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REAL TIME CONTROL OF ARSINE AND PHOSPHINE PURIFICATION PROCESS USING TDLS

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Introduction

High-purity AsH_3 and PH_3 are used for semiconductors production (GaAs, GaP, AlAs, InAs).

Quality of semiconductors manufactured depends on impurities presence. For required current carrier concentration below 10^{15} cm^{-3}, impurity concentration in hydrides has to be below 10 ppb.

There are many possible impurities in hydrides. H_2O, NH_3, H_2S, CO_2, and C_2H_4 are considered as most important. In present paper we'll present result for ammonia.

Goal: investigate possibility to use TDLS for real time ammonia concentration measurement in phosphine and arsine during their syntheses and purification.

High-purity arsine and phosphine production stages

Syntheses → **Cryo-filtration** → **Rectification**

There are 3 steps of high purity AsH_3 and PH_3 production:

1. Syntheses

Phosphine

$Mg_3P_2 + 6HCl \rightarrow 2PH_3 + 3MgCl_2$

Arsine

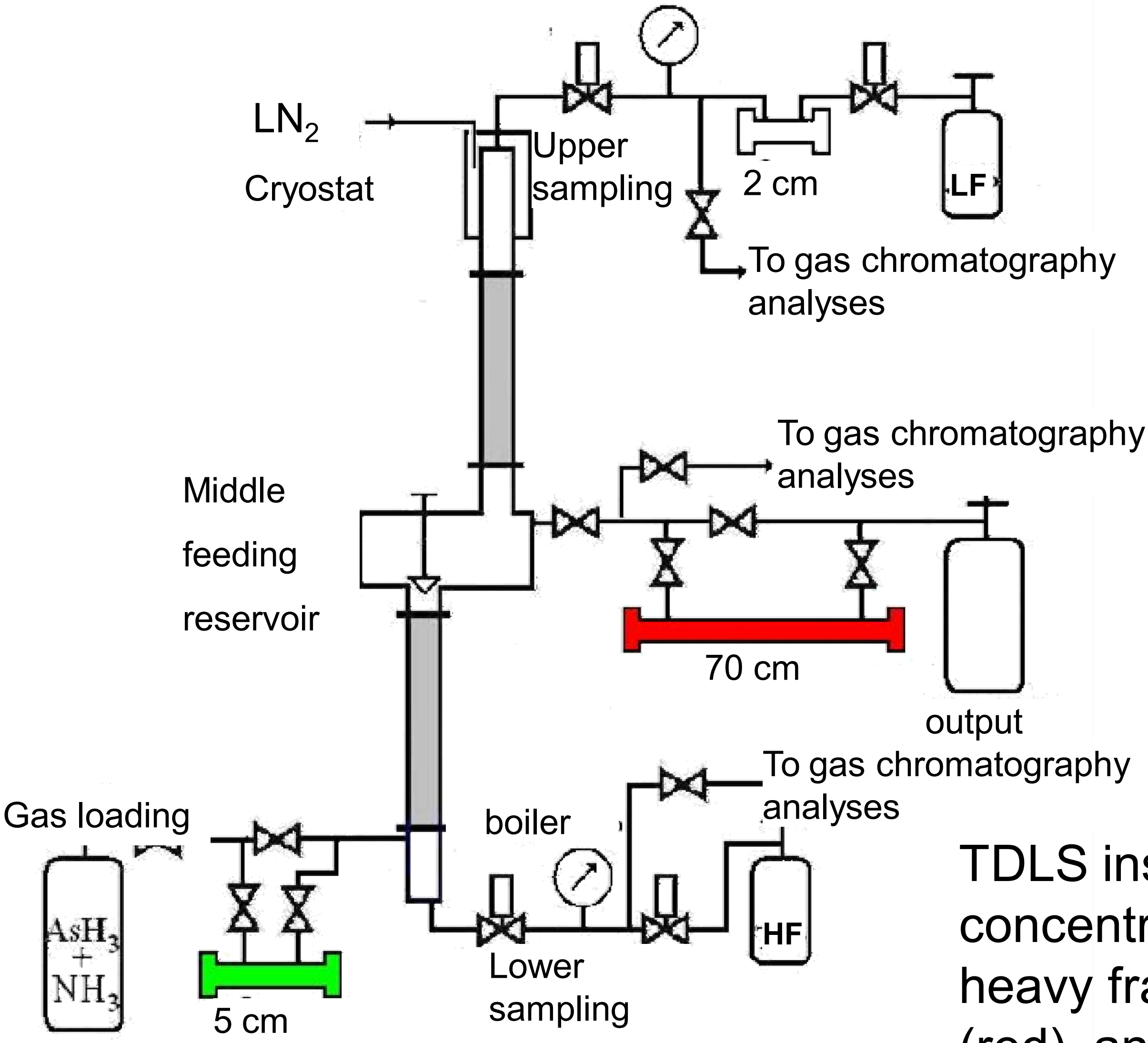
$Mg_3As_2 + 6HCl \rightarrow 2AsH_3 + 3MgCl_2$

$AsCl_3 + 3NaBH_4 + 9\ H_2O \rightarrow AsH_3 + 3NaCl + 3H_3BO_3 + 9H_2$

2. Cryo-filtration
3. Rectification

Two last steps are subject for TDLS complexes application.

