A Turnkey and Autonomous System for the On-line Monitoring of Industrial Processes

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KEYWORDS

ABSTRACT

The ability to monitor industrial processes and obtain real-time data is crucial for many reasons such as a better understanding of the process, control of emission regulations, or even safety reasons. To this end, industries are often in need of systems able to realize fast on-line analysis with built-in alarms if necessary. On-line gas chromatography is a tool of choice because of the large variety of compounds that can be analyzed, the precision and reliability of the results. However, such systems usually demand controlled laboratory conditions and data treatment. In this paper, we present an autonomous, on-line and turnkey solution designed for the monitoring of odorous compounds before and after an odor treatment system. This complete solution is composed of several gas chromatographs (GCs) for the measurement of volatile organic compounds (VOCs), aldehydes and ketones, H_2S and mercaptans, NH_3 and total volatile organic compounds (TVOCs). Two gas generators (hydrogen and pure air) allow the module to function autonomously and continuously. The GCs and gas generators are all installed in a temperature-controlled cabinet designed for harsh environmental conditions. Analytes are automatically identified and quantified and the reliability of the results is checked daily thanks to integrated gaseous standards.

INTRODUCTION

The analysis of volatile organic compounds (VOCs) is of increasing interest due to their impact on human health and the environment (Yu, et al, 2022; Zhang, et al, 2021). VOCs include a wide variety of compounds and many of them are harmful for human health and/or the environment, even at low concentrations (Hu, et al, 2019). Their harmful effects range from minor discomfort to various diseases (asthma, cancers, …) depending on the concentration and time of exposure (Almetwally, et al, 2020). In addition to their hazardous nature, many VOCs are also considered as odorous compounds and can often be the source of unpleasant smell. VOCs and odorous VOCs can be generated by many different sources such as traffic activities, chemical, agricultural, food processing or waste production processes (Han, et al, 2018). Industrial areas are subjected to greater VOCs concentrations. Considering all of this, there is a need to monitor VOCs and odorous VOCs in industrial areas to ensure a better control and regulations of these compounds. The most common technique for VOCs measurements in industrial area is done by off-line sampling in traps or canisters, followed by gas chromatography analysis. The main drawback of this technique is the delay between sampling and analysis. We present a turnkey and fully autonomous system for continuous monitoring of some VOCs at ppm level for an industrial process. In this particular case, the goal is to monitor some odorous compounds before and after a deodorization process.

DESCRIPTION OF THE ANALYTICAL SYSTEMS

COMPOUNDS TO BE MONITORED

As mentioned before, odorous VOCs are numerous and belong to various chemical families. Table 1 summarizes the compounds to be monitored and their expected concentrations at each sampling point (before and after the deodorization process):

Table 1: Description of the monitored compounds with their target concentrations and low detection limit

Compounds/Compound families	Max concentration before the deodorization process (ppm)	Max concentration after the deodorization process (ppm)	Low Detection Limit (ppm)
CH_4/NMTHC	150 ± 0.05	2 ± 0.05	0.1
Aldehydes/ketones	10 ± 0.10	1 ± 0.10	0.1
Amines	10 ± 0.07		0.07
H_2S	50 ± 1	1 ± 0.005	0.005
Mercaptans	10 ± 1	1 ± 0.005	0.005
NH_3	50 ± 1	1 ± 0.1	0.2
CO_2	$5\ 000 \pm 10$	$3\ 000 \pm 10$	10
N_2O	10 ± 0.2		0.5
Cl_2	10 ± 0.1		0.5

To monitor all these different compounds, several GCs are used, each designed to target a specific type of compounds. In total, three GCs equipped with a flame ionization detector (FID) were used for the continuous and automatic measurement of CH_4/NMTHC (non-methane total hydrocarbons), aldehydes and ketones and amines. A GC coupled to an electrochemical detector was used to monitor H_2S and sulfur compounds and an FT-UV detector was used for NH_3. CO_2, N_2O and Cl_2 were monitored by specific sensors.

