

Cryogenic Hydrogen Ultra-Purification System (CHUPS) tests.

1. Hydrogen flux calibration.

The typical procedure of the hydrogen flux calibration ($Q_{H_2} \left[\frac{l}{min} \right]$) is the following:

- we create the pressure difference $\Delta P = P_2 - P_1$ at the mass flow controller. $\Delta P = 3 \text{ bar}$ – maximum possible pressure difference for the mass-flow controller.
- we set the fixed and constant flux on the mass-flow controller and measure the outlet pressure $P_1(t)$.

In this case the real hydrogen flux will be:

$$Q_{H_2}(P_1) = V_1 \frac{\partial P_1}{\partial t}$$

For the formula of purification we need only ratio $J = \frac{Q_{H_2}}{V_1}$:

$$J = \frac{Q_{H_2}(P_1)}{V_1} = \frac{\partial P_1}{\partial t} = u(P)$$

We do not need to know test volume capacity or TPC capacity (which is difficult to measure because of complex shape and unknown total volume of internal elements).

Figure 1 shows the $u(P)$ dependence for the constant flux of $1.2 \frac{nl}{min}$ ([nl] stands for litre at standard conditions).

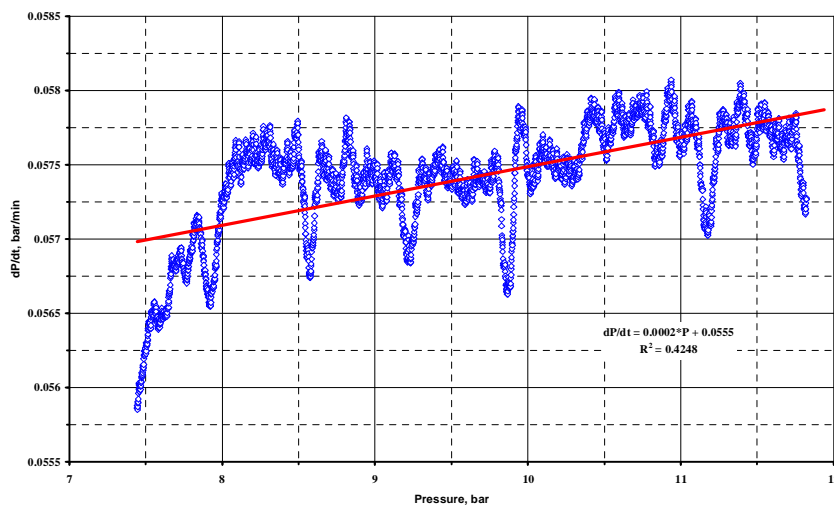


Figure 1. Pressure dependence of the $\frac{\partial P}{\partial t}$ at the constant flux of hydrogen $1.2 \frac{nl}{min}$.

Taking into account test volume capacity of 30l gives the real flux of hydrogen at 10bar
 $Q_{H_2}(10bar) = 1.725l/min$ and correction factor is 1.44.

2. Investigation of the gas purification procedure at the fixed average hydrogen flux.

2.1. Assumptions

1.

In the closed chamber with the volume $V[l]$ admixture of N_2 and O_2 is the linear function of the time:

$$P_{N_2} = P_{0N_2} + x_{N_2}(t - t_0) \quad P_{N_2} [ppm] \quad x_{N_2} \left[\frac{ppm}{min} \right]$$

$$P_{O_2} = P_{0O_2} + x_{O_2}(t - t_0)$$

This assumption corresponds to the constant mass flow of the admixture into the chamber.

2.

Pressure of the admixture after absorber (filter) does not depend on the hydrogen flux $Q_{H_2} \left[\frac{bar \cdot l}{min} \right]$, pressure $P_{H_2} [bar]$ and inlet partial pressure of the admixture. These assumptions are correct if the absorber is far from the saturation and transport gas velocity in the absorber is much smaller than the diffusion velocity. After absorber we have $P_{N_2end} [ppm]$ and P_{O_2end} pressures.

3.

We have a homogeneous distribution of the admixtures in the chamber volume.

