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C_2H_4 detection in SiH_4 purification using TDLS

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Introduction

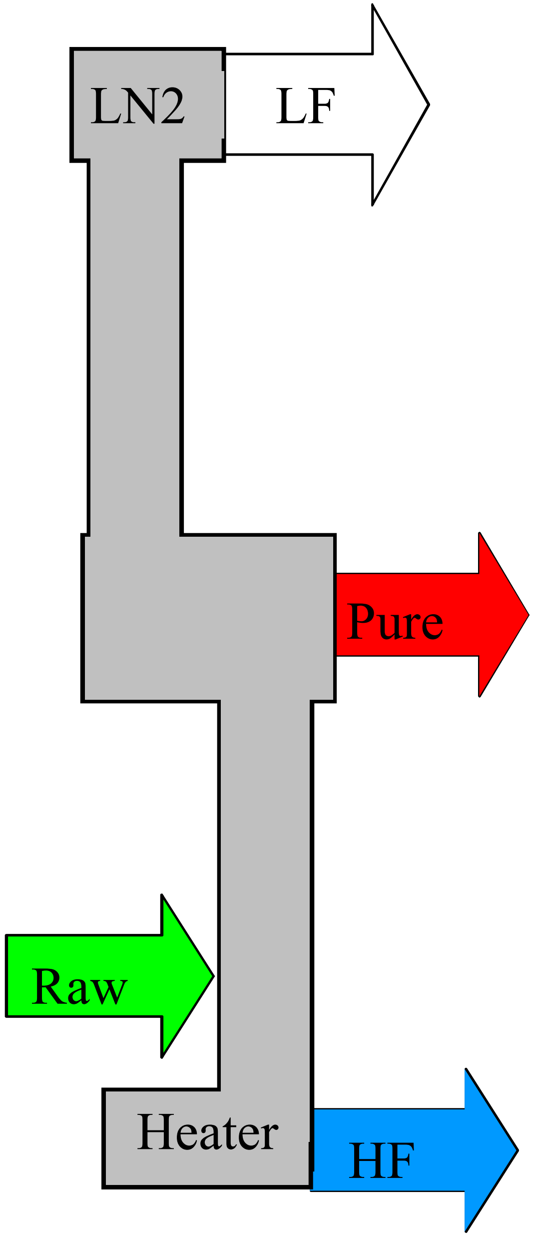
SiH_4 is main source to produce Si of highest purity necessary for modern electronics. Requirements for SiH_4 purity: concentration of electrically active impurities (B, P, As, Al) < 10^{-9} %, and for gaseous impurities < 10^{-5} -10^{-6} %. To produce high purity SiH_4 low temperature rectification is using.

Volatile hydrides (diboran, arsine, phosphine) sources of electrically active impurities have physical – chemical properties close to SiH_4. As result it is difficult both to remove and control them during rectification process. Due to the problem mentioned above SiH_4 purification efficiency can be controlled by C_2H_4 having in purification process under consideration separation factor close to 1 (1.26).

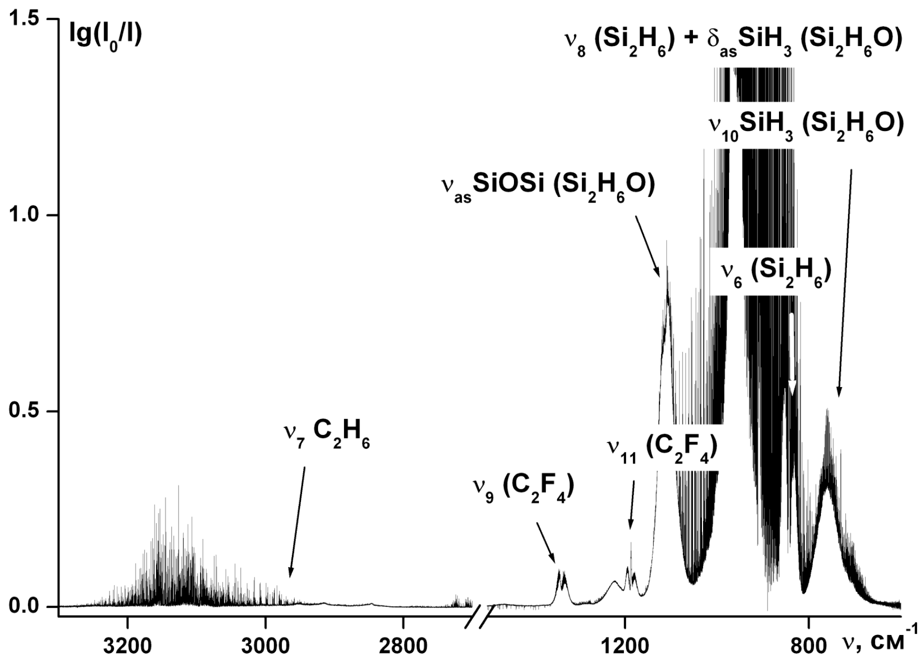
Goal of present work: to development apparatus and technique for ethylene detection in silane with detection limit 1 ppm.

