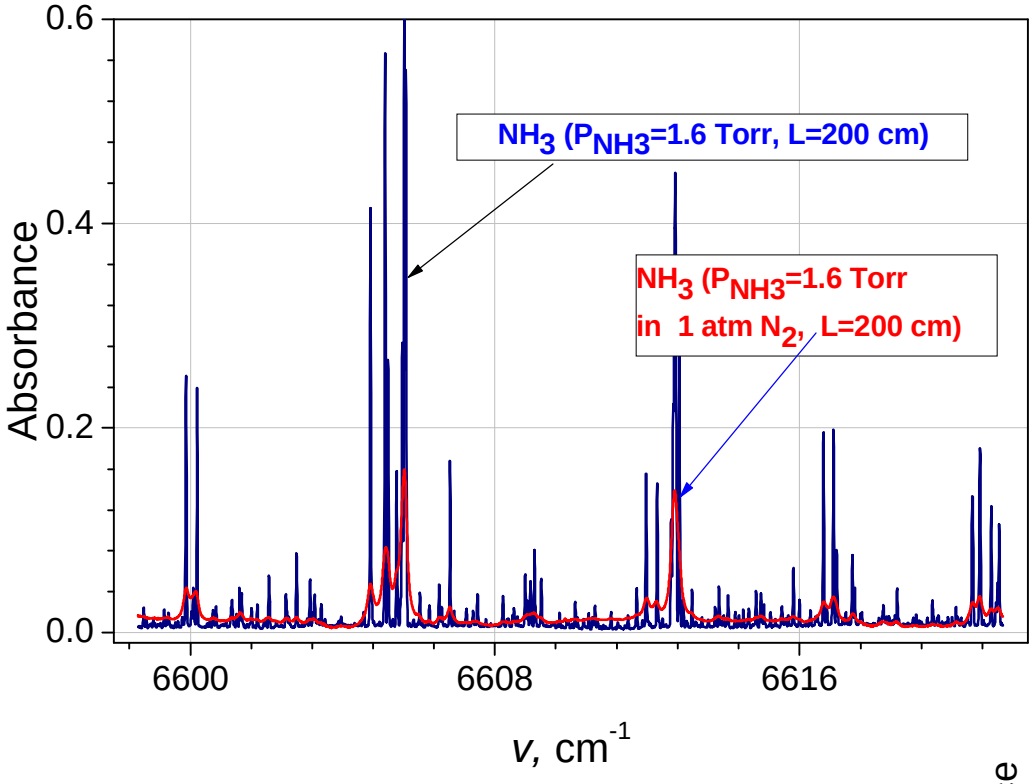


View of TDLS complex developed to measure water vapor concentration in NH_3

Water concentration measurement in heavy fraction (HF) during purification process