Rectification column



Block scheme and view of rectification column.

TDLS instrument measured NH_3 concentration in raw material or heavy fraction (HF) (green), pure (red), and light fraction (LF) (white) points of rectification column.

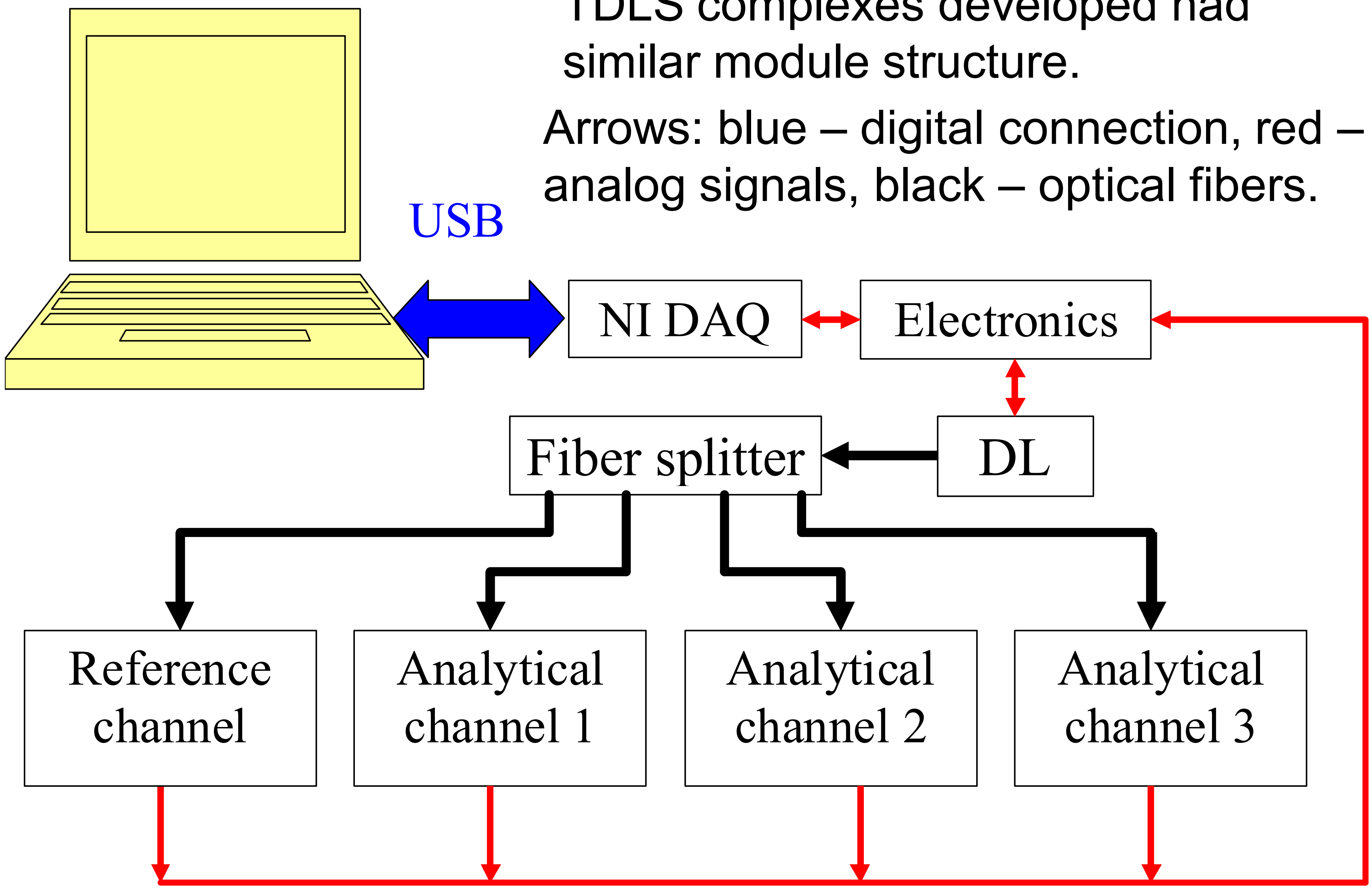
Impurities in AsH_3 and PH_3

Controlled impurities	Impurity content, ppb			
	Arsine		Phosphine	
	99,99994 % Solkatronic Chemicals	SPE "Salut"	99,9999 % Solkatronic Chemicals	SPE "Salut"""
N_2, Ar, O_2	<50	<200	<100	<500
CO, CO_2	<50	–	<100	<1000
CH_4, C_2H_6; C_3H_8	<50	<100	<100	<100
C_2H_4, C_3H_6	–	<70,<100	–	<70,<100
H_2O	<100	<1000	<100	<1000
GeH_4, SiH_4	<50, <100	–	–	–
PH_3	<50	<200	–	–
AsH_3	–	–	<100	<1000
NH_3	<50	<200	<100	<1000

TDLS complex block-scheme

TDLS complexes developed had similar module structure.