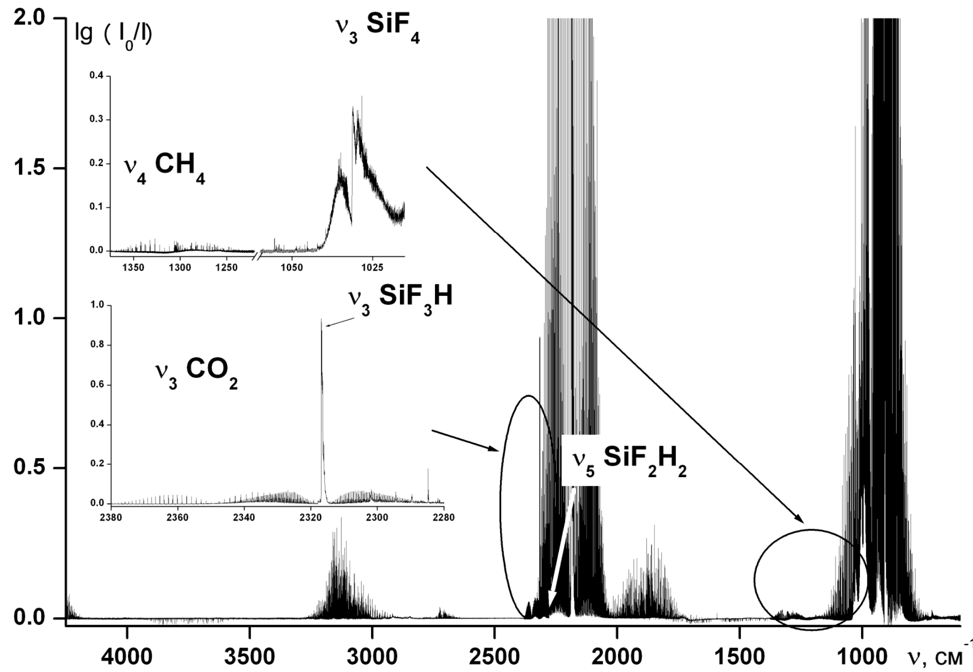
Rectification column

Rectification column view and diagram. Raw material is loaded in rectification column. Due to heater and LN2 cooling condensation evaporation processes took place inside column. As result impurities are concentrated at bottom (Heavy Fraction - HF) and upper (Light Fraction - LF) parts of rectification column. Central part - pure material.



Impurities





FTS spectra (resolution 0.01 cm^{-1}) of HF - Heavy Fraction (left) and LF - Light Fraction (right) with impurities absorption bands identification.

P = 30 mBar, L = 20 cm.

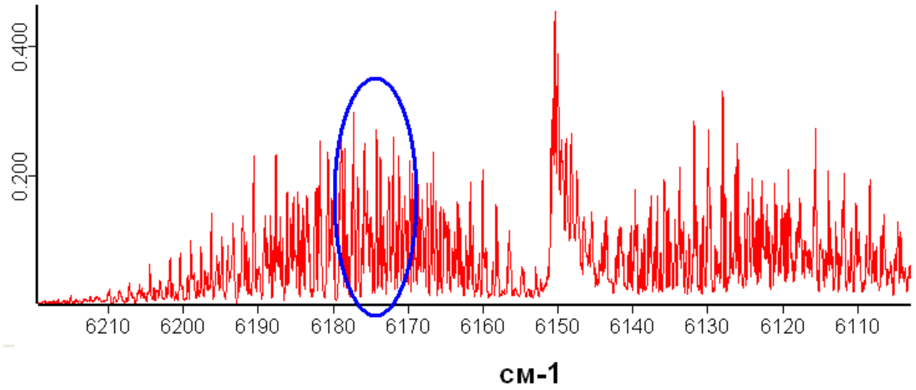
Ethylene selection as indicator

	T_b, °C						
SiH_4	-111.6						
LF	T_b, °C	SF	SF exp.	HF	T_b, °C	SF	SF exp.
CH_4	-161,4	16	15,3	C_2H_4	-103,5	1,68	1,26
SiF_4	-91			C_2H_6	-88,5	4,24	3,2
$SiHF_3$	-			B_2H_6	-92,4		1,37
SiH_3F	-97.5			PH_3	-85,8	5,2	4,4
SiH_2F_2	-77.8			AsH_3	-62,3	19	12,8
CO_2	-78.5			GeH_4	-88,5		2,26

Boiling temperature (T_b) and separation factor (SF) of different impurities in SiH_4.

Volatile hydrides (blue) sources of electrically active impurities in Si (B, P, As) have physical – chemical properties close to SiH_4. As result it is difficult both to remove and to control them during rectification process. Ethylene - C_2H_4 (red) has physical – chemical properties even closer to SiH_4, separation factor close to 1. Hence, ethylene can be used as indicator of removing electrically active impurities during SiH_4 rectification.