2.2. Differential equation

Let $P[ppm]$ is the admixture pressure. We can write:

$$P \cdot P_{H_2} V = \frac{m}{m} RT,$$

where m is the mass of the admixture and m is the molar mass of the admixture. In case of constant hydrogen pressure and temperature we can write:

$$P_{H_2} V \cdot \frac{\partial P}{\partial t} = \frac{RT}{m} \frac{\partial m}{\partial t}$$

We have two sources of the positive flux of the admixtures:

1. rest impurities in the inlet hydrogen:

$$P_{end} Q_{H_2} = \frac{RT}{m} \frac{\partial m_1}{\partial t},$$

where $\frac{\partial m_1}{\partial t}$ is the inlet mass flux of the admixture.

2. impurities flux from the chamber surface:

$$xP_{H_2} V = \frac{RT}{m} \frac{\partial m_2}{\partial t},$$

where $\frac{\partial m_2}{\partial t}$ is the mass flux of the admixture from the chamber surface.

Negative flux of admixtures is absorber outlet flux which depends on the partial pressure:

$$PQ_{H_2} = \frac{RT}{m} \frac{\partial m_3}{\partial t}$$

Finally we can write

$$P_{H_2} V \cdot \frac{\partial P}{\partial t} = \frac{RT}{m} \frac{\partial m}{\partial t} = \frac{RT}{m} \left(\frac{\partial m_1}{\partial t} + \frac{\partial m_2}{\partial t} - \frac{\partial m_3}{\partial t} \right) =$$

$$= P_{end} Q_{H_2} + xP_{H_2} V - PQ_{H_2}$$

$$P_{H_2} V \cdot \frac{\partial P}{\partial t} = -Q_{H_2} \left(P - P_{end} - x \frac{P_{H_2} V}{Q_{H_2}} \right)$$

$$\frac{\partial P}{\partial t} = -\frac{Q_{H_2}}{P_{H_2} V} \left(P - P_{end} - x \frac{P_{H_2} V}{Q_{H_2}} \right)$$

$$P = P_{end} + x \frac{P_{H_2} V}{Q_{H_2}} + A e^{-\frac{Q_{H_2}}{P_{H_2} V} t},$$

where $A[ppm]$ is free coefficient which is defined by the starting conditions.

If $P_0[ppm]$ - initial impurity of the gas, we can write

$$A = P_0 - \left(P_{end} + x \frac{P_{H_2} V}{Q_{H_2}} \right)$$

And finally the pressure will be written as:

$$\begin{aligned}
P &= P_{end} + x \frac{P_{H_2} V}{Q_{H_2}} + \left[P_0 - \left(P_{end} + x \frac{P_{H_2} V}{Q_{H_2}} \right) \right] e^{-\frac{Q_{H_2} t}{P_{H_2} V}} = \\
&= \left(P_{end} + x \frac{P_{H_2} V}{Q_{H_2}} \right) \left(1 - e^{-\frac{Q_{H_2} t}{P_{H_2} V}} \right) + P_0 e^{-\frac{Q_{H_2} t}{P_{H_2} V}}
\end{aligned}$$

2.3. Experimental data

In the test device we can assume very low outgassing rate. It means we can put $x = 0$. This allows one to evaluate the pressure formula to:

$$P = P_{end} \cdot \left(1 - e^{-\frac{Q_{H_2} t}{P_{H_2} V}} \right) + P_0 e^{-\frac{Q_{H_2} t}{P_{H_2} V}} = P_{end} + (P_0 - P_{end}) e^{-\frac{Q_{H_2} t}{P_{H_2} V}}$$

At the real experiment conditions initial pressure of the impurity is few orders of magnitude more than P_{end} . In this case we can write:

$$P = P_{end} + P_0 e^{-\frac{Q_{H_2} t}{P_{H_2} V}}$$

This formula is correct only if the hydrogen flux is time independent. In our conditions it is not a constant value (the flux is changing for pressure stabilization). But the cleaning procedure takes dozens of hours while the normal oscillations of the hydrogen flux take only some minutes. It means that we can use adiabatic approximation and use the average flux. It is more convenient to connect the cleaning effect with the volume of the hydrogen has been passed through the chamber. In adiabatic approximation we can use this volume as:

$$V_{H_2} = \int_0^t Q_{H_2} dt$$

“Purification” dependence in this case will be:

$$P = P_{end} + P_0 e^{-\frac{V_{H_2}}{P_{H_2} V}}$$

Table 1 presents the experimental data of the impurities at the average hydrogen flux $1.73 \frac{l}{min}$ through the volume of the test chamber $30l$.