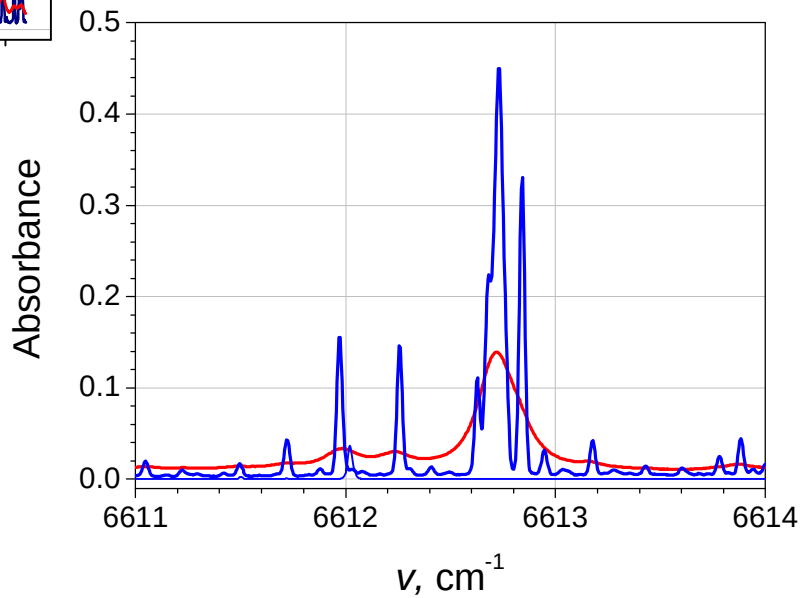


Analytical NH_3 line in 1.51 μ range

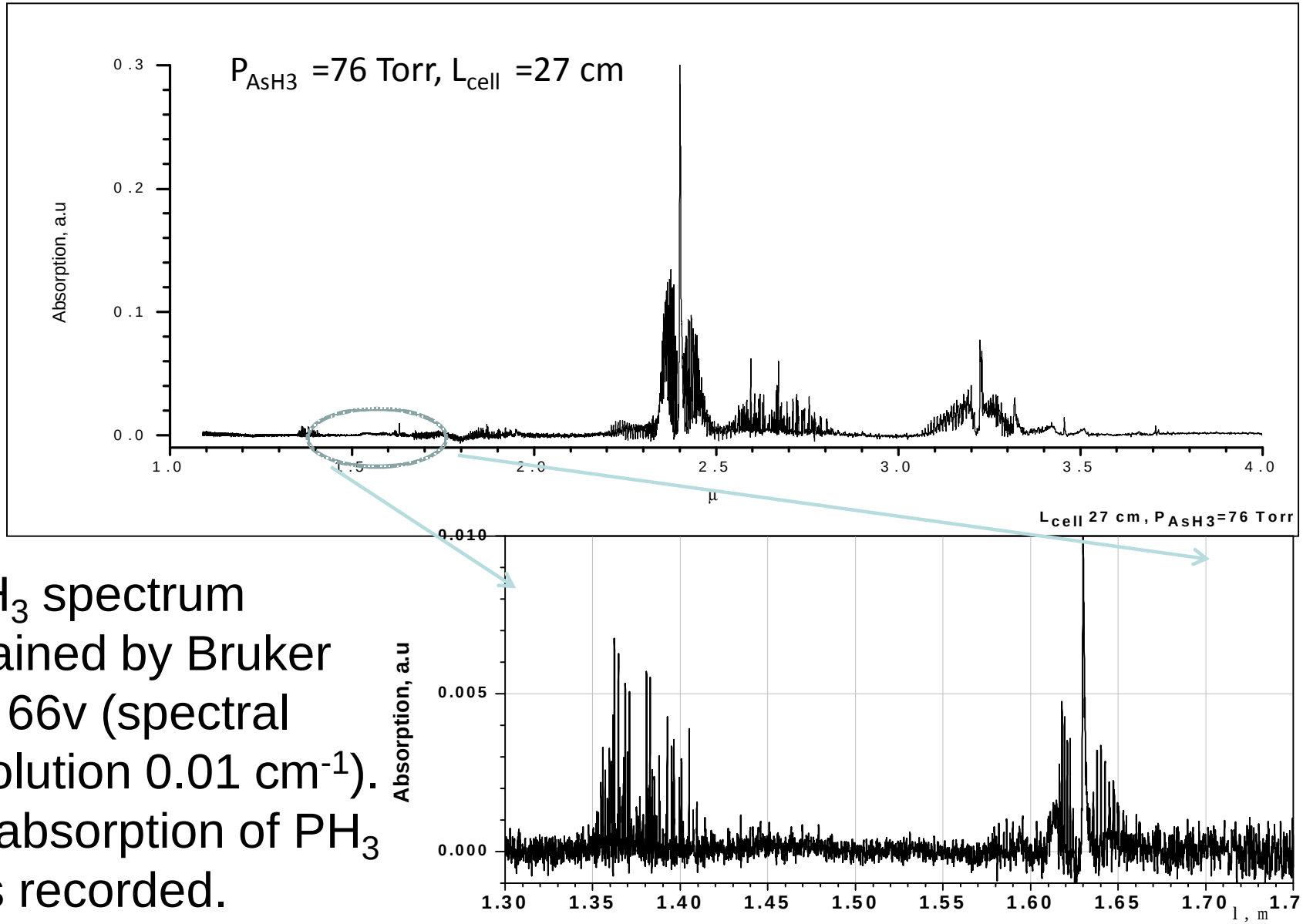


NH_3 spectra recorded using TDLS and software Panorama (see C2)

