BTEX-GC

MINI GAS-CHROMATOGRAPH

SHORT TECHNICAL DESCRIPTION

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Introduction

Benzene, toluene, ethylbenzene and xylene are volatile organic compounds. Due to their toxicity and ambient air concentrations, they are regarded as significant air pollutants. Environmental pollution due to vehicular traffic and industrial activities is a growing problem, especially in larger cities and industrial areas, and capillary air quality monitoring has become mandatory in many locations to ensure healthy living conditions.

Simple low-cost systems based on solid-state gas sensors have recently been proposed. However, the lack of selectivity of metal oxide (MOX) gas sensors is still a major issue in applications where single compounds within complex mixtures must be detected reliably and quantified. Although harmless to humans some compounds typically found in air quality samples, like water vapour, are present at high concentrations and can vary rapidly with time, producing significant shifts in the baseline of MOX sensors. Conversely, other compounds, like benzene, are toxic or even carcinogenic at ppb concentrations, mandating accurate, precise and reliable selective monitoring.

For quantifying environmental pollutants, certain analytic techniques are already widely employed. In particular, gas chromatographic (GC) techniques are currently used for analysing outdoor air samples. GC achieves high selectivity through the spatiotemporal separation of complex gas mixtures into individual chemical components.

In automatic air-quality monitoring stations, specialized gas-chromatographs are usually deployed for the in-field quantification of aromatic volatiles, such as benzene, toluene, xylenes, ethyl benzene. Conventional GC equipment is utilized either on capillary or packed columns, comprising several meters of fused silica or stainless steel tubing functionalized with a specific stationary phase. The GC columns separate the gas mixtures into their components by exploiting their different affinities towards the stationary and mobile phases. As a result, the individual gas species travel at different speeds through the column, when forced by a carrier gas flow. In addition, a GC system consists of several other components: the detector, which responds to the separated components at the column outlet; the injection system, which inputs sample mixture at a given rate; and an optional pre-concentration system, which increases the amount of injected samples, increasing the sensitivity.

What is BTEX-GC

The BTEX-GC for real-time environmental monitoring of aromatic Volatile Organic Compounds (VOCs) is an **innovative smart integrated sensing system based on silicon micromachined Gas-Chromatographic (GC) components**.

Originally developed at the Institute for Microelectronics and Microsystems of the Italian National Research Council (CNR-IMM) in Bologna, it combines Micro-Electro-Mechanical-System (MEMS) micro-fluidics for selective pre-concentration and GC separation, and peak quantification with a miniaturized Photo-ionization detector.

The main break-through beyond state-of-the-art environmental aromatic VOC monitoring is the stand-alone operability of the BTEX-GC system, which does not require carrier gas cylinders to perform the analytical sequence.

It can be operated anywhere, installed inside a small temperature controlled housing, with a 12V power supply, and has reduced maintenance requirements with respect to conventional GC/PID systems.

Equipped with optional integrated signal processing and data transmission hardware, it is suitable to be integrated into wireless sensing networks.

Specifications

Column Temperature	Ramp up to 180°C
Carrier gas	Air, on board generated: <20 mL/min
Lower detection limit	<0.25ppb BTEX for 15min analysis time
Span drift (24Hr)	<3%
Sample flow rate	100-250 mL/min typical
Power rating	12V, 10W average, <30W peak
Analysed compounds	Benzene (C6H6), Toluene (C7H8), Ethylbenzene (C8H10) and Xylenes (C8H10)
Analysis time	User configurable: 15-60min
Operating temperature	10-30 °C
Detector	PID 10.6eV
Column	MEMS, packed
Size	12 x 11 x 6,5 cm
Weight	1,9 kg

Overview of the BTEX-GC system

The BTEX-GC consists of the following main blocks:
   A. Sampling and pre-concentration unit
   B. Gas-chromatographic (GC) separation unit
   C. PID detector unit
   D. Manifolds for flow distribution and filter
   E. Housing, including cooling fans and electrical connectors
   F. Embedded mini-PC for control, acquisition and data processing

BTEX-GC operating principle

The operating principle of the BTEX-GC is described in the following. An analytical cycle consists of a complete set of sequential system states which implement a complete measurement. The result of each single measurement cycle is a chromatogram, which is processed to extract the height of the peaks of the aromatics, namely benzene, toluene, ethylbenzene and xylene.