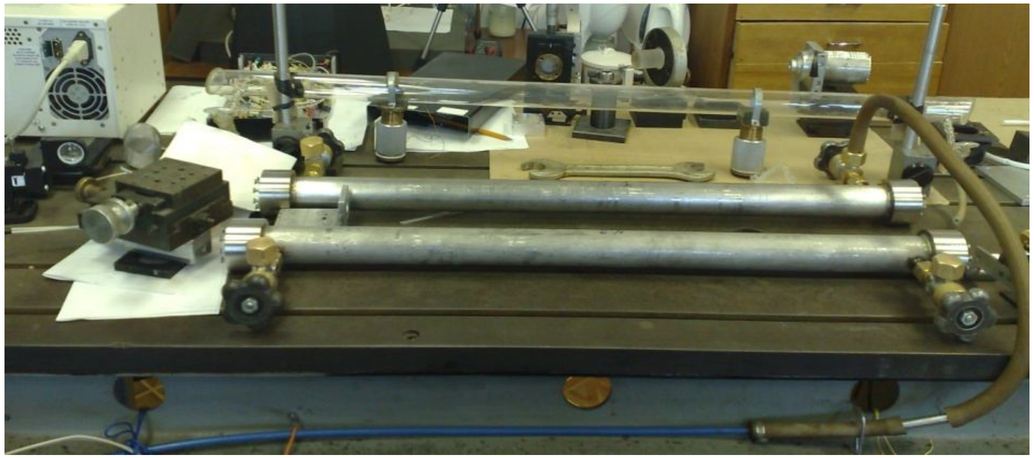
Arrows: blue – digital connection, red – analog signals, black – optical fibers.



TDLS complex view

Three cannels TDLS complex to detect ammonia in arsine and phosphine view.

Analytical cells

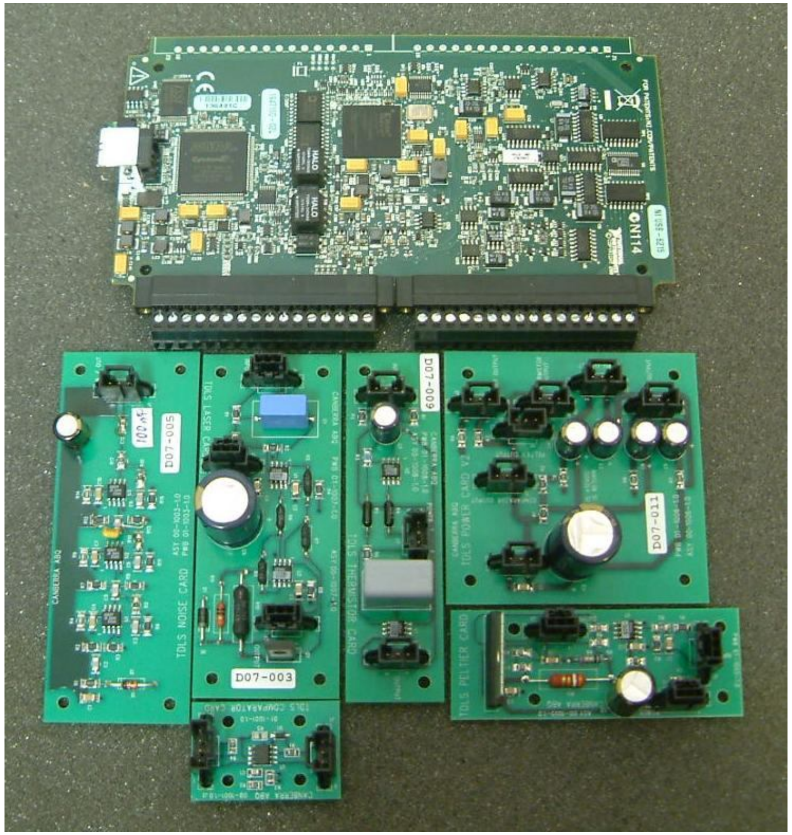


L=70, 140 cm

L=3, 5 cm

TDLS complex

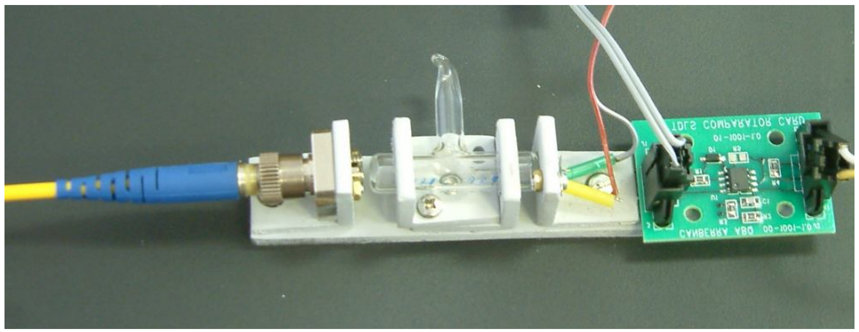
All TDLS complexes contain the same set of components