Analytical line selection

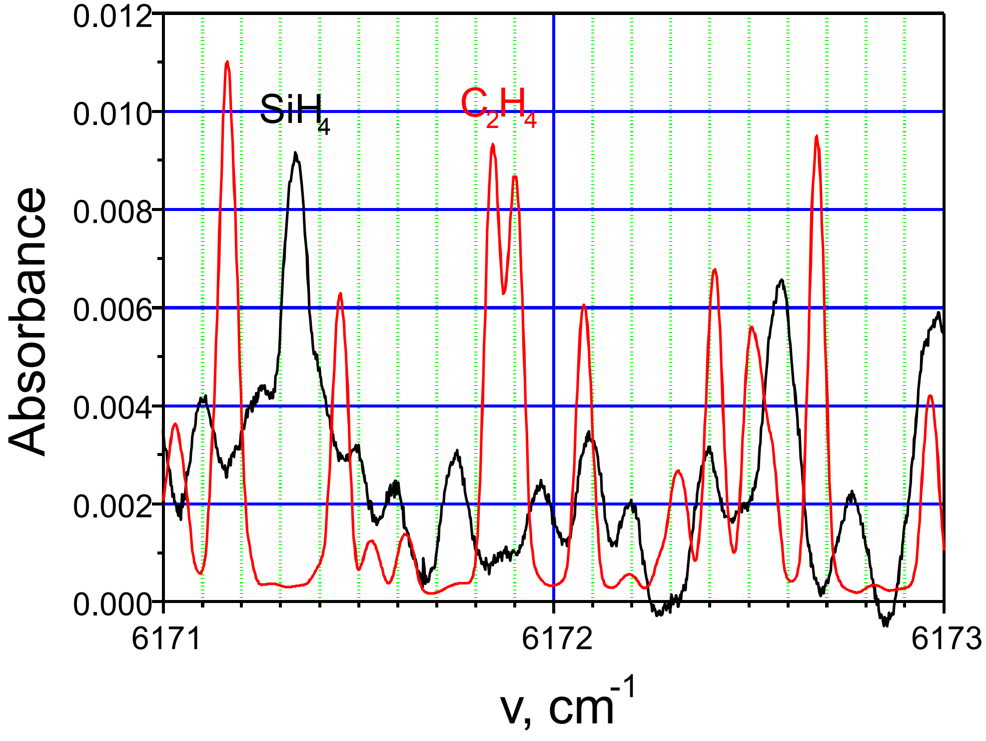


FTS ethylene spectrum in near IR.

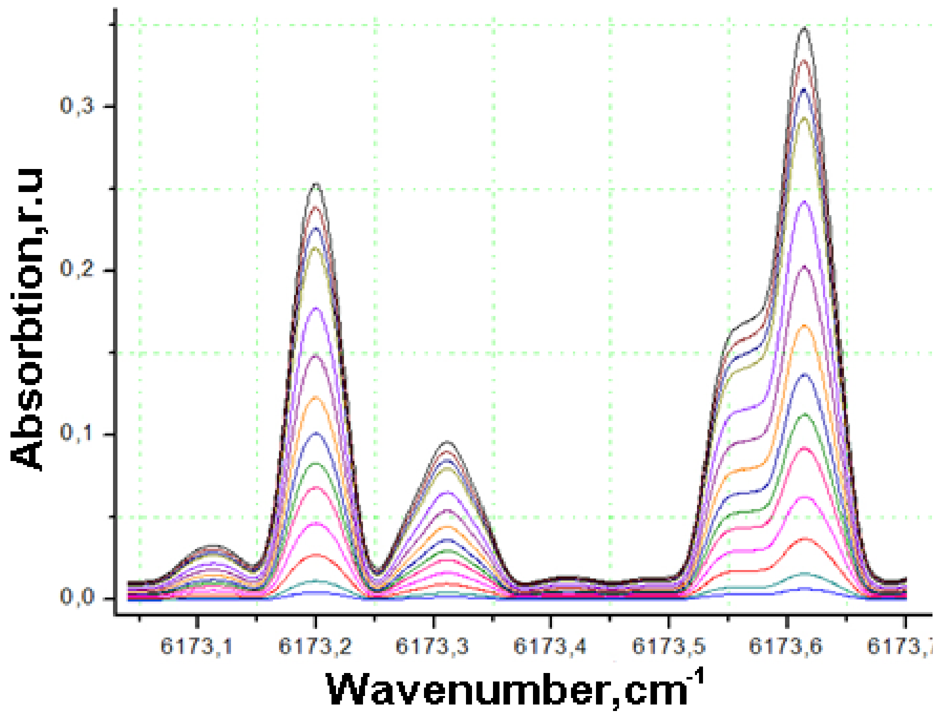
Analytical spectral range was selected (blue).