The height of each peak is linearly correlated, by means of a calibration factor, to the concentration of each single aromatic component sampled during a sampling cycle.

In the current set-up, the BTEX-GC has a cycle duration of 15 minutes.

This means that the height of each of the BTEX peaks is computed 4 times every hour.
The height of each peak is proportional to an average concentration of the compound, as sampled during approximately 10.5 minutes during a 15 minutes cycle. The remaining 4 minutes are used for the cleaning of the pre-concentrator between successive measurement cycles.

This means that the chromatogram peaks acquired by the PID detector refer mostly to the air sampled during the previous cycle!

A typical example of a chromatogram, as acquired by the PID detector, is shown below in figure 1a. In this example, the benzene peak elutes with a maximum signal at T=142s after injection, and has a height of 15.835mV. The toluene peak elutes at 276s and is 29.858mV high, etc.
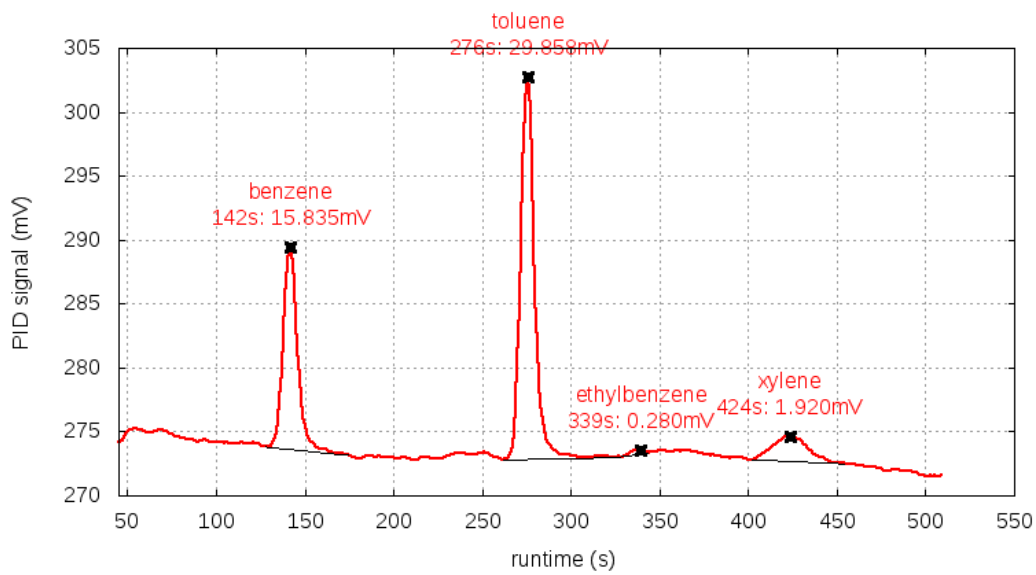Daily trends of sub-ppb benzene and toluene concentrations are shown in figure 1b.