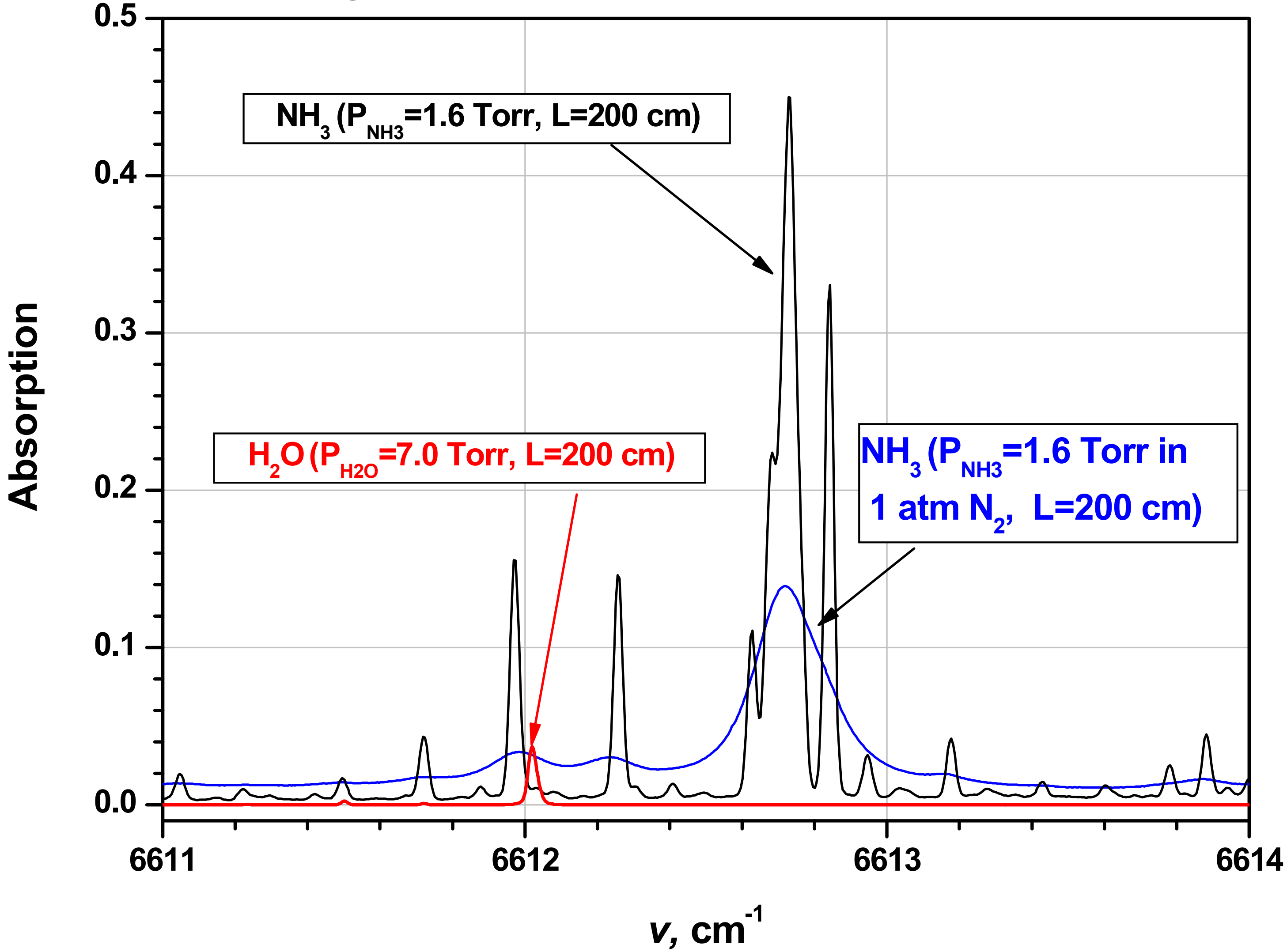
National Instrument USB DAQ

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

View of reference channel

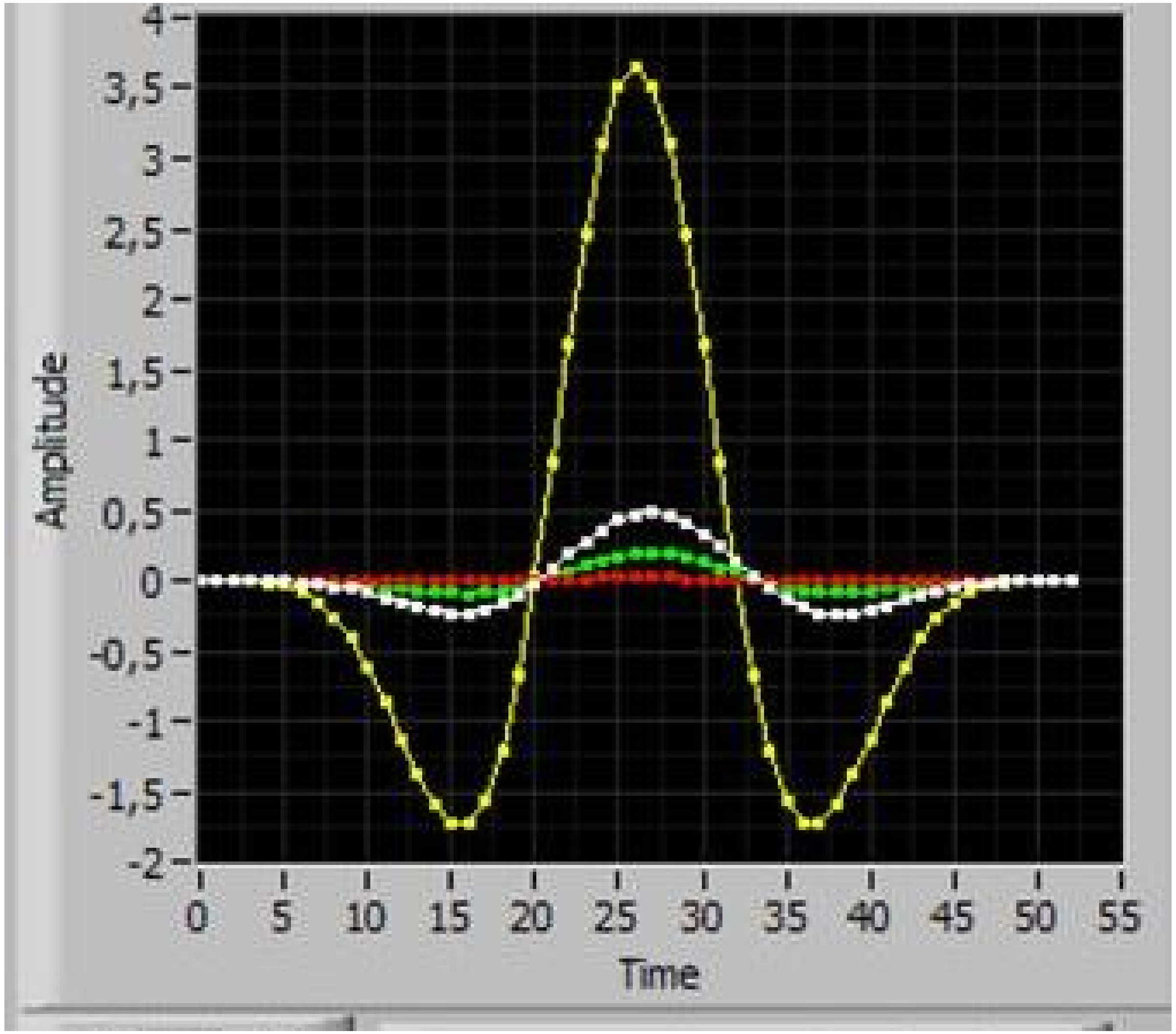


Analytical line selection



No significant AsH_3 and PH_3 absorption was observed in this spectral range.