NH_3 analytical line 1.51 μ spectral range



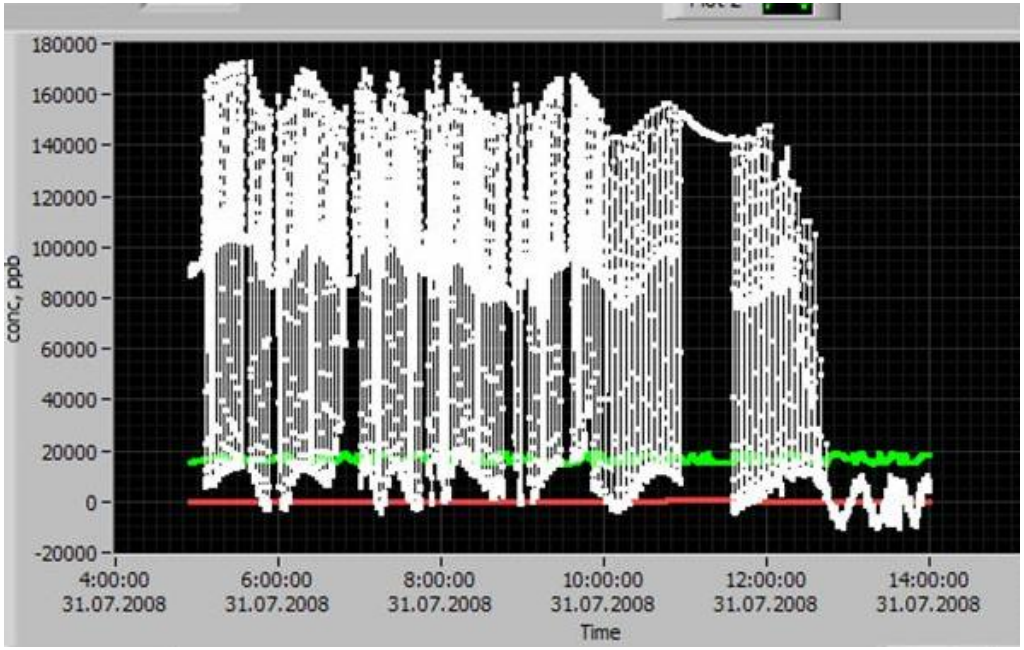
AsH_3 spectrum



AsH_3 spectrum obtained by Bruker IFS 66v (spectral resolution 0.01 cm^{-1}). No absorption of PH_3 was recorded.

NH_3 in AsH_3 and PH_3

View of 3 channels TDLS complex developed to measure NH_3 in AsH_3 and PH_3.