At the beginning strongest line in selected spectral range was considered as analytical one. However, during preliminary experiments it was found that SiH_4 has also absorbance here.

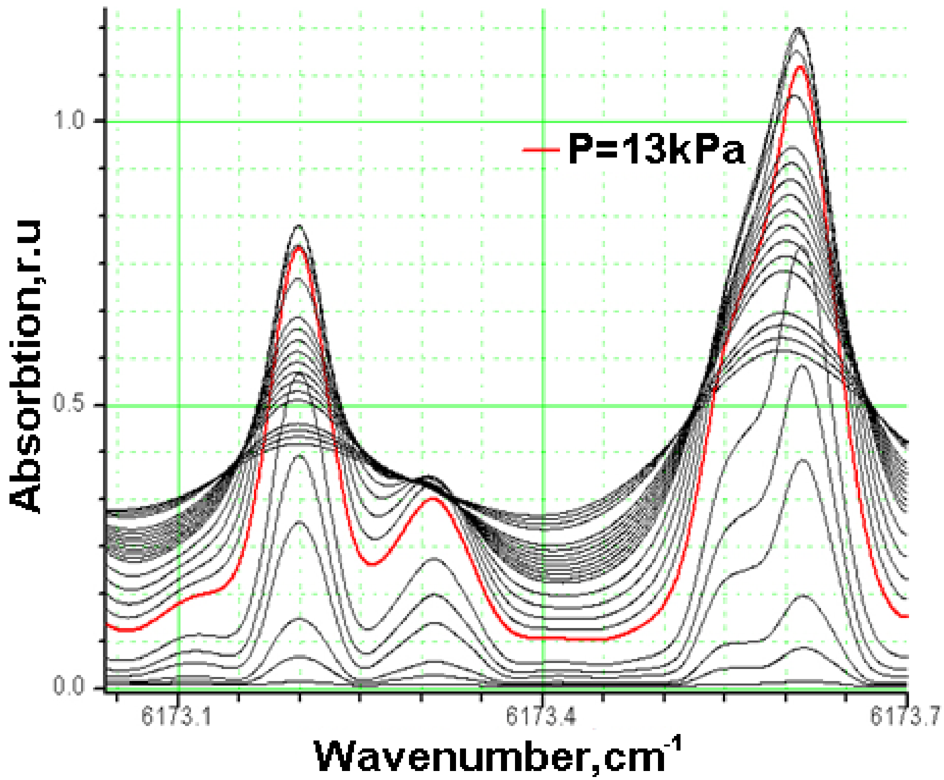
Spectra of both C_2H_4 and SiH_4 were recorded by DL in use. Ethylene analytical line was selected having minority interference with SiH_4.



Optimal sample pressure determination



Pure ethylene absorbance spectra
for P = 1 – 10 mBar.



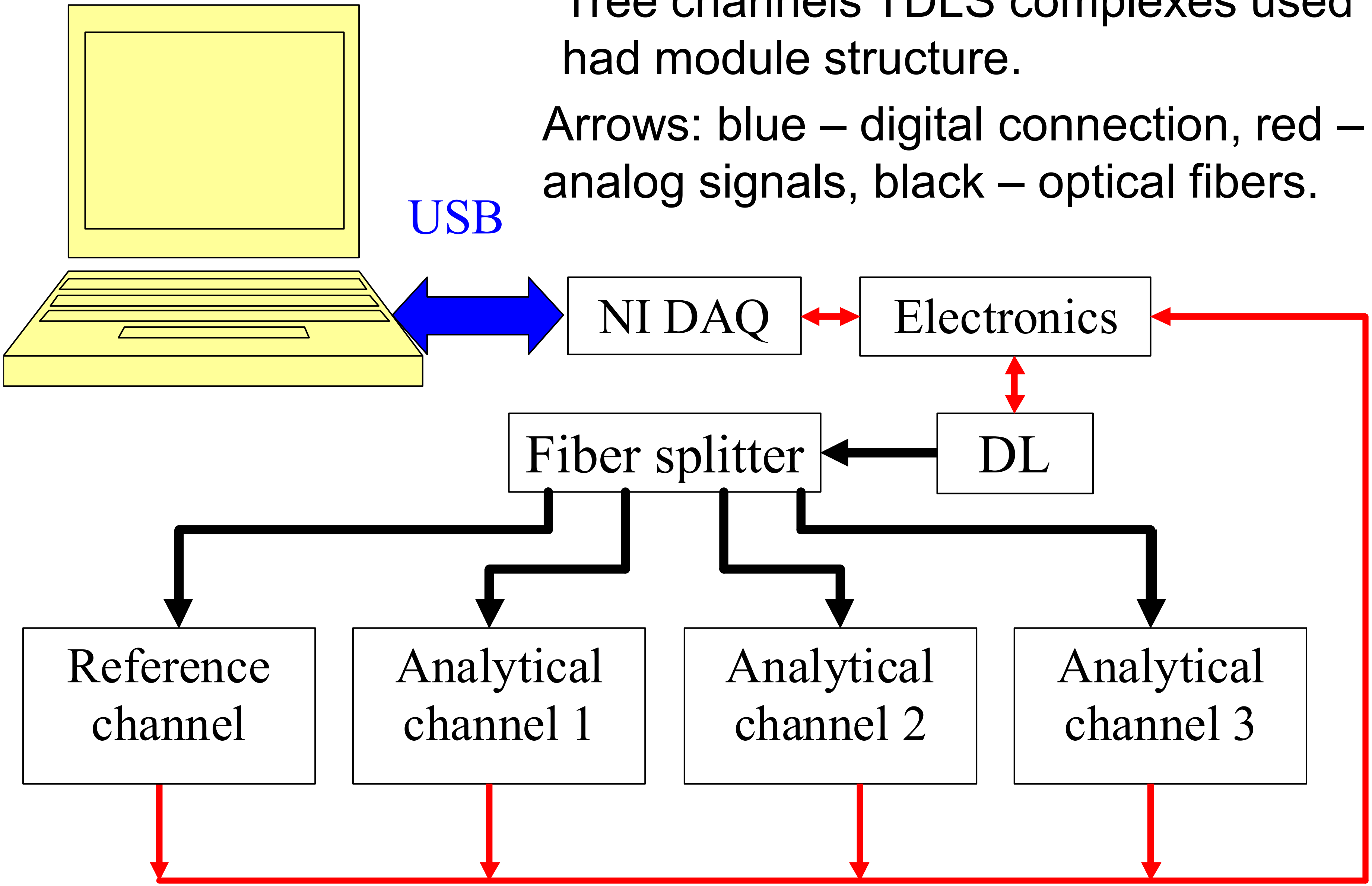
Gas mixture ethylene : nitrogen = 5%
spectra for P = 1 – 1000 mBar.