Table 1.

Time, hours	Volume of hydrogen passed through the chamber, nl	Impurity of N_2 , ppm	Impurity of O_2 , ppm
0.0	0	14	6.4
1.4	156	7.5	3.4
5.0	552	1.8	0.75
8.4	927	0.82	0.25
9.4	1039	0.1	0.04
11.4	1255	0.09	0.06
14.9	1638	0.15	0.04
15.9	1745	0.03	<0.01
17.3	1901	0.029	<0.01
19.6	2155	0.01	<0.01
20.9	2299	<0.008	<0.01
23.0	2533	0.06	<0.01
31.6	3478	<0.005	<0.01

If we will find the parameters of this formula it will be very easy to recalculate purification speed to any hydrogen flux. Figures 2, 3 show the dependence of the nitrogen and oxygen admixtures as function of the hydrogen flux through the chamber. Calculated and measured $P_{H_2}V$ are presented in table 2.

Table 2.

	$P_{H_2}V$	$\Delta P_{H_2}V$
Calculated	285	± 3
From N_2 purification	258	± 8
From O_2 purification	250	± 4

Measured and calculated values are not equal inside the error bars. We have to explain this discrepancy (or to make new measurements). The measured asymptotes are present in table 3.

Table 3.

	$P_{end} [ppm]$	ΔP_{End}
From N_2 purification	0.05	± 0.05
From O_2 purification	0.014	± 0.013

100% uncertainty is mainly defined by the impurities level which is less than the resolution of the analyzer.

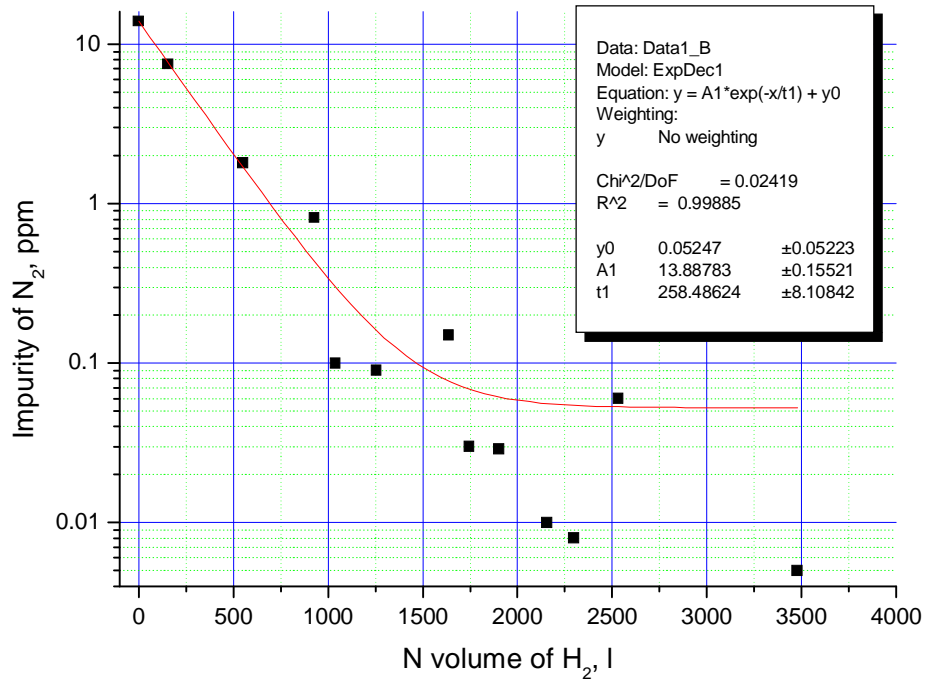


Figure 2. Purification of nitrogen.