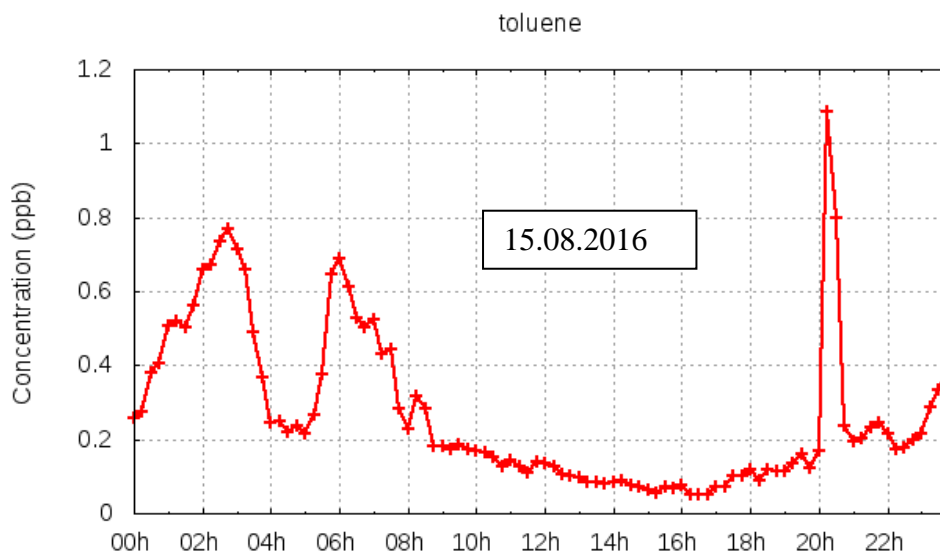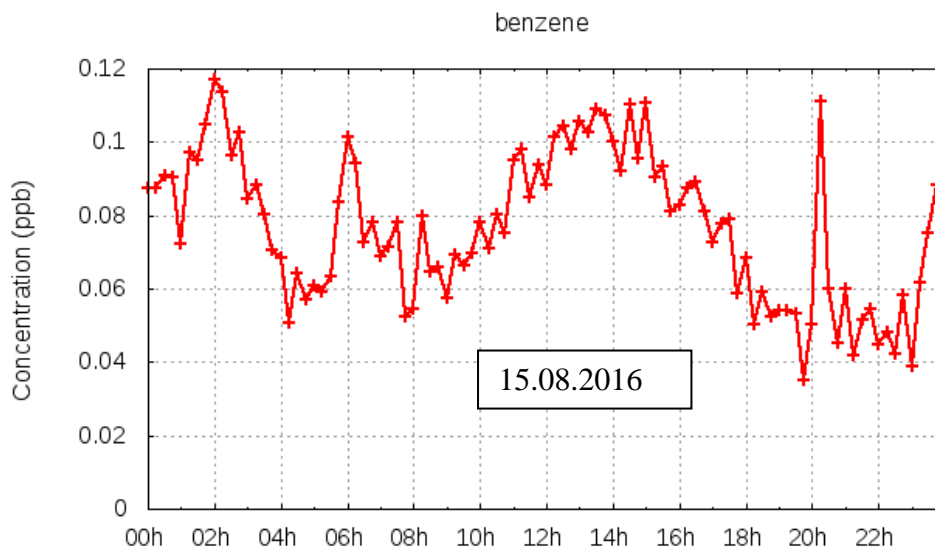Figure 1a: example of chromatograph acquired by a BTEX-GC system.

benzene

15.08.2016

toluene

15.08.2016

Figure 1b: daily trend of benzene (top) and toluene (bottom) concentrations

BTEX-GC connections

The following figure 2 shows a complete BTEX-GC device inside its housing, with the different fluidic in- and outlet connectors and the electrical connections.
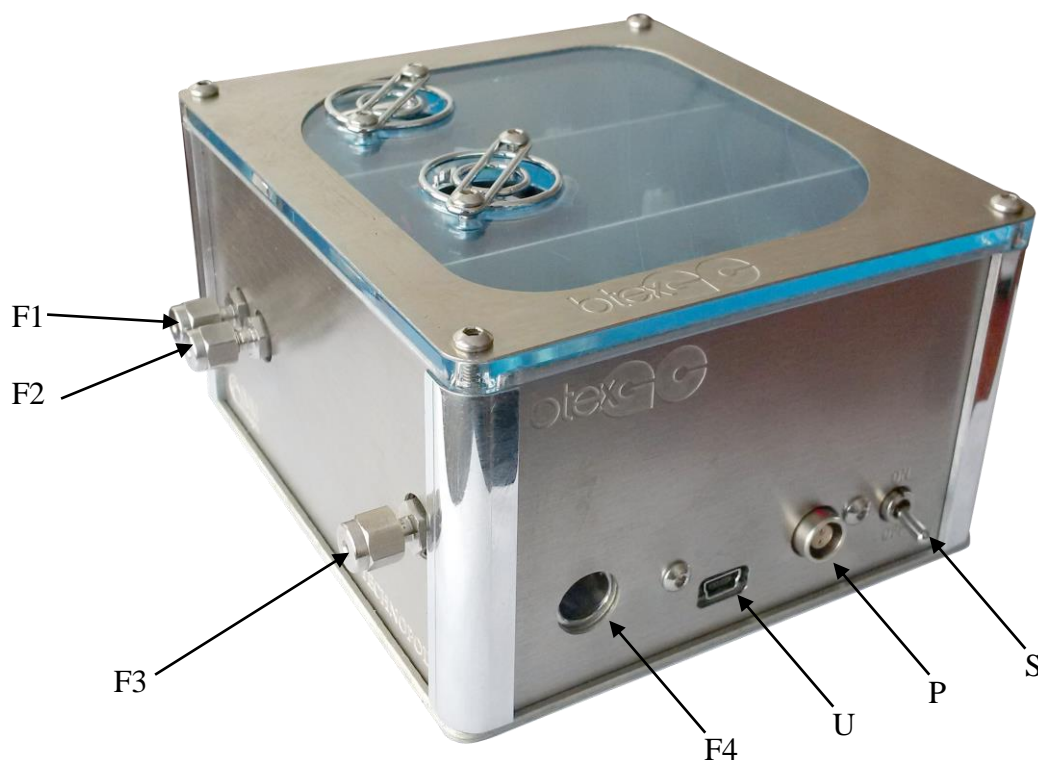