GC/FID FOR THE MONITORING OF CH4/NMTHC

For each analysis, a 250µl sampling loop is filled and its content injected into the columns. For the separation, two Porapak Q columns (100/120 mesh, 1m) followed by a 10 m MXT 624 column (0.53 mm ID, 3 µm dF) are used. Only the second Porapak Q and the MXT 624 column are located inside an oven set at 80 °C. An internal gas standard of benzene is also integrated in the form of a permeation tube located in an oven set at 45 °C. This oven is permanently flushed by 50 ml/min of air and an additional 200 ml/min is added for the analysis. Figure 1 represents an example of chromatogram obtained in ambient air.
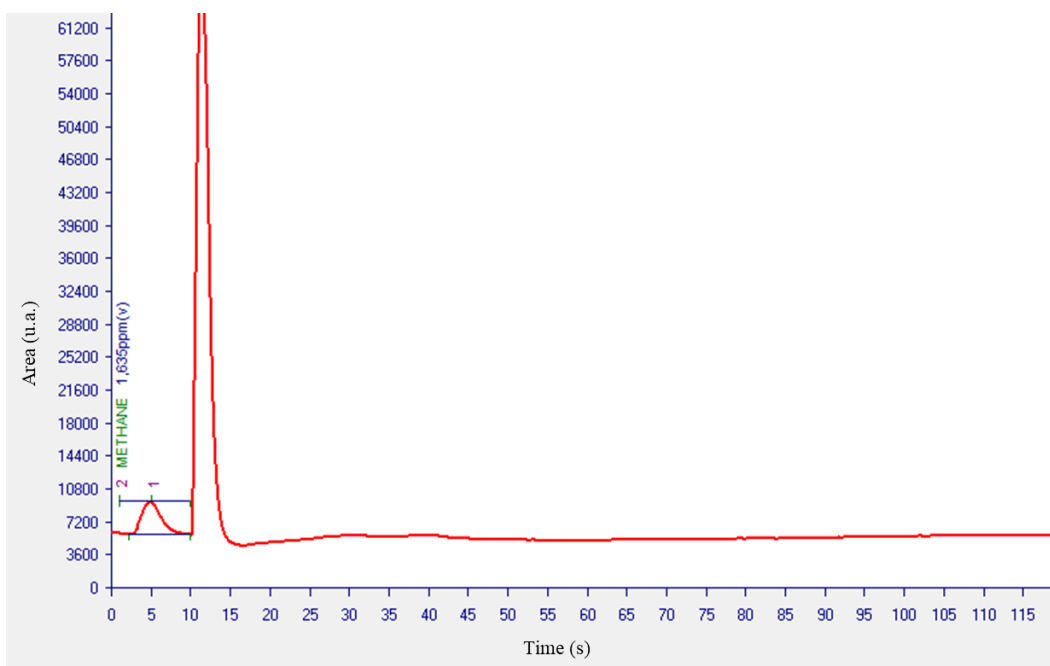
Figure 1: Chromatogram of CH$_4$/NMTHC obtained in ambient air

GC/FID FOR THE MONITORING OF ALDEHYDES AND KETONES

For each analysis, a 250µl Teflon sampling loop is filled and its content injected into the columns. The columns are positioned in a specific backflush mode, called CP backflush, to prevent potential matrix impurities from going into the analytical column. The CP backflush column is a 1 m MXT 624 (0.53 mm ID, 3 µm dF) and the analytical column is a 29 m MXT 624 (0.53 mm ID, 3 µm dF) located inside the heated oven of the GC. During the first 7 minutes of the analytical procedure, the temperature rose from 36 °C to 50 °C with a heating rate of 2 °C/min. Afterwards, a constant heating rate of 10 °C/min was applied for 3 minutes followed by a heating rate of 12 °C/min for 8,3 minutes. Finally, a heating rate of 20 °C/min was applied for 1 minute to reach a temperature of 199°C. The temperature was kept at this value for 2 minutes. For this application, an oven containing permeation tubes of benzene at 1.2 ppm, acetaldehyde at 1.6 ppm and 2-hexanone 0.3 ppm was used to check the stability of the analyzer over time. Figure 2 shows the chromatogram obtained for the analysis of the standard gas from the permeation oven. Many aldehydes and ketones including acetaldehyde, acrolein, acetone, isopropyl alcohol, methyl tert-butyl ether, vinyl acetate, methyl ethyl ketone, ethyl acetate, 1,4-dioxane, methyl methacrylate and methyl isobutyl ketone can be identified and quantified with this method.
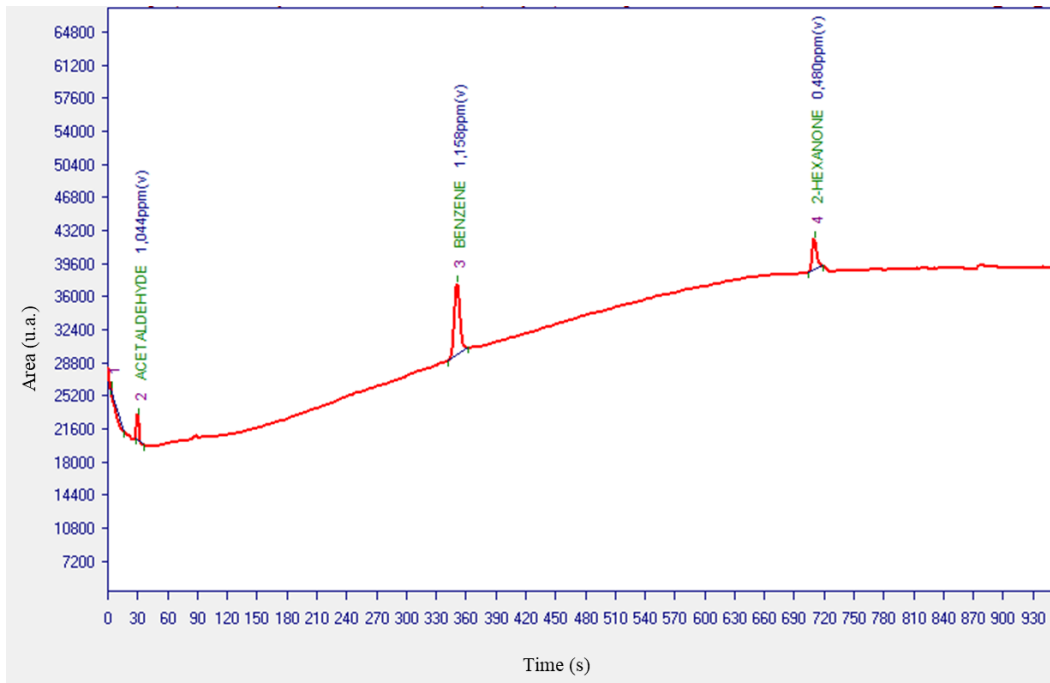
Figure 2: Chromatogram obtained for the analysis of the permeation oven