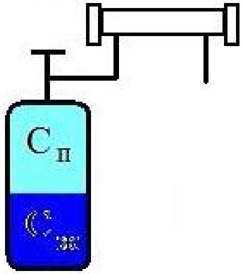
Analytical signal



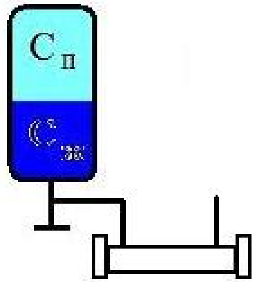
NH_3 line correlation functions in 4 channels: reference (yellow); raw (green), LF (white), pure (red).

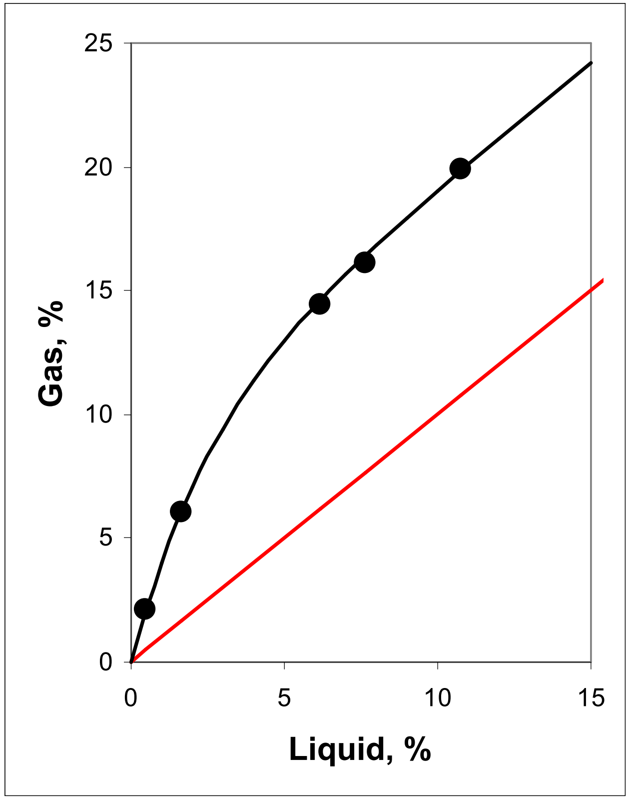
Vapor above solution (Raoult law)