Figure 2: boxed BTEX-GC with fluidic and electric connections

The fluidic connections identified in figure 2 are:

F1   **sample inlet**. The sample air flows INTO this connector all the time the pump of the pre-concentration unit (A1) is on.

F2   **sample outlet**. The sample air flows OUT OF this connector while the pre-concentrator is in sampling state. In these states, the flow out of this connector should be in the 100-200mL/min range. During the injection step the flow out of this connector must drop to 0 mL/min.

F3   **PID outlet.** The flow eluting from the GC column and flowing through the PID chamber flows OUT OF this connector whenever the GC unit pump is on. In these states, the flow out of this connector should be in the 10-20mL/min range. This flow increases to >20mL/min when the pre-concentrator unit is injecting into the GC separation unit.

F4   **carrier gas inlet.** The air flowing through this activated carbon filter is used as GC carrier gas. Ambient air flows INTO this connector whenever the sampling pump of the GC unit (B1) is on and the system is not in injecting.

F1, F2 and F3 are 1/16" Swagelok® connectors, part# SS-100-1-1.
The filter connection OD is compatible with 1/4" or 6mm Teflon® tube fittings.

The following table 2 resumes the target flow-rates out of F2 and F3.

These flow-rates can be measured with portable flow meters of floating-sphere rotameters to debug malfunctioning BTEX-GC devices. Zero or much lower flow-rates than those shown blow are indications pump or valve failure, please contact manufacturer for assistance.

State	Valves and pumps	Flow out of F2	Flow out of F3
S1	Both pumps on Valves in sampling state	100-200 mL/min	**F** = 10-20 mL/min
S2	Both pumps on Valves in injection state	0 mL/min	> **F**

Note: S1 can be found at the intervals   T = [0..40]s and [80..880]s   of the cycle.
S2 can be found at the interval   T = [60..80]s   of the cycle.

The electrical connections identified in figure 3 are:

U   Mini-USB port for controlling the BTEX-GC
P   Power supply: DC 12V 3A max rating. Use the power supply delivered with the units.
S   Power switch turns off only the pre-concentrator and GC units

The embedded mini-PC for control, acquisition and data processing

The BTEX-GC devices are shipped each with a Raspberry-Pi 2 or 3 model B embedded single-board computer (SBC) for system control, acquisition and data processing. The SBC runs a standard Debian-based Linux distribution and an application-specific software package written in C.

In the following, details on the software implementation are reported, as necessary to run the BTEX-GC devices and access the data acquired and processed.

The Linux user related to the BTEX-GC device is user: "pi"
The default password of "pi" user is   *****************
CAUTION: The user "pi" has administrative privileges.

At delivery, the SBC is configured for automatic IP configuration via DHCP.

For initial access to the SBC, the use of external USB mouse and keyboard and the HDMI connection to a suitable display are suggested, in order to log into the SBC (which may have an unknown IP address) and do the necessary configurations (e.g. static IP address).

Once the SBC is set-up with a known IP configuration, it can be accessed at any time via SSH, SFTP and Samba (Microsoft Windows shared folders) connections. Please note that SSH, SFTP and Samba servers are already running on the SBC OS.

The following is the relevant directory structure inside the SBC:

/home/pi/misure   contains all the data acquired, with daily subdirectories which are created automatically by the control software.

/home/pi/miniGC   contains all the control and processing software binaries and scripts.

The Linux cron deamon "crond" is used to start a single measurement cycle at 00, 15, 30, and 45 minutes of each hour. This automates the start of the whole measurement system whenever the SBC is powered up.

The start of the measurement cycles will always be synchronized to the four 15min quarters of each hour by the SBC integrated Real-time-clock (RTC). All data files will refer the time and date information corresponding to the system RTC.