The permeation tubes used were certified at ± 50% that is why the relative standard deviation obtained are between 3.8% for benzene and 50% for 2-hexanone. Here, the permeation tubes are mainly used to verify the stability of the system and the retention time stability.

To demonstrate the system stability, the internal standard gas was periodically analyzed and Figure 3 shows the concentrations measured during 48 hours of monitoring:
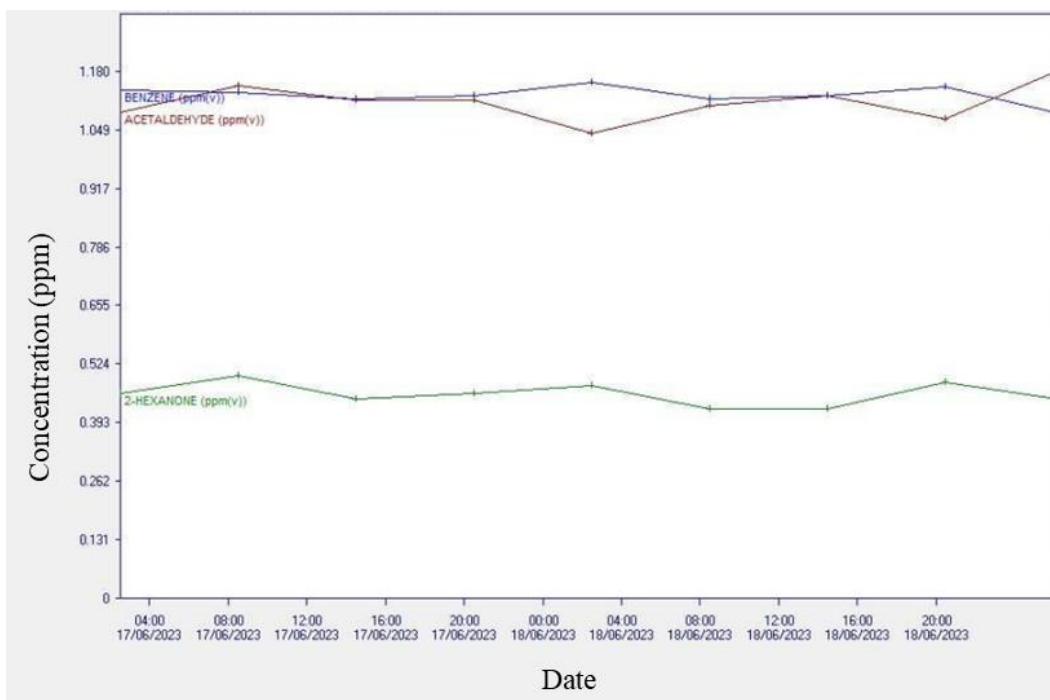
Figure 3: 48 hour trend on the internal standard gas

The relative standard deviation for benzene, acetaldehyde and 2-hexanone are 1.79 %, 3.84 % and 5.36 % respectively.