Optimal sample pressure was determined as 100 mBar.

TDLS complex block-scheme

Tree channels TDLS complexes used had module structure.

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



TDLS complex view

Three channels TDLS complex view.

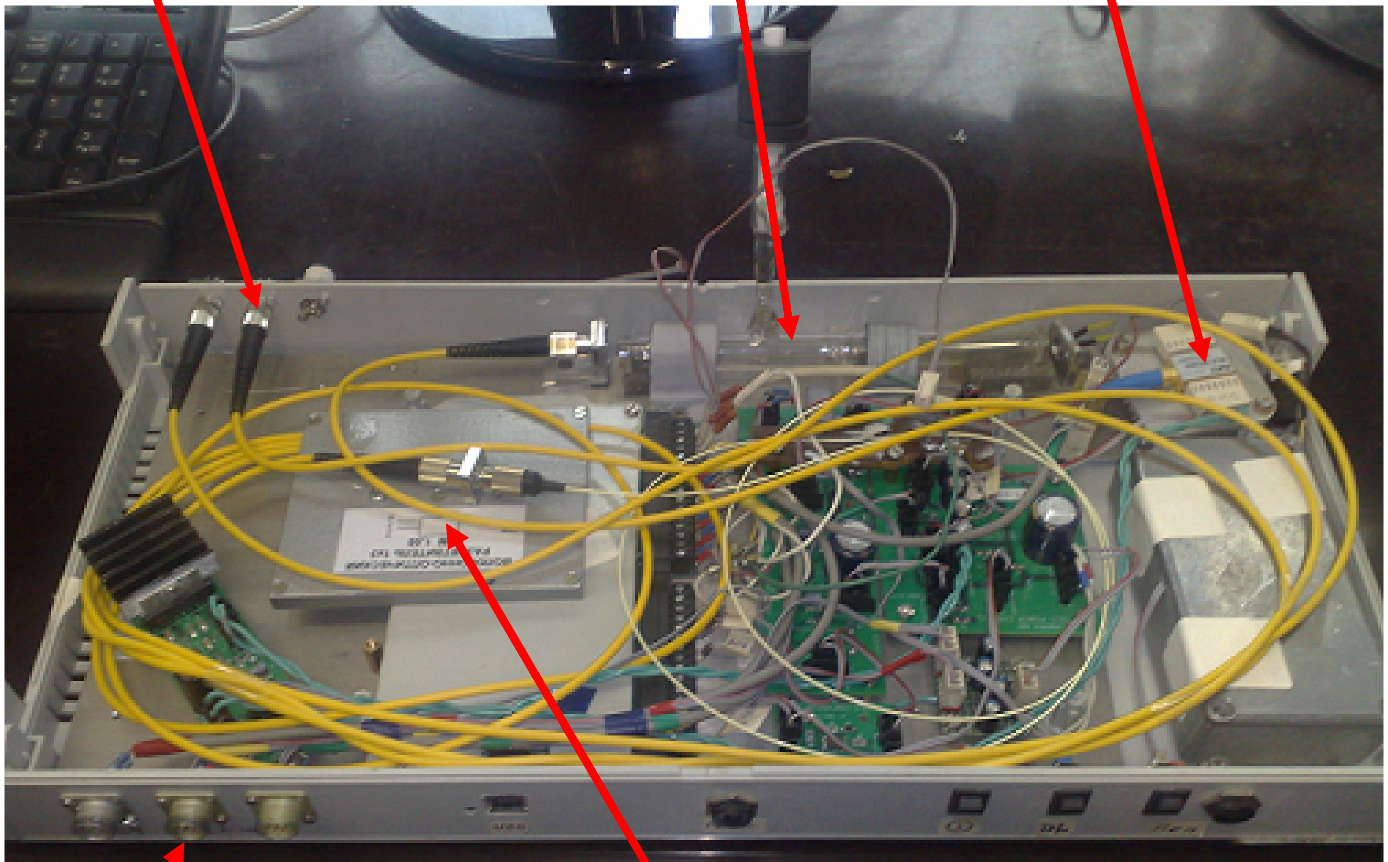
Two complexes were used to detect H_2O and CH_4 in NH_3.
LF was directed to cells with L = 2 cm, L = 150 cm and multipath cell with L = 15.2 m to measure CH_4 concentration.
HF was directed to cell with L = 150 cm to measure H_2O concentration. To remove atmosphere water absorption dry nitrogen flow was used.