Inside the /home/pi/miniGC directory, the following scripts are to be called by the user:
miniGC_enable   enables the BTEX-GC to run and acquire data, as triggered by crond.
miniGC_disable   disables the BTEX-GC. The cron deamon trigger will not start the BTEX-GC.

Furthermore, the shell script **miniGC_start** can be modified by the user, e.g. through a secure shell connection (SSH) using the "nano" editor. Inside this script, the chromatogram processing parameters can be modified to compensate peak position changes, which rarely occur.

Please use caution when modifying the **miniGC_start** script:
if changes to this script are necessary, please make a back-up copy first.

As an example, please note the following line inside the miniGC_start script:

```
./processor $LASTFILE benzene 96 160 6 125 12 toluene 260 310 15 275 10
   ethylbenzene 320 355 15 333 20 xylene 400 440 15 420 15 > file_to_plot
```

As can be disclosed, the four aromatics, whose peaks need to be identified and quantified (benzene, toluene, ethylbenzene and xylene) are listed, together with their 5 peak integration parameters each. If necessary, further peaks may be defined, making sure to add, in the correct sequence:

      i)   the peak name
      ii)   the 5 peak integration timings, as described below

As an example, please consider the definition of the first peak "benzene"

```
./processor $LASTFILE benzene 96 160 6 125 12 … … … … …
                         |    |   |  |  |   |
                         |    |   |  |  |   PMW=12
                         |    |   |  | PMP=125
                         |    |   | PBW=6
                         |    |  PBE=160
                         |   PBS=96
                        PN="benzene"
```

In the following, the 6 parameters of the benzene peak are explained, as shown below in figure 3.

    PN   = Peak name
    PBS   = Peak base start time (in seconds)
    PBE   = Peak base end time (in seconds)
    PBW = Peak base search width (in seconds)
    PMP = Peak maximum position (in seconds)
    PMW = Peak maximum search width (in seconds)

Peak height calculation procedure:

The peak height is calculated as the difference between the PID signal at the peak maximum time and a baseline, which is constructed at the base of the peak by finding two PID signal minima.
The peak minima are searched close to the times **PBS** and **PBE**, at a maximum distance of **PBW** seconds. The baseline is a straight line connecting the two minima found close to **PBS** and **PBE**.
The peak maximum is searched close to the time **PMP**, at a maximum distance of **PMW** seconds. Once the exact position of the peak is found, it is subtracted by the baseline at the same position, resulting in the peak height.
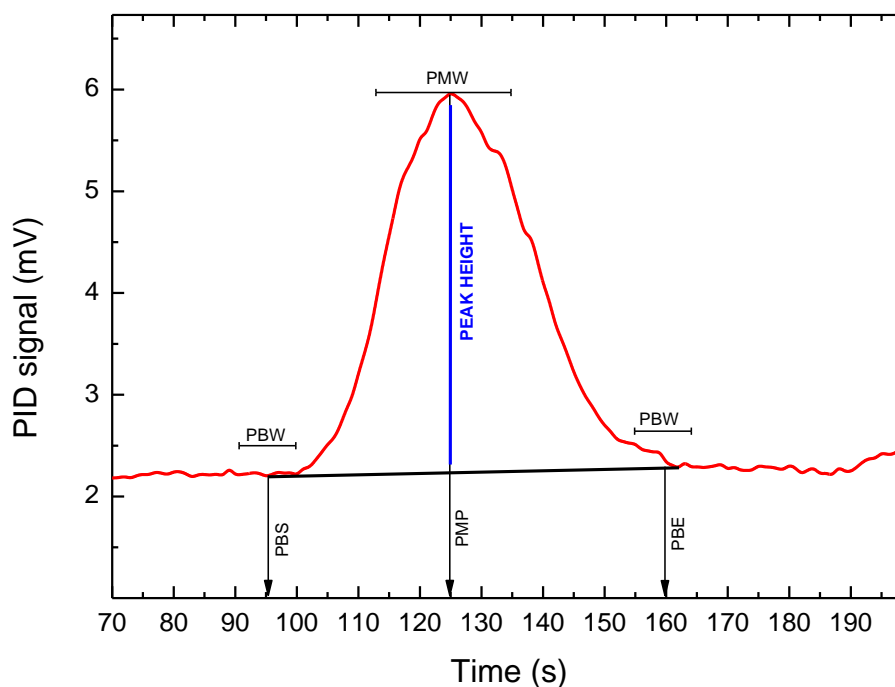
Figure 3: visual representation of the peak integration parameters

The structure of the acquired data

Inside the folder /home/pi/misure, all the data acquired by the software package are stored. The following list reports all files and their contents.