GC/FID FOR THE MONITORING OF AMINES

For each analysis, a 125 µl PEEK sampling loop is filled and its content injected into the columns. The columns are positioned in a CP backflush mode to prevent potential matrix impurities to go into the analytical column. The CP backflush includes a 1 m Rtx volatile amines column (0.32 mm ID, 5 µm dF) and a 30 m Rtx volatile amines column (0.32 mm ID, 5 µm dF) located inside the heated oven of the GC. During the first 2.5 minutes of the analytical procedure, the temperature rose from 45 °C to 50 °C with a heating rate of 2 °C/min. The oven was kept at 50 °C for 5 minutes. Afterwards, a constant heating rate of 20 °C/min was applied for 6.5 minutes. The temperature reached was 180 °C and the oven was kept at this temperature for 10.3 minutes. For this application, an oven containing permeation tubes of benzene at 1.2 ppm, trimethylamine at 2.2 ppm and diethylamine at 1.4 ppm was used to check the stability of the analyzer over time. Figure 4 shows a chromatogram obtained for the standard gas analysis from the permeation oven and Figure 5 shows the chromatogram obtained for an injection of trimethylamine and diethylamine in a heated glass bulb. Amines such as methylamine, dimethylamine, trimethylamine, ethylamine and diethylamine can be identified and quantified with this method.
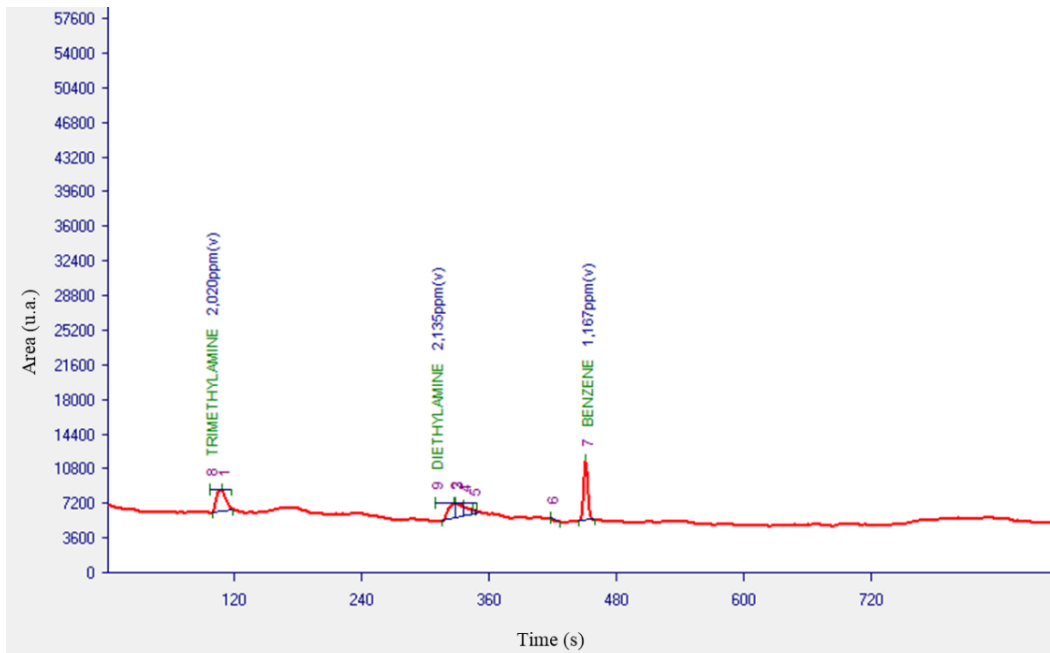
Figure 4: Chromatogram obtained for the analysis of the permeation oven