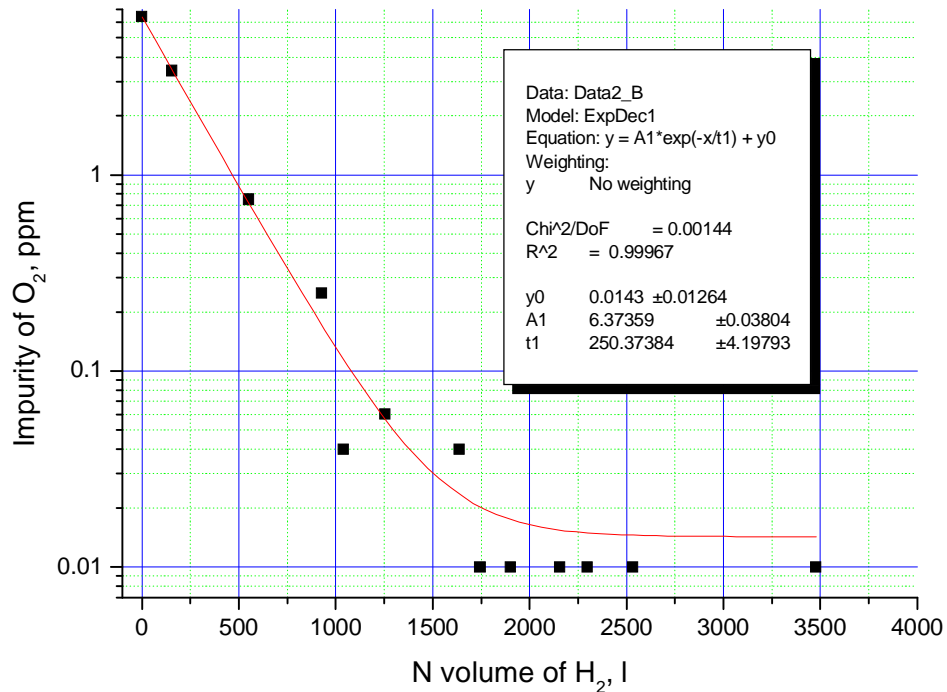


Figure 3. Purification of oxygen.

3. Parameters of the cryo compressor.

Heating and cooling process in the cryo compressors are responsible for the circulation of hydrogen in the system. We have 3 independent compressors with check valves which enable the hydrogen flux only in one direction. The temperature dependence of every compressor is presented in figure 4.