TDLS complex

3 fiber outputs. In present case 2 outputs are in use

Reference cell

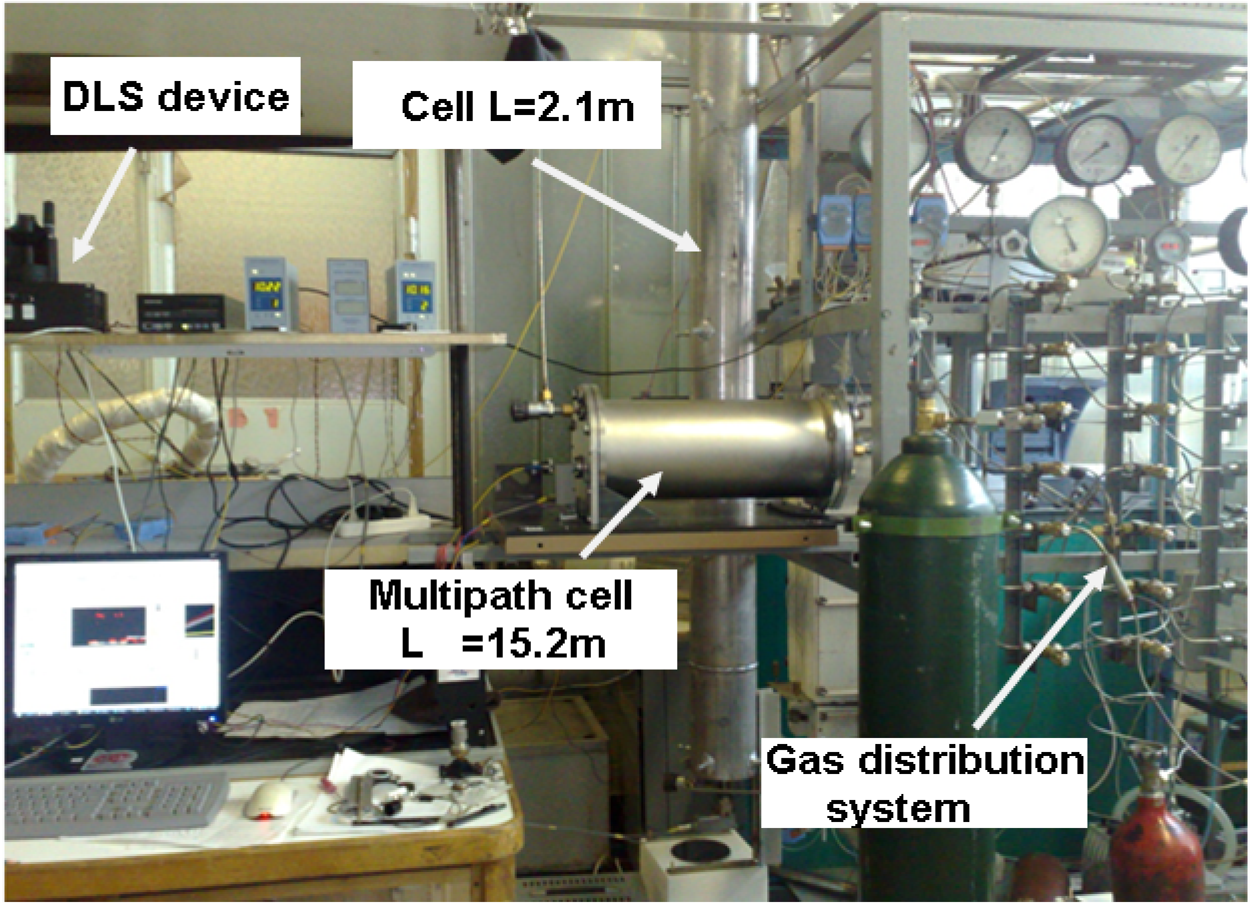
DL



3 PD inputs.

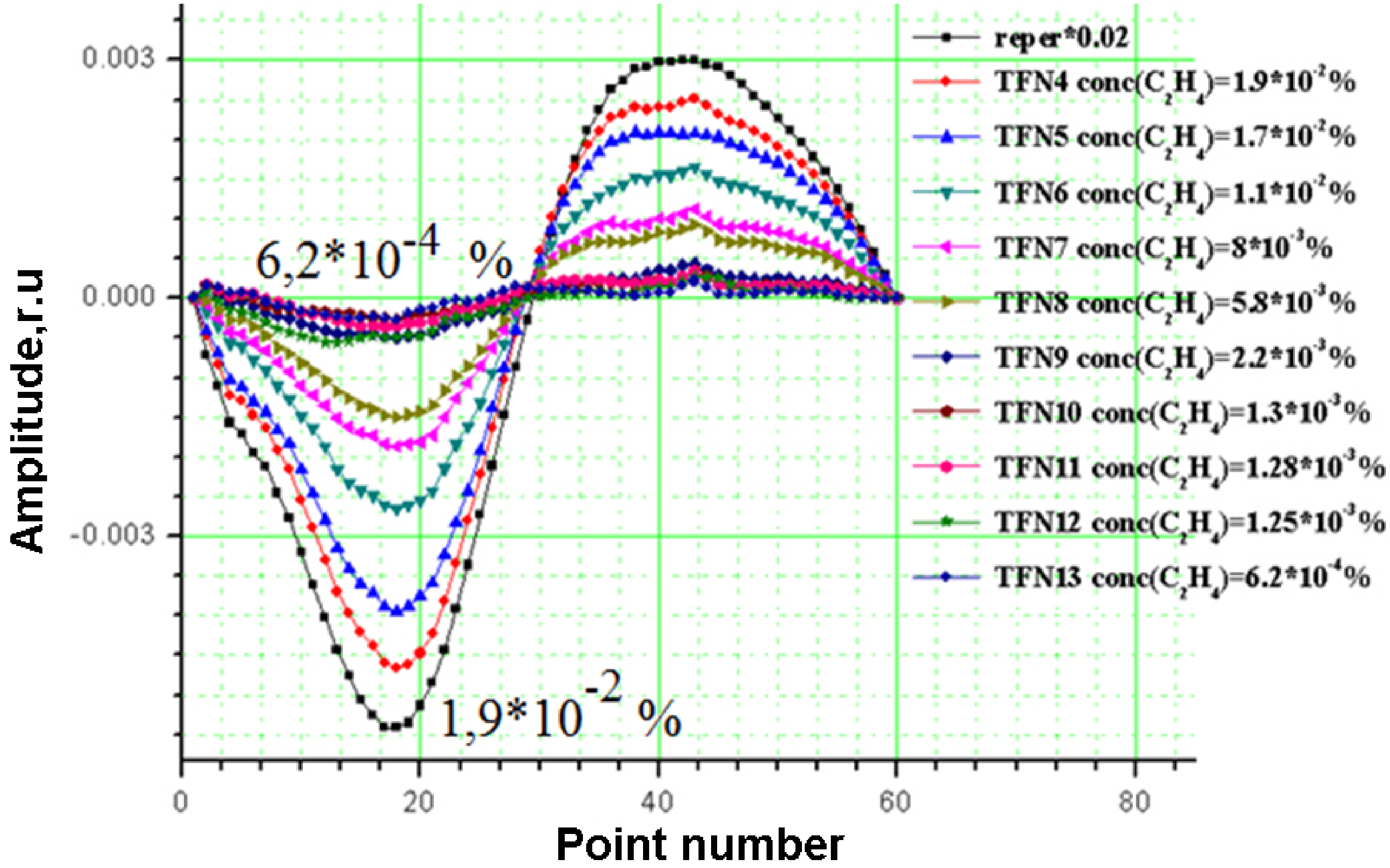
1 to 3 fiber splitter

TDLS complex installation



TDLS complex to measure ethylene concentration during SiH_4 rectification process was installed in SIE “Salut” (NN).
Rectification HF was directed to two cells: single path cell (L = 2.1. m) and multipath cell (L = 15.2 m).