Again, the permeation tubes are certified at ±50% and are used to control the retention time stability and the repeatability of the system.
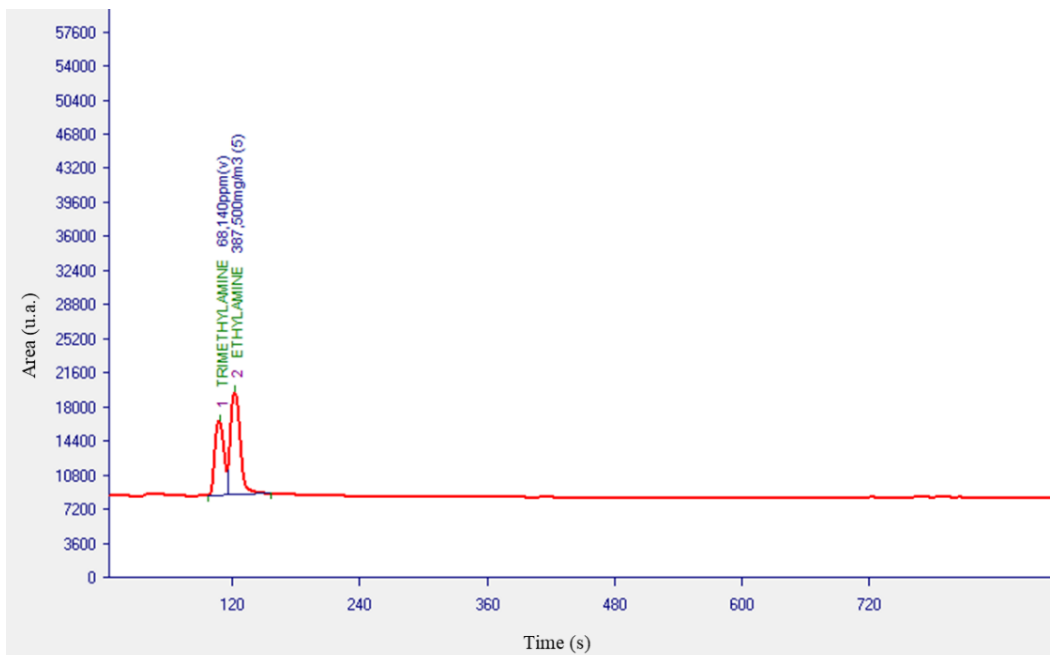

Figure 5: Chromatogram obtained for an injection of trimethylamine and ethylamine in a heated glass bulb

To demonstrate the stability of the system, the internal standard gas was periodically analyzed and Figure 6 shows the concentration measured for 48 hours.
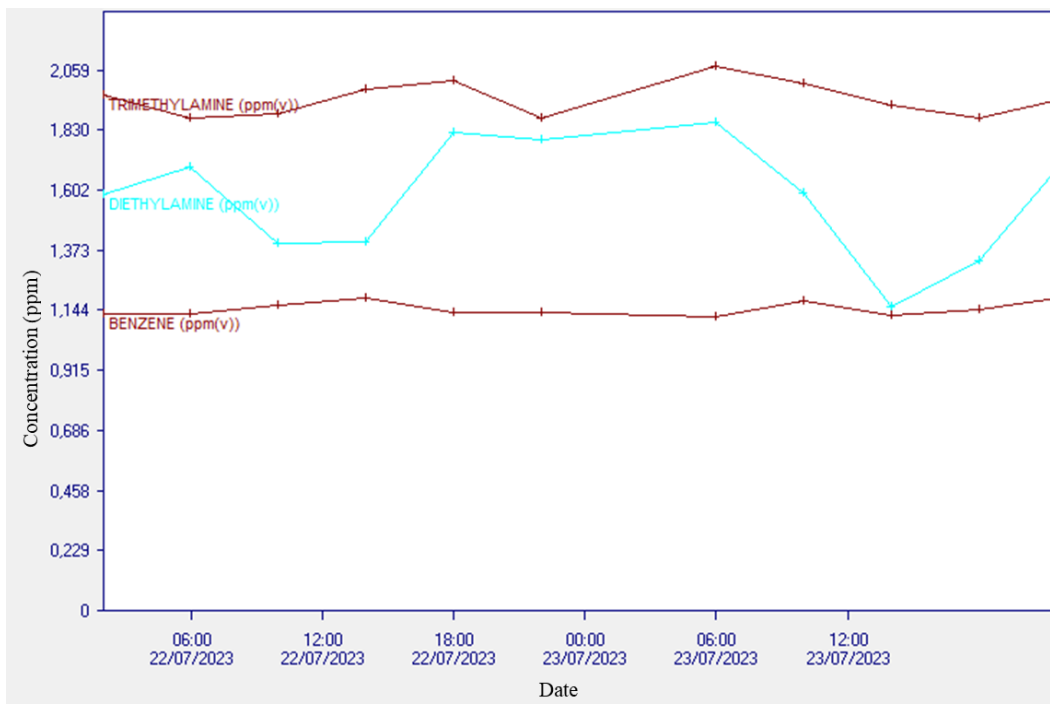

Figure 6: 48 hours trend on the internal standard gas

Compared to the other compounds, diethylamine shows a poorer repeatability. That is mainly due to the integration of the peak which is tailing. The relative standard deviation calculated for benzene, trimethylamine and diethylamine are respectively 2.2 %, 3.4 % and 17.0 %.