Raw material gas phase analyses



Raw material liquid phase analyses



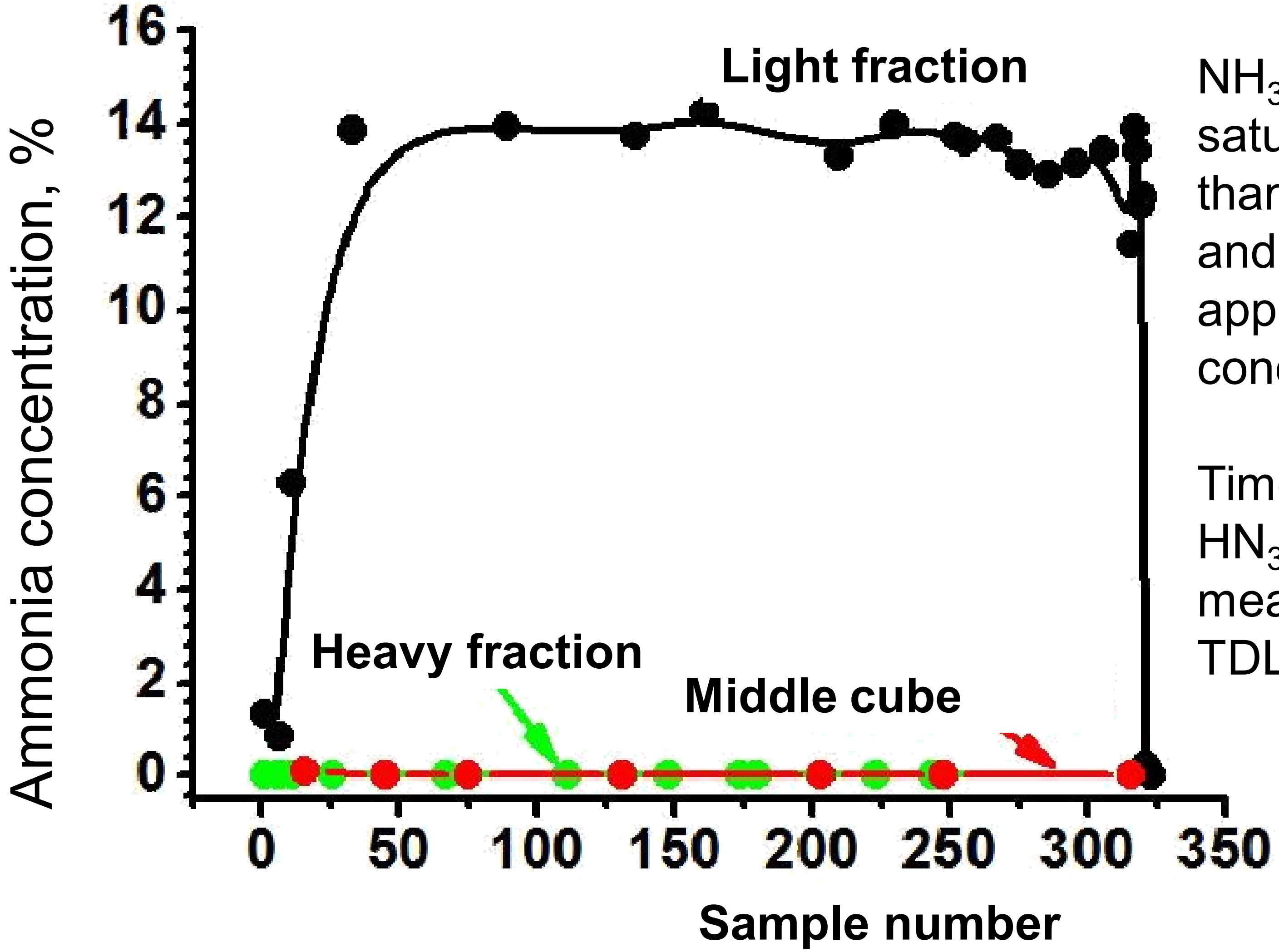


NH_3 concentration in gas phase as function of its concentration in liquid phase as measured by TDLS in arsine. Red – Raoult law (concentrations are equal).

<u>Raul law is not valid for NH_3 in hydrides.</u>

One more law is not valid

Traditional approach: Impurities having lower or higher vapor pressure than main molecule will concentrated in HF and LF, respectively.

