CHEMICAL ENGINEERING TRANSACTIONS Volume 23, 2010
Editor Renato Del Rosso

DOI: 10.3303/CET1023040

Miniature And Low-Cost Devices For The Precise And Reliable Monitoring Of Low Concentrations Of H_2s In Changing Environments

Nazaré Pereira-Rodrigues*, Jean-Michel Guillot**, Jean-Louis Fanlo**, Christophe Renner***, Bruno Aubert*
* Cairpol, CC Rocade Sud, av. Olivier de Serres, 30100 Alès, France
** LGEI, Ecole des Mines d'Alès, 6 av. De Clavières, 30319 Alès, France
*** Veolia Environnement, chemin de la Digue BP76, 78603 Maisons Lafitte, France

Gas detection instruments are increasingly needed for industrial health and safety, environmental monitoring and process control. International recommendations and laws for limiting environmental pollution (toxic gases) and annoyance (malodorous gases) are becoming stricter for both industrial and domestic sources of pollution. Public organizations for environmental control and industries require therefore new tools for a cheaper and more effective monitoring of gas emissions. Among air pollutants, reduced sulfur compounds and especially hydrogen sulfide (H_2S), which mainly results from industrial activities and anaerobic manure decomposition in commercial livestock animal operations, is an offensive malodorous and toxic gas even in small concentrations, causing serious discomfort and health and social problems. There is therefore a need to be able to detect the presence of this pollutant at low concentration (ppb level).

Today, the most common industrial gas sensors available on the market are based on semiconductor oxides. However, issues with sensitivity (ppb range), selectivity and stability have limited their use, often in favor of more expensive approaches. Another limitation of these commonly used gas sensors is their lack of reliability while measurements are made on the field, especially during rapid changes of environmental conditions (like sudden variations of relative humidity).

We developed an ultraportable and low-cost monitoring gas device that allows the continuous detection of low concentrations of H_2S:

- The selectivity of measurement was obtained with specific amperometric gas sensors, which have also the advantage to be low consumers of energy and to be miniaturized.
- The sensitivity of detection was enhanced (from ppm to ppb range) thanks to a dynamic uptake of the target gas to the amperometric sensor.
- The low-cost of the developed monitor provides a higher potential to install arrays of devices to precisely map the levels of this malodorous gas in extended areas. A map reporting H_2S real-time levels in the field (location: Wastewater Treatment Plant (WWTP) in the south of France) was carried out.

Please cite this article as: Pereira-Rodrigues N., Guillot J.M., Fanlo J.L., Renner C. and Aubert B., (2010), Miniature and low-cost devices for the precise and reliable monitoring of low concentrations of h2s in changing environments, Chemical Engineering Transactions, 23, 237-242
DOI: 10.3303/CET1023040

- The reliability of measurement was drastically improved during field measurements (the studied WWTP was close from the sea) by using a filter based on a buffer effect against any environmental interference (like rapid change of relative humidity) during gas monitoring.

An evaluation of odorous H_2S emissions could be precisely estimated in real-time conditions by performing simultaneous H_2S monitoring in the WWTP.

Keywords: H_2S detection, electrochemical sensors, humidity-insensitive buffer, dynamic uptake system, field measurements

Introduction

In France the Law on air and the rational use of energy (the LAURE Law), repealed the Law of 1961 and has become the basic French legislation on the environment. In 2000, the provisions of this law were integrated into the Environmental Code through the regulations. The Environmental Code states that each person has a right to breathe air which is not harmful to health. This provision for the general welfare consists of preventing, monitoring, reducing or eliminating atmospheric pollution. Odor is considered an atmospheric pollutant and the code provides a definition of atmospheric pollution: “Atmospheric pollution […] is the direct or indirect introduction of substances with harmful consequences into the atmosphere and enclosed spaces and which [...], can provoke excessive olfactory pollution”. Through the idea of excessive olfactory pollution, the French legislator refers to the concept of tolerable annoyances, introducing the principle of acceptability of the annoyance, as in the case of sound pollution. Up to now, there is no general value for the acceptability level of odors. However, the regulation for Classified Facilities for Environmental Protection (ICPE) provides, in certain cases, odor concentrations or odor flow rates beyond which olfactory discomfort may be presumed for residents (Bokowa et al, 2010).

Wastewater collection and treatment systems often generate offensive odors that elicit complaints from neighbors. Collection systems transport wastewater from commercial and industrial facilities and residences to Wastewater Treatment Plants (WWTP) for processing. Collection systems can include both force mains, through which wastewater is pumped, and gravity sewers, through which the wastewater flows without pumping. This wastewater can create collection system odors and related corrosion that sometimes must be collected and treated.