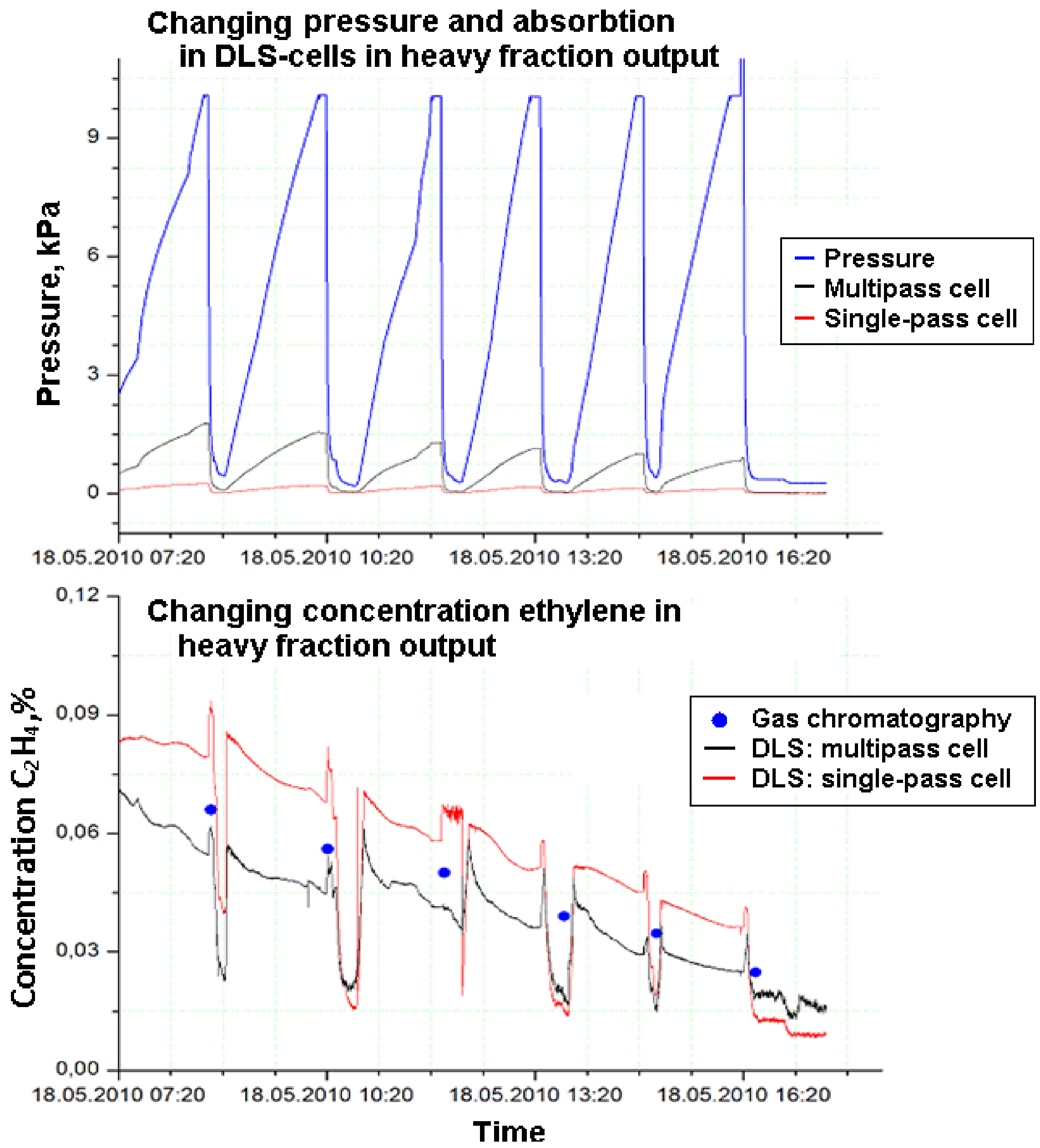
Minimum detectable concentration



Processed analytical signal for different ethylene concentrations in SiH_4.

Minimum detectable concentration was determined as 1 ppm close to instrument requirements.

Rectification process control



Silicon manufacture from SiH_4 obtained

Si manufacturing was performed in Chemistry of high purity materials institute of RAS (NN).

Si single crystal growing

Crystals parameters

Parameters of manufactured Si crystals as function of ethylene concentration in SiH_4.

	Initial SiH_4	Rectified SiH_4
Ethylene content, % vol.	$4,5 \cdot 10^{-3}$	$8 \cdot 10^{-7}$
Specific resistance, Ohm /cm	$(2 \div 4) \cdot 10^{-2}$	$100 \div 200$
Carriers concentration, cm^{-3}	10^{19}	10^{13}

Conclusion

1. Usage of ethylene monitoring in heavy fraction during SiH_4 rectification to control electro active impurities removing was proposed.
2. Analytical line was selected and investigated.
3. TDLS complex was developed and installed.
4. Minimum detectable concentration 1 ppm is close to the instrument requirements.
5. SiH_4 rectification using ethylene monitoring was performed.
6. Si crystals were manufactured from SiH_4 obtained.
7. Electrical parameters of manufactured crystals were measured.
8. Results obtained proved item #1.