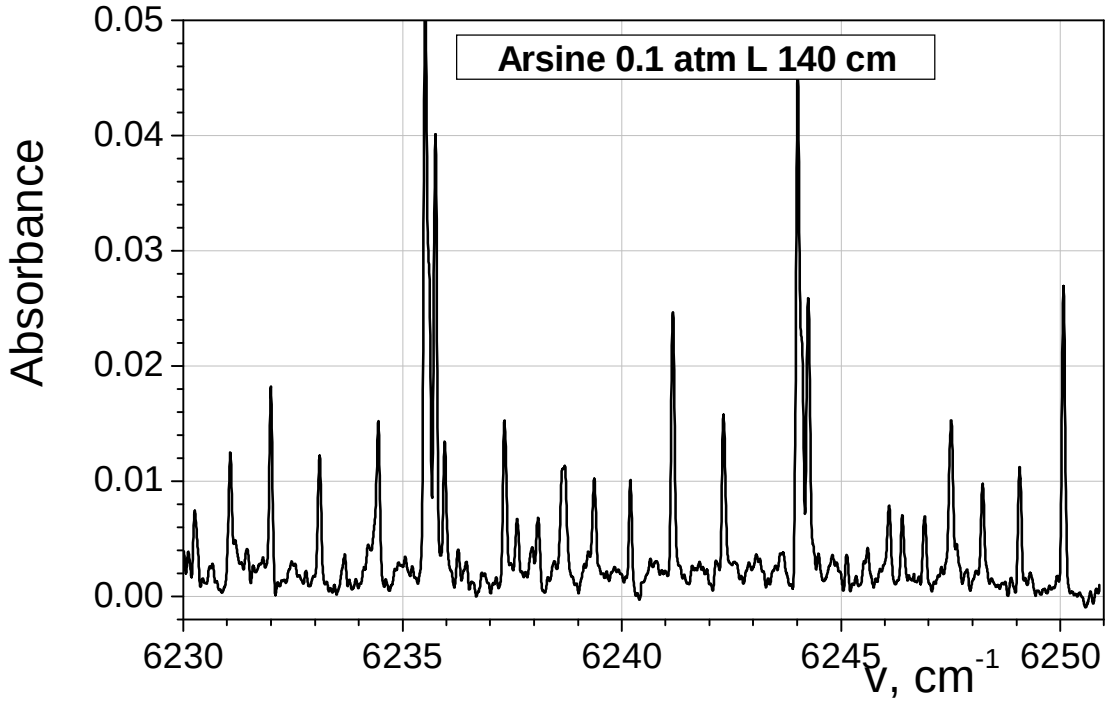


NH_3 detection in 3 channels: raw (green), pure (red), LF (white).

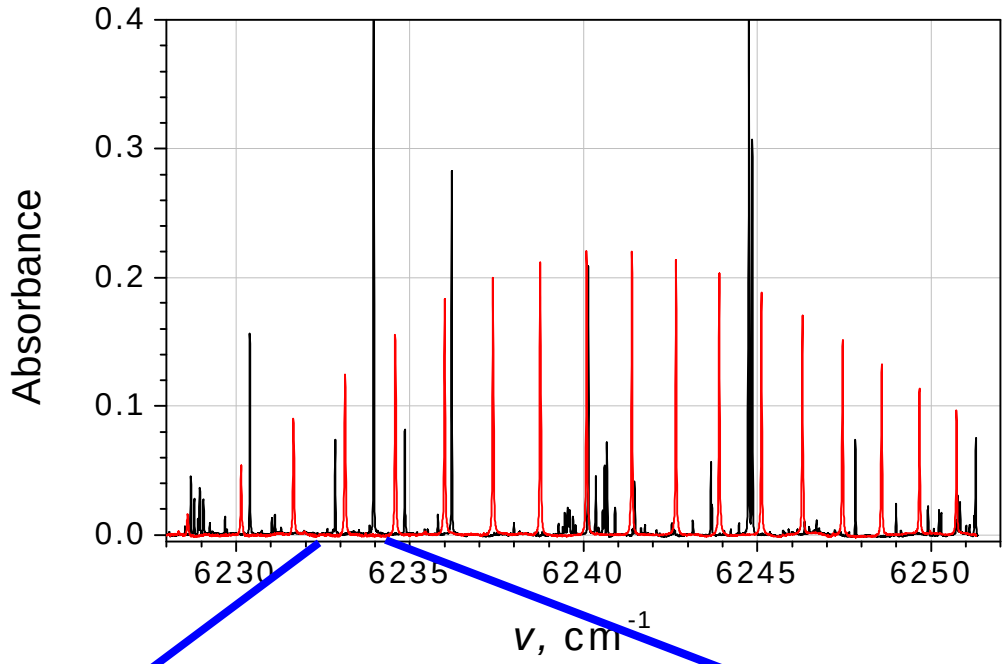
CO_2 and H_2S in AsH_3 and PH_3

Both CO_2 and H_2S have absorption in 1.6 μ range and can be detected using the same DL. There was no information about AsH_3 and PH_3 in this spectral range. Spectra were recorded using 3 channel DL spectrometer developed.