Reduced sulfur compounds such as hydrogen sulfide (H_2S) and methylmercaptan (CH_3SH) are prevalent at industrial facilities where anaerobic degradation of organic material is taking place. All of these reduced compounds are a main cause of nuisance odors due to their extremely low odor detection thresholds. It has been shown that H_2S is the most prevalent odorant at wastewater facilities (Yuwono et al, 2004)

Various sampling and analytical approaches exist for low level measurement of these compounds. Traditional techniques of measuring hydrogen sulfide include sample collection in Tedlar® bags and/or specially treated canisters and subsequent laboratory analysis by gas chromatography with sulfur chemiluminescence detection, pulsed flame photometric detection, or other specialized detection technique. The sulfur chemiluminescence detector (SCD) is one of the most selective sulfur detectors available. Therefore the response of the volatile sulfur compounds is not affected by the co-elution of hydrocarbons in the sample matrix. Coupled with a traditional gas chromatograph (GC), the SCD is used to detect reduced sulfur compounds as hydrogen sulfide. Typical reporting limits for laboratories performing low-level reduced sulfur (i.e. odor related) testing are in the range of 2.5-5.0 ppb. However, sampling and analysis of hydrogen sulfide (H_2S) in air is a challenge due to its reactive nature and low concentration (ppb to ppm range).

For accurate monitoring of pollution exposure, it is therefore necessary to measure air pollution gases continuously, either at several points in a plant or in the occupant's breathing zone. Today, the most common industrial gas sensors available on the market are based on semiconductor oxides. However, issues with sensitivity (ppb range), selectivity and stability have limited their use, often in favor of more expensive approaches. Another limitation of these commonly used gas sensors is their lack of reliability while measurements are made on the field, especially during rapid changes of environmental conditions (like sudden variations of relative humidity). The use of electrochemical (EC) sensors is an excellent alternative for accurate and low-level monitoring of H_2S at the ppb range. Improvements in EC sensor technology can combine the sensitivity and selectivity gas chromatography techniques with advantages in size, portability, and low-cost. However, very low range concentrations are hard to reach if no dynamic uptake of the sample is performed.

We developed a low-cost and miniaturized H_2S monitor called CairHaz that can perform real-time and highly sensitive measurements by combining a miniaturized amperometric sensor with a dynamic air uptake, as well as an enhanced stability of the signal with a filter that enhanced the measurement reliability (especially during rapid changes of relative humidity). This allows CairHaz to achieve a lowest detection limit, improved response times, and stability over an extended lifetime. First tests made in the field in a WWTP in the south of France demonstrate the high accuracy of reduced sulfur compounds as H_2S measurements in the field.

Methodology

CairHaz (**Figure 1**) is a highly compact monitoring system that has been developed to simultaneously monitor very low levels (ppb range) of reduced sulfur compounds as hydrogen sulfide (H_2S) and methylmercaptan (CH_3SH).

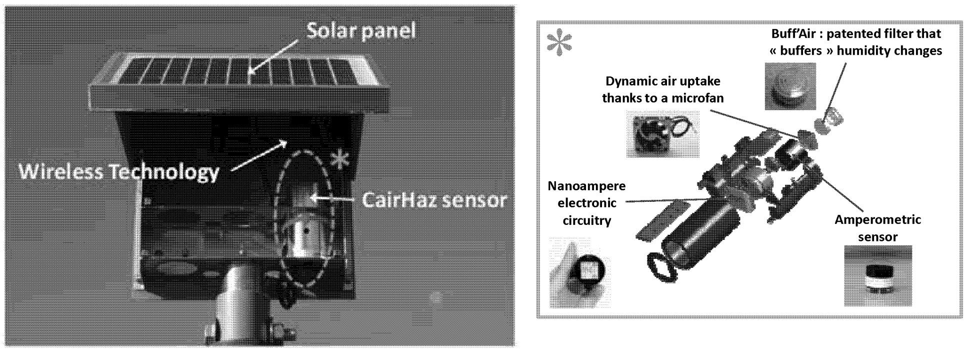

Figure 1: Description of the Cairbox and CairHaz (*)

The principle of pollutant gases detection is based on the use of a miniaturized electrochemical sensor inserted in a compact system that includes a microfan that allows a continuous and dynamic uptake of air sample (3 $L.min^{-1}$), as well as a patented inlet filter that was developed to ensure response stability by minimizing interferences

induced by quick changes of humidity. The integrated fan was previously shown to enhance the sensitivity of the amperometric sensing response in the case of other gases like ozone (Ebeling et al, 2009).
An enhanced stability of gas sensing response is one of the most important parameter to consider, especially in the case of odor monitoring and also for long-term measurements in changing environments. To monitor sulfur reduced compounds in the field, our CairHaz monitor as been coupled with a solar panel to insure a permanent power supply and with a radio-based network technology to insure an on-line datalogging, the overall system being called Cairbox (**Figure 1**).
Low-levels of gas concentrations could be detected thanks to the integrated electronics, which was designed to detect current levels of the target gas at the nanoampere range. The instrument was designed to continuously display real-time reduced sulfur compounds concentrations. Total gas exposure (expressed in ppb) was monitored in real-time thanks to the associated radio-based wireless technology and power was supplied through solar panels.
The overall performances of the amperometric sensors integrated in the CairHaz (sensitivity, selectivity, stability) were first evaluated in our laboratory and reduced sulphur compounds (H_2S and CH_3SH) levels were compared with those measured by gas chromatography analysis (that could precisely evaluate the real concentration injected in the test bench). Relative humidity in the experimental room was monitored and controlled by a commercial humidifier.
Tests were then performed in the field by assessing a network of 30 Cairboxes in a wastewater treatment plant (WWTP) in the South of France (**Figure 2**). All data were collected in real-time thanks to the wireless technology included in each Cairbox.