MONITORING OF H₂S AND MERCAPTANS WITH GC COUPLED TO AN ELECTROCHEMICAL DETECTOR

For H$_2$S and sulfur compounds, the concentration range is wide enough so that two injection loops are needed: 50 (MXT deactivated sampling loop) µL for the high concentrations (before the deodorization process) and 400 µL (Sulfinert sampling loop) for the smaller concentrations (after the deodorization process). The content of the selected loop is injected into the columns. A first MXT-5 column (4m, 0.53 mm ID, 1.5 µm dF) is used to separate the light sulfur compounds from the heavier one. The light compounds are then sent into a 30 m MXT 624 column (0.53 mm ID, 3 µm dF). Both columns are located inside an isothermal oven set at 40 °C. For this application, an oven containing permeation tubes of H$_2$S at 112.2 ppb and dimethylsulfide at 54.3 ppb was used to check the analyzer stability. H$_2$S and sulfur compounds such as methyl and ethyl mercaptan, dimethyl sulfide, diethyl sulfide and dimethyl disulfide can be identified and quantified. Figure 7

shows the chromatogram obtained for a mixture of sulfur compounds and Figure 8 shows the concentration measured for 30 hours of analysis of the same mixture.
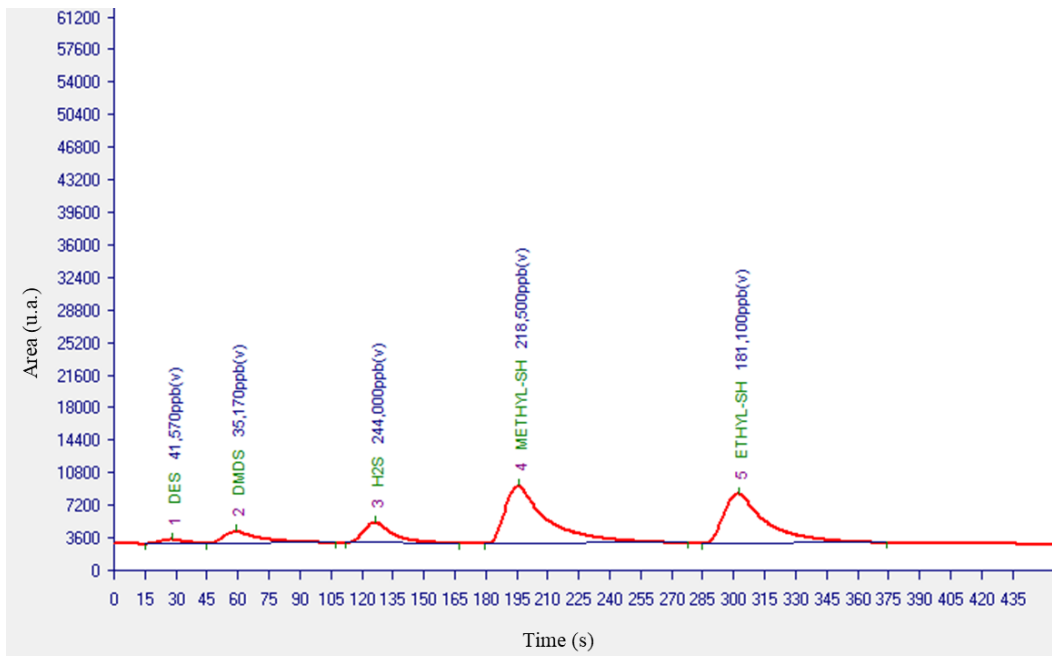