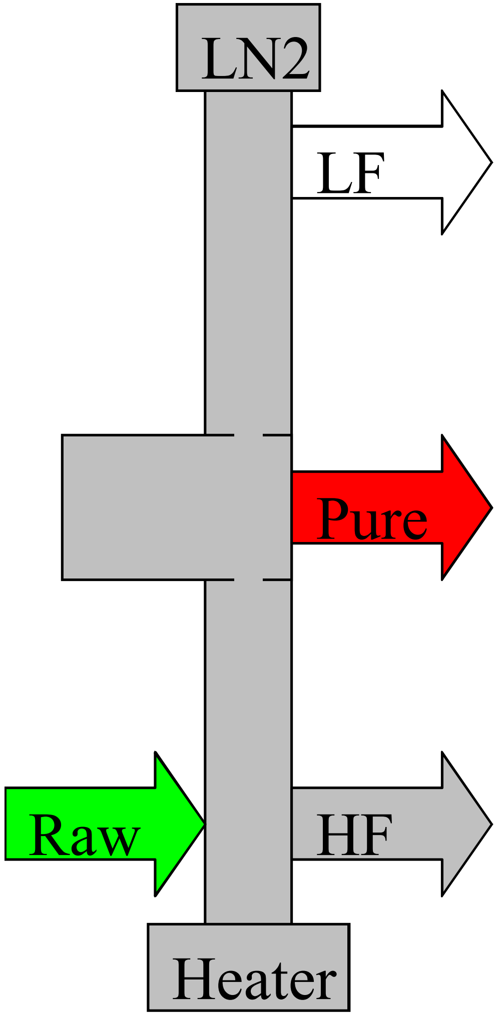


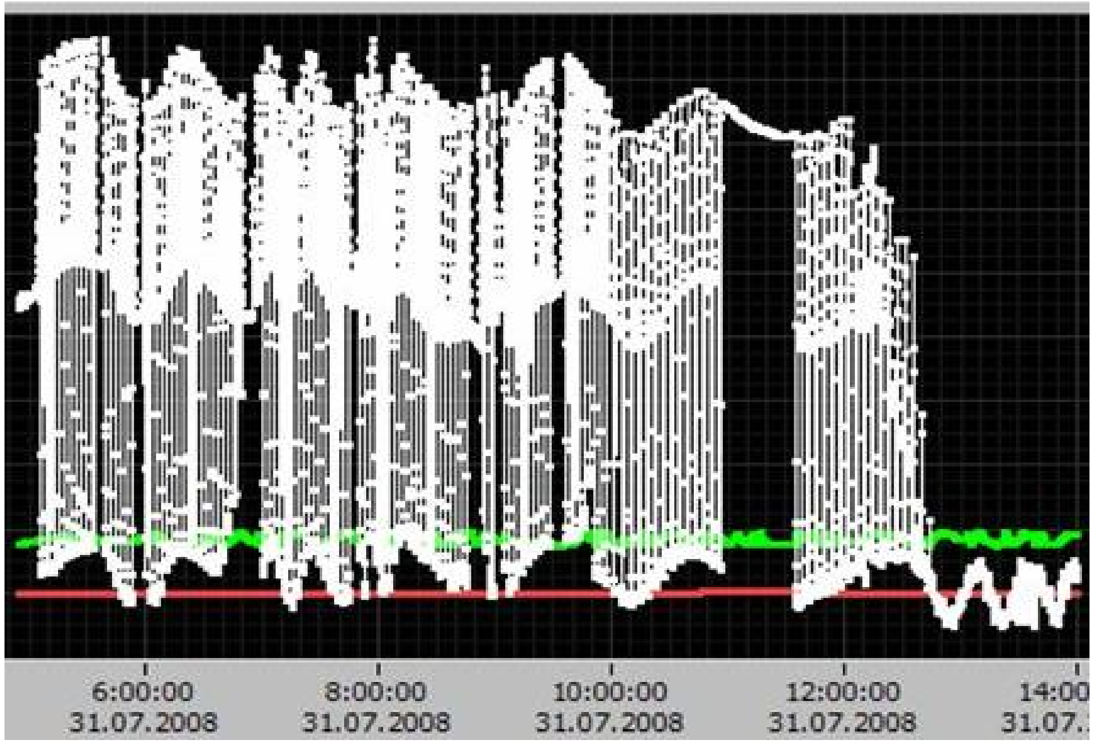
NH_3 has lower vapor saturated pressure than AsH_3 and PH_3 and due to traditional approach has to be concentrated in HF.

Time dependence of HN_3 concentration as measured in three TDLS channels.

<u>NH_3 in AsH_3 and PH_3 is concentrated in light fraction</u>

System operation



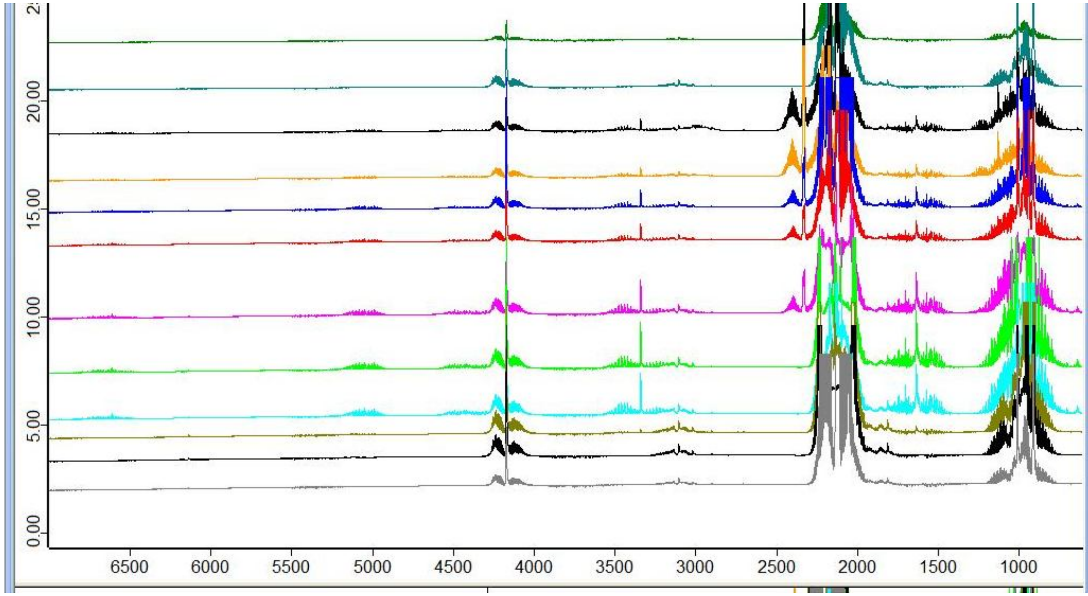


Time dependence of NH_3 concentrations in three points of rectification column: raw (green), LF (white), pure (red).