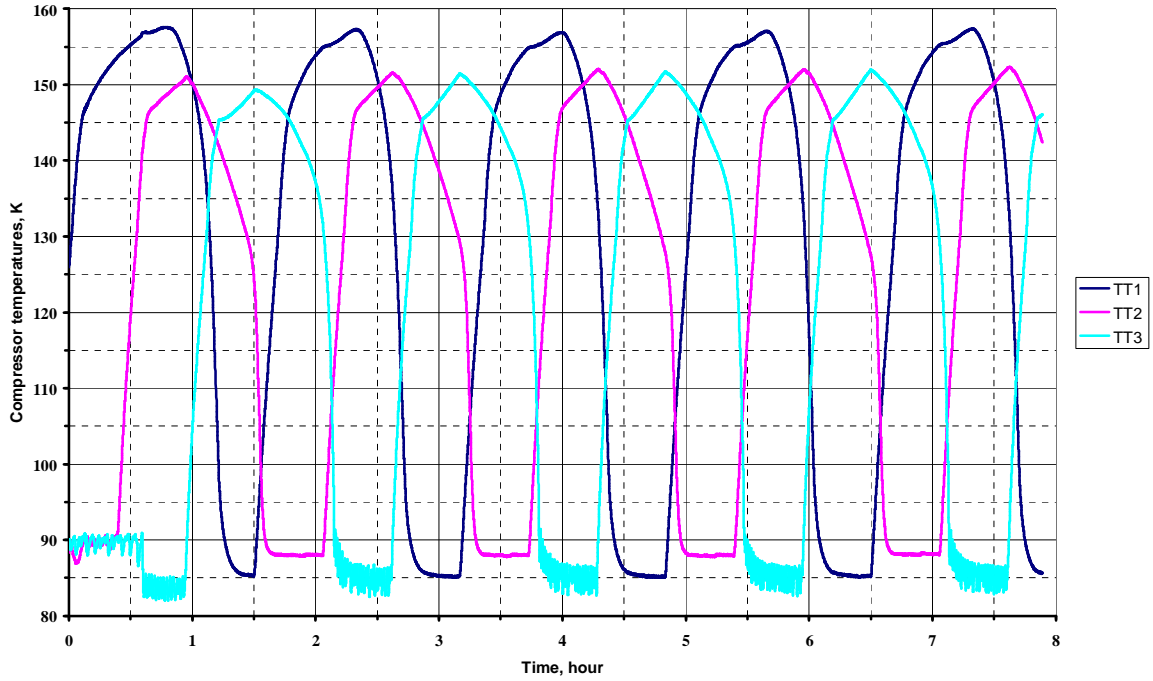


Figure 4. Time dependence of the cryo-compressor temperatures.

The temperature of the compressors oscillates between 85K and 150K. The difference of the upper and lower temperatures for the different compressors depends on the different position of the temperature sensors respect to the heaters and heat exchangers. The total cycle of each compressor is 6000 s (1 hour 40 min). It means that with the measured average hydrogen flux

$1.87 \frac{l}{min}$ for 3 compressors we have in one cycle of the compressor

$$\frac{1.87 \frac{l}{min} \cdot 100 \frac{min}{cycle}}{3 compressors} = 62.3 \frac{l}{cycle}$$

This value connected with the upper and lower temperatures and with the hydrogen pressure in the system. This value does not depend (in the equilibrium case) on the cycle length. We did not carry out systematic optimization of the cycles parameters. This is very long procedure. Normalization of the cycles takes more then 3 hours with these parameters. Figure 5 shows the fluxes of the liquid nitrogen, which is used for the cryo-compressor cooling.

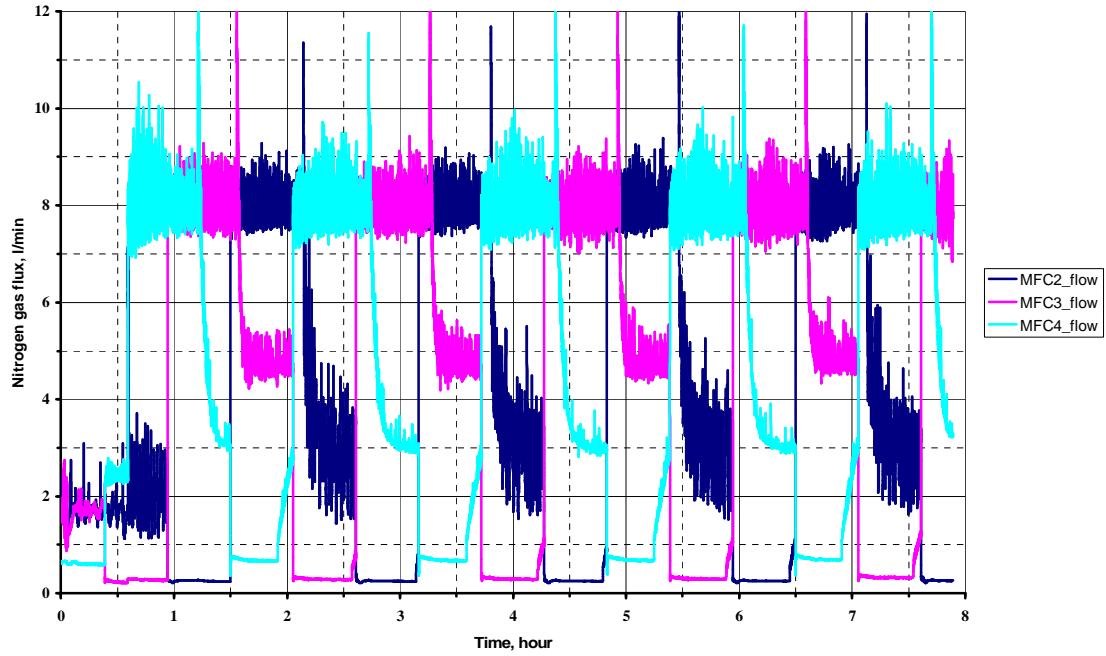


Figure 5. Fluxes of the liquid nitrogen. Flux is presented in the equivalent gas volume at normal pressure and temperature.