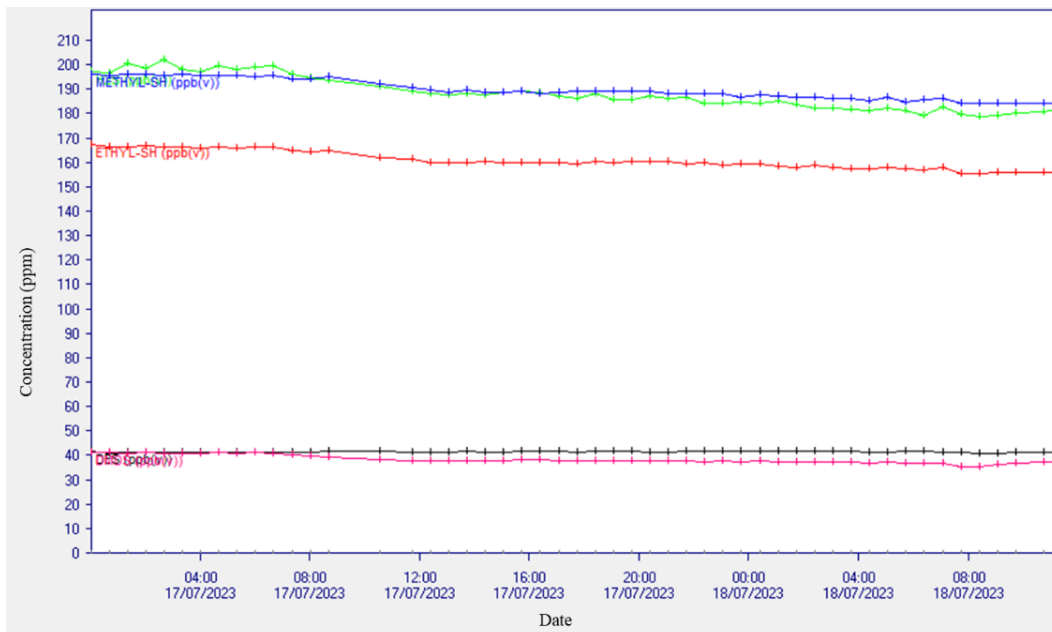Figure 7: Chromatogram obtained for the analysis of a mixture of sulfur compounds

Figure 8: Trend for 30 hours for the analysis of the mixture of sulfur compounds (in green, H_2S – in blue, methyl mercaptan – in red, ethyl mercaptan – in black, diethylsulfide – in pink, dimethyl disulfide)

The relative standard deviation calculated for H2S, methyl mercaptan, ethyl mercaptan, diethylsulfide and dimethyl disulfide are respectively 1.3 %, 1.0 %, 0.9 %, 0.9 % and 1.8 %.

AUTONOMOUS SOLUTION IN SHELTER FOR INDUSTRIAL PROCESS MONITORING

To provide a completely autonomous solution, gas generators were used to supply the analyzers. Hydrogen, zero air and nitrogen were continuously produced, in quantity and quality sufficient for all modules. A multiplexer was added to enable monitoring the two streams: before and after the deodorization process.

The GCs, gas generators and other modules (sensors, sampling pumps) were integrated inside two shelters. A shelter consists of a big cabinet in which the analyzers and gas generators can be placed. The shelter can be located outdoor because it is designed to protect its content from the outside (extreme temperatures, rain). A climatization module regulates the temperature of the shelter thus preventing its content to be influenced by outdoor conditions. This was verified experimentally on one GC placed in a shelter located in Bordeaux. The shelter was located outside, without any particular protection. The experiment was made in July and the shelter was directly exposed to the sun for about 8 hours. Temperature measurements were made using two temperatures sensors, one located in the shelter (close to the GC) and another directly inside the GC. The temperature was measured and recorded every second for 24 hours. Every 30 minutes (the GC cycle time), a file containing the measured temperatures of both sensors was created. To simplify the data treatment, for each file, the maximum, minimum and average temperature was reported. This treatment was done for 24 hours. Figures 9 shows the temperature measured in the shelter and in the GC compared to the outdoor temperature.
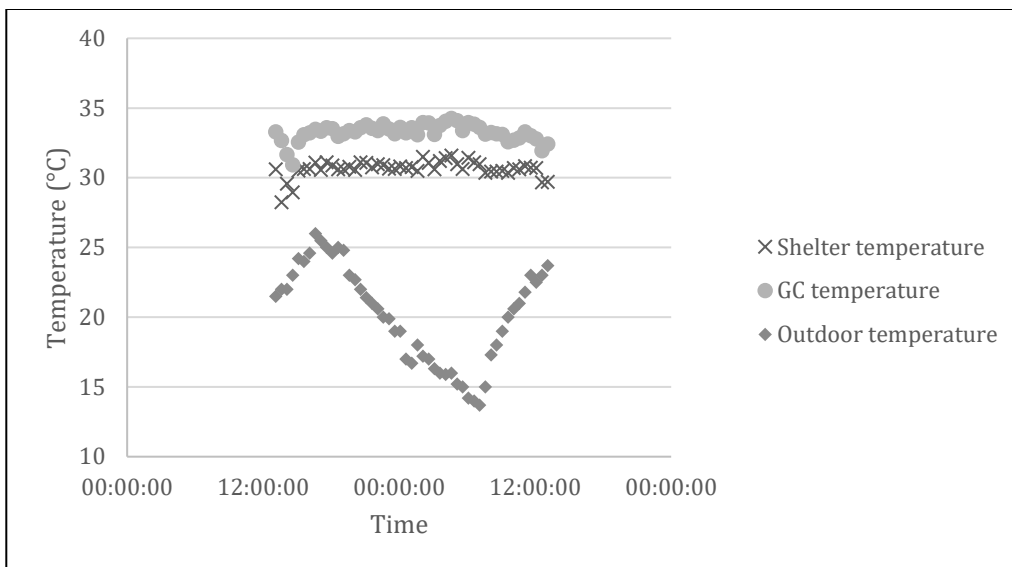
Figure 9: shelter, rack and outdoor temperature