<u>End of purification can be easily identified</u>

Additional diagnostics

Rectification columns have addition diagnostics: FTS, gas chromatography, and dew point temperature measurement.



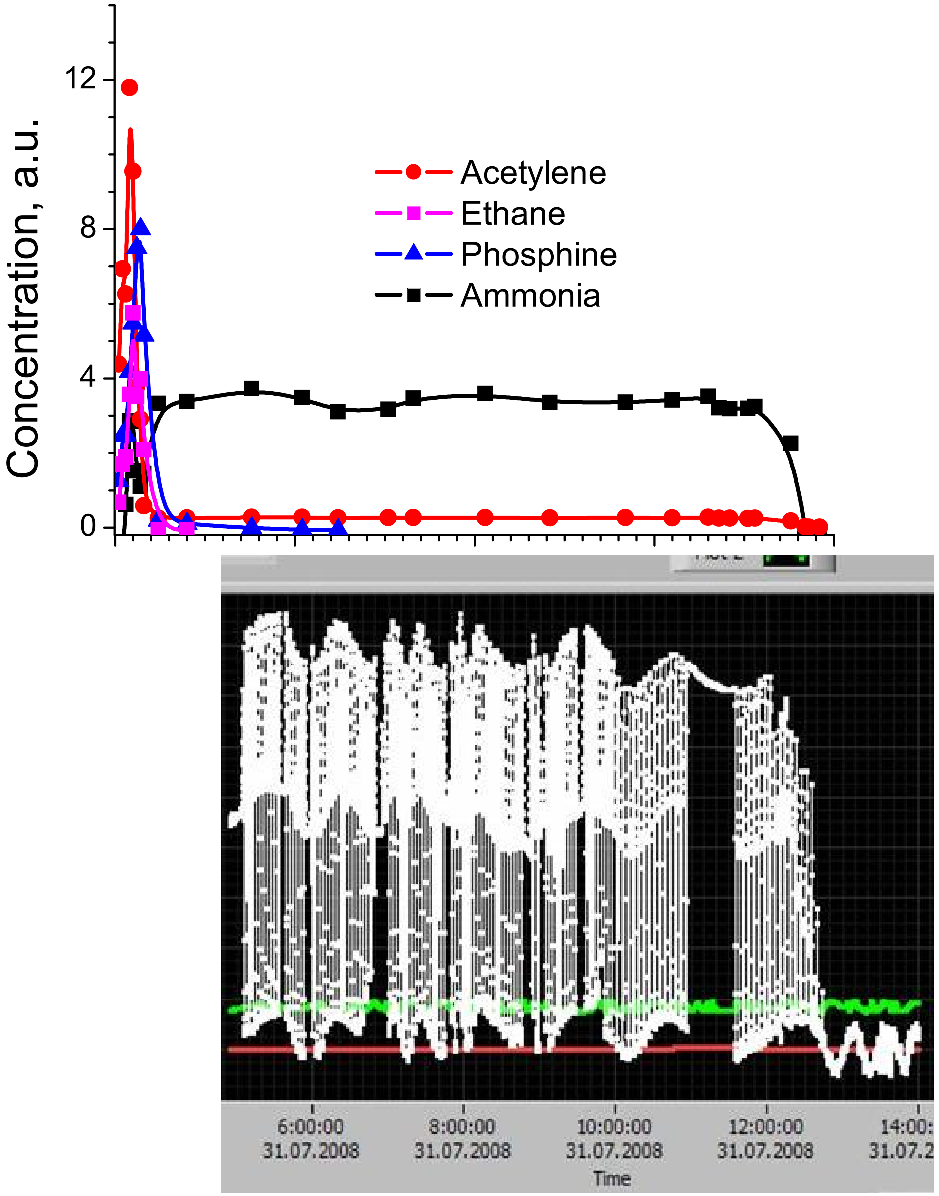
FTS spectra at different moments of rectification process.

Presence of different impurities can be observed.

Intercomparison results of different diagnostic techniques of NH_3 detection: TDLS is 1-2 orders more sensitive than FTS and gas chromatography, is more operative in time scale, and can detect impurity in different points of rectification column.

FTS and gas chromatography can detect simultaneously several impurities and give TDLS information of impurities to be detected.

TDLS and FTS together



Simultaneous analysis of LF content during arsine rectification process using FTS (upper) and TDLS (lower - ammonia concentration).
For ammonia both techniques show similar behavior.
Due to FTS results it was found that some impurities are removed from main purified material very quickly, some remained in it – subject for future TDLS development.

Conclusion

1. TDLS based complexes were developed to measure NH_3 in hydrides (see A3).
2. NH_3 was detected in raw samples of AsH_3 и PH_3.
3. It was discovered that Raul law is invalid for NH_3 in hydrides.
4. It was discovered that traditional approach can not explain NH_3 behavior during AsH_3 , PH_3 и GeH_4 rectification.
5. TDLS technique was developed to control NH_3 behavior during AsH_3 and PH_3 rectification.
6. Technique developed was compared with FTS and gas chromatography. TDLS is 1-2 orders more sensitive than FTS and gas chromatography, is more operative in time scale, and can detect impurity in different points of rectification column. FTS and gas chromatography can detect simultaneously several impurities and give TDLS information of impurities to be detected.