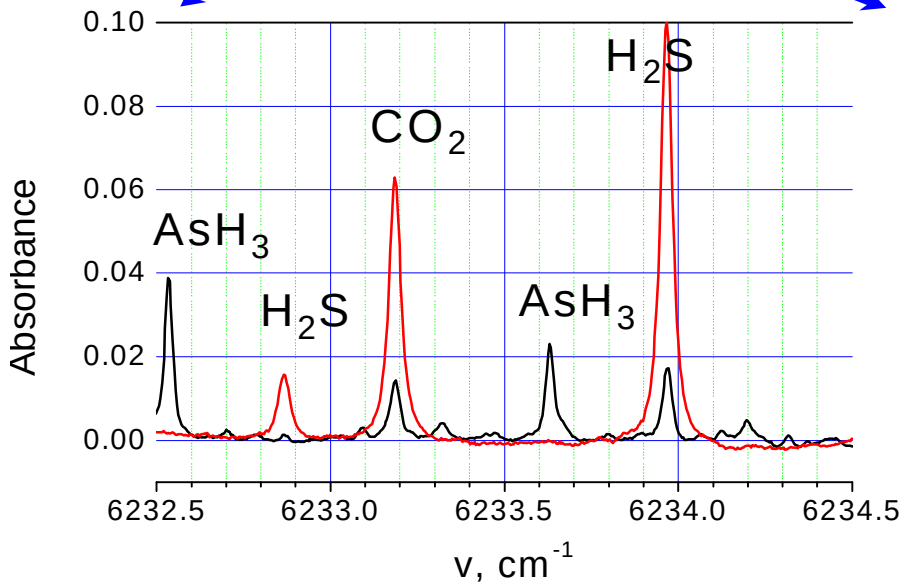
AsH_3 absorption in spectral range under consideration. Raw AsH_3 sample was used having CO_2 and H_2S impurities.
No significant PH_3 absorption was observed.



Analytical line selection



Absorption spectra of CO_2 (red) and H_2S (black) in spectral range under consideration as recorded by TDLS.

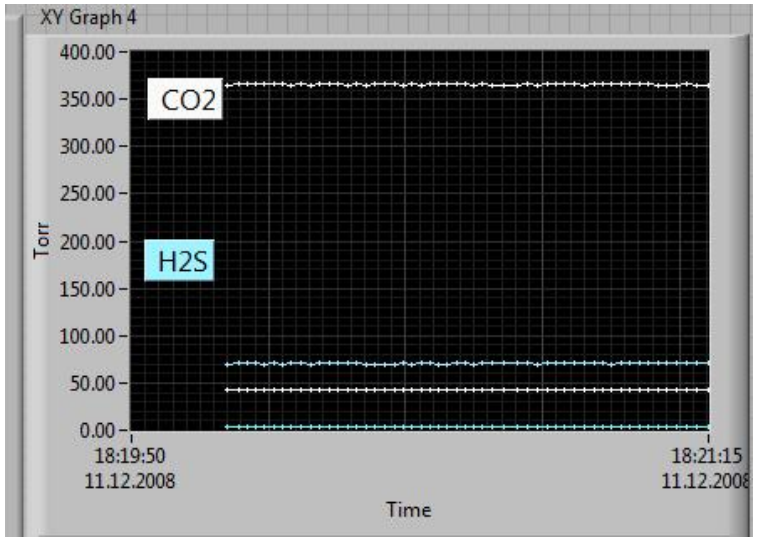


Analytical lines to detect CO_2 and H_2S were selected to have no interference with AsH_3 absorption.
Spectra recorded L=140 cm:
red - P=0.2 Bar of gas mixture $Ar:CO_2:H_2S=1:0.46:0.054$.
black - P=0.1 Bar of raw AsH_3 sample.
Impurities presence can be easily observed.

CO_2 and H_2S in AsH_3 and PH_3

View of 3 channels TDLS complex developed to measure CO_2 and H_2S in AsH_3 and PH_3.

Simultaneous measurement of CO_2 (white) and H_2S (blue) in two channels containing cells with following gas mixtures:
Upper – 365 Torr CO_2 and 70 Torr H_2S.
Lower – 43 Torr CO_2 and 3.6 Torr H_2S.



Conclusion

Spectra of molecules under consideration (hydrides and impurities) were recorded in near IR spectral range (some of them for the first time). Analytical lines to detect different impurities in hydrides were selected.
6 TDLS complexes were developed and installed in Scientific-industrial enterprise “Salut” (Nizhnii Novgorod) to control process of hydrides purification in real time.