The long term equivalent average **liquid** nitrogen flux is $0.4 \frac{l}{hour}$. If we take into account the vaporization of the liquid nitrogen in the tank this value will be about $0.6 \frac{l}{hour}$. Taking into account total capacity of liquid nitrogen volume (20 l), this gives a possibility to work at least 24 hours without refilling.

4. Pressure stabilization.

The system has to stabilize the pressure in the chamber. This is done by the mass-flow controller which vary the flux of hydrogen from the reserve volume (pressure P_2) to the chamber (pressure P_1). The flux of hydrogen as a function of time is shown in figure 6. Flux is varied between 0 and $3.7 \frac{l}{min}$ (upper limit set by operator). The long term average flux is $1.87 \frac{l}{min}$.

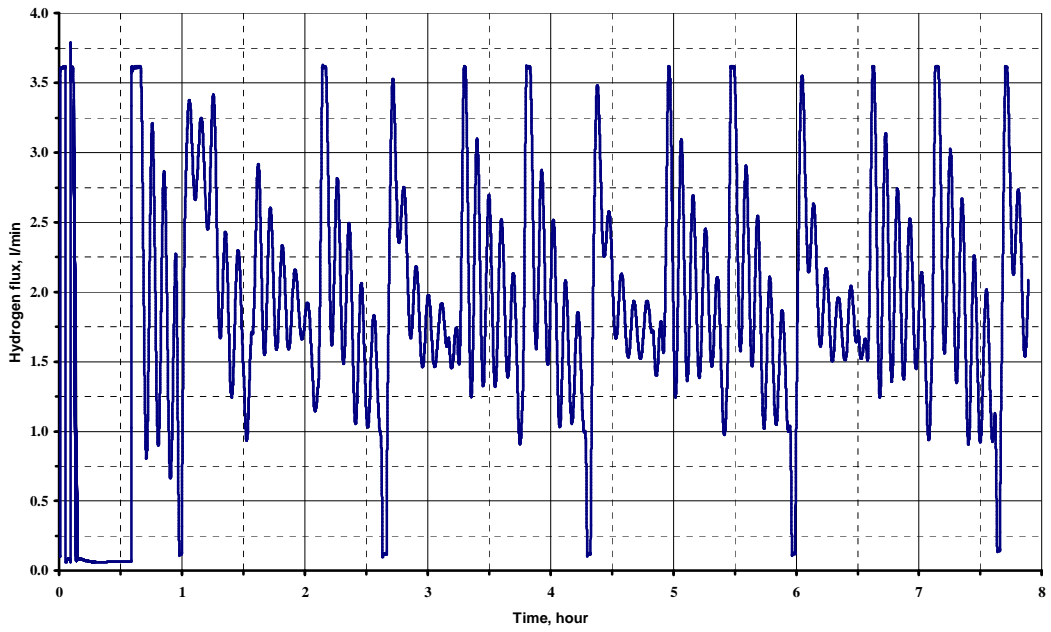


Figure 6. Hydrogen flux in the system.

Figure 7 shows pressures in the system.