For each day of measurement   a sub-folder is created with the name "**YYYY-MM-DD/**"

For each chromatogram/cycle   the following 4 files are created

PID_YYYY-MM-DD_HH:MM:SS.dat   contains the PID signal of the chromatogram.
                                 PID sampling interval is 1s.
                                 Column1   time in seconds
                                 Column2   PID signal in mV
                                 Columns3-4   discard (for compatibility)

PID_YYYY-MM-DD_HH:MM:SS.dat.png   bitmap of the processed chromatogram in png format, plotted by gnuplot. See figure 2.

GCSep_YYYY-MM-DD_HH:MM:SS.Tlog   contains a log of the GC unit states.
                                 Contents are relevant only for debugging.

PreC_YYYY-MM-DD_HH:MM:SS.Tlog   contains a log of the pre-conc. unit states.
                                 Contents are relevant only for debugging.

For each chromatogram/cycle   the following 3 files are updated, by appending a line

benzene	contains the height of the benzene peaks, 1 line per measurement.
toluene	the height of the toluene peaks, 1 line per measurement.
ethylbenzene	the height of the ethylbenzene peaks, 1 line per measurement.
xylene	the height of the xylene peaks, 1 line per measurement.

NOTE: more files will exist if more peaks are defined inside the miniGC_start script.

The detailed format of the four files reported above is:

Column1	Chromatogram start time in Julian-time format
Column2	Full path to processed PID data-file
Column3	Peak height in mV
Column4	Peak maximum value in mV

```
2457065.59375      /home/pi/misure/2015-02-12/PID_2015-02-12_14:15:02.dat   1.408  2.354
2457065.60417      /home/pi/misure/2015-02-12/PID_2015-02-12_14:30:02.dat   1.490  2.452
2457065.61458      /home/pi/misure/2015-02-12/PID_2015-02-12_14:45:02.dat   1.581  2.334
2457065.62500      /home/pi/misure/2015-02-12/PID_2015-02-12_15:00:03.dat   1.536  2.452
2457065.63542      /home/pi/misure/2015-02-12/PID_2015-02-12_15:15:02.dat   1.583  2.227
2457065.64583      /home/pi/misure/2015-02-12/PID_2015-02-12_15:30:02.dat   1.478  2.435
...                ...                                                      ...    ...
```

The peak height indicated in the third column is <u>proportional to the concentration</u> of the single aromatic, through a PID sensitivity coefficient S:

Concentration = S * peak_height

Said sensitivity coefficient S will slowly decrease during the BTEX-GC operation time, until the PID lamp will need to be replaced when the peak signal-to-noise ratio will be too low for peak processing.

To perform autonomous long-term measurements (>2 weeks), periodic sensitivity re-calibration will be necessary to determine the sensitivity coefficient S. Special equipment may be necessary for sensitivity re-calibration.

<u>Every 2 chromatograms/cycles</u>   the following 3 files are updated, by redrawing

benzene.png	a plot of the daily benzene peak height trend
toluene.png	a plot of the daily toluene peak height trend
ethylbenzene.png	a plot of the daily ethylbenzene peak height trend

NOTE: more files will exist if more peaks are defined inside the miniGC_start script.

It is suggested that the user access the data acquired by a SFTP connection to the SBC. A SFTP server is up by default configuration. Access to the daily subdirectories should allow for easy periodic download of the acquired data. Optionally, samba file sharing protocol can be implemented.

Appendix 1: list of BTEX-GC LEDs

Supply IN
Supply IN Fused

+5V USB
TX/RX UART
Internal supply regulated +3.3V

Blink 10Hz during normal operation
Light 1.3sec on every Tx/Rx I²C interface

Supply PID ON

Exciting polarization EV

Front fan ON

Internal supply regulated +3.3V

Hardware Status

Electrical Column continuity
Heating Column ON

Supply IN

Internal supply regulated +3.3V analog section
Internal supply regulated +2.5V analog section
Internal supply regulated +3.3V digital section
Internal supply before internal regulator
Supply input
Supply input fused

Heating Fluidic part ON
Pump ON