This figure shows good temperature stability in both the shelter and the GC. The small decrease of temperature observed at the beginning in the shelter and in the GC corresponds to a brief opening of the shelter. This clearly demonstrates the ability of the shelter to protect its content from outdoor conditions. Despite the important temperature variations measured outdoor (from 13.7 °C to 25.5 °C), the temperatures measured in the shelter and in the rack are very stable. The relative standard deviation calculated in the shelter and in the GC are respectively 1.3 % and 1.4 %.

In parallel, the stability of the benzene retention time was verified. Figure 10 shows the retention time of benzene over the 24 hours monitored (the chromatogram where the shelter was opened are not considered in this case).
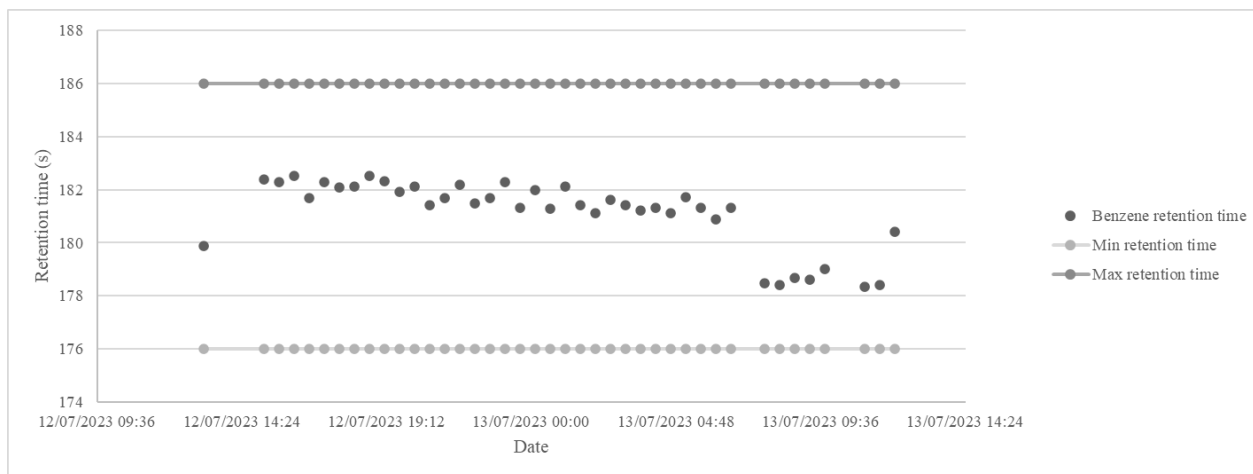
Figure 10: Trend on the benzene retention time

The relative standard deviation for benzene retention time is 0.7% which is very good. A small temperature drop of less than 3 °C is observed. Minimum retention time and maximum retention time represent the retention time window used for benzene identification. The overall retention time of benzene is quite stable, enough to enable an automatic identification of the compound based on its retention time.

SUMMARY

In this paper, we presented a fully autonomous solution for continuous and automatic monitoring of an industrial deodorization process. Given the complexity and the differences in the compounds to be monitored, several GCs and a few specific sensors were needed. To make the solution fully autonomous, hydrogen, air and nitrogen generators were provided to supply the various analyzers. All of the modules (analyzers, gas generators, sensors and sampling pumps) were integrated into two shelters. These shelters are specifically designed to enable the GCs to work even under harsh environmental conditions. Temperature tests in the shelter and in a GC located in the shelter have shown temperature stability in both the shelter and the GC on a hot summer day. This type of installation is ideal for the monitoring of industrial processes were there is a need for autonomous, robust systems that provide automatic identification and quantification.

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