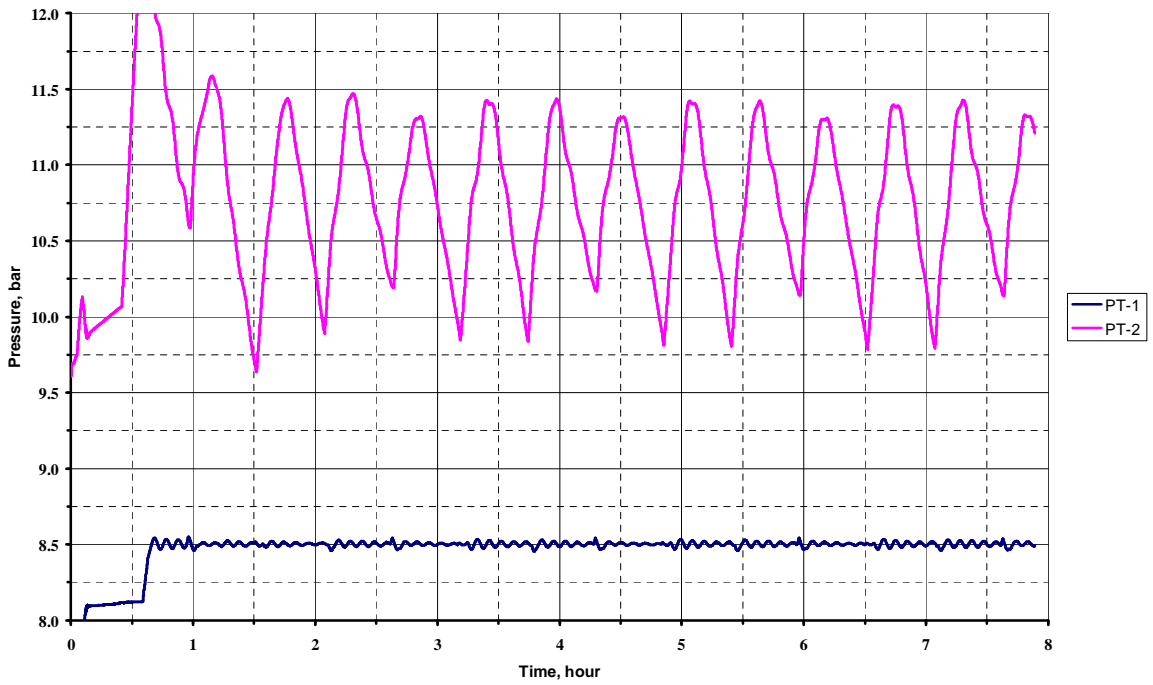


Figure 7. Pressures in the system. PT-1 – pressure in the chamber, PT-2 – pressure in the reserve volume.

The most important value is “quality” of the PT-1 stabilization. Figure 8 presents the pressure distribution histogram. Pressure setpoint is 8.5 bar.

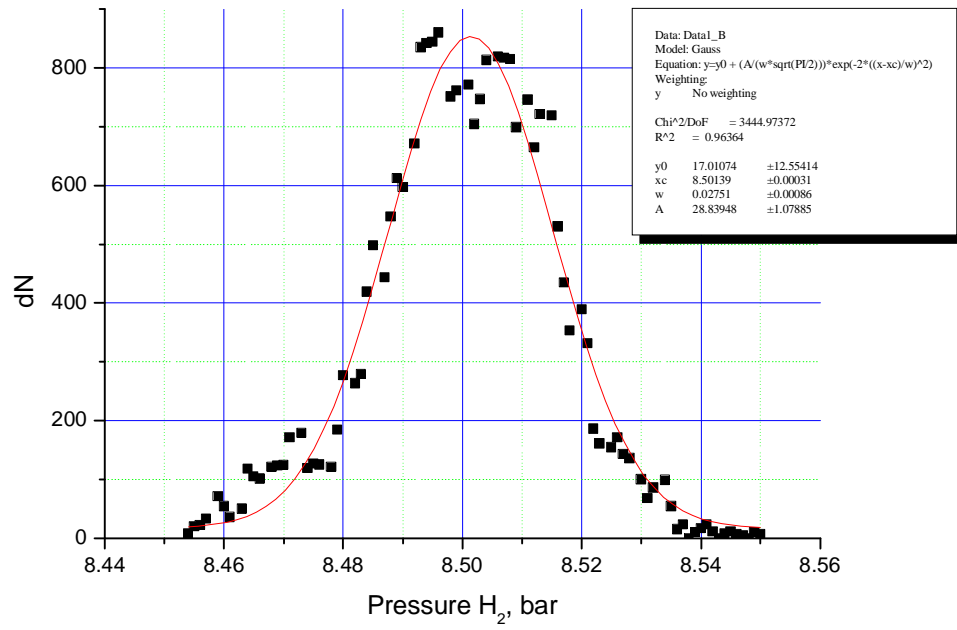


Figure 8. 7 hours histogram of the pressure stabilization.

Finally, we can say that TPC pressure is kept in the following region:

$$P_1 = 8.501 \pm 0.014 \text{ bar}$$