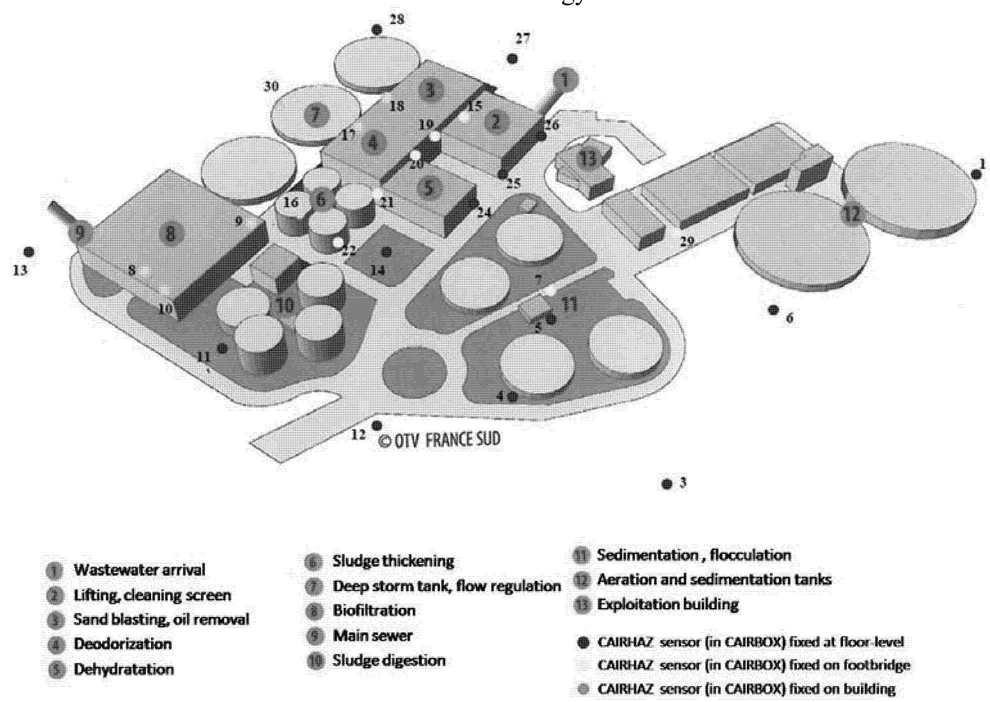

Figure 2: Map of the WWTP with the position of all Cairboxes in the field

Tests were then performed in the field by assessing a network of 30 Cairboxes in a wastewater treatment plant (WWTP) in the South of France (**Figure 2**). All data were collected in real-time thanks to the wireless technology included in each Cairbox.

Results And Discussion

Performances of CairHaz

The results in **Figure 3** show a high linearity (r^2>0.99) and sensitivity of response in the low-concentration range of H_2S (here 0-2500 ppb) with a resolution of 4 ppb. Interestingly, we found a cross-sensitivity to methylmercaptan (CH_3SH) with the same performances. This point is particularly important, as it is known that other reduced sulfur compounds as methylmercaptan are present in WWTP, and are as important as H_2S due to their nuisance odor effect. Therefore, our monitor will also be able to detect these both reduced sulfur compounds in the field.

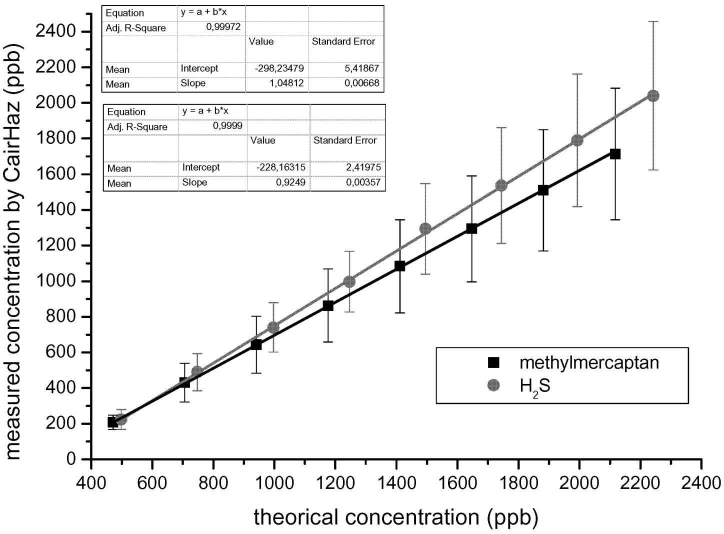

Figure 3: Calibration curve of total sulphur coumponds (here H2S and CH3SH) by CairHaz. "Theorical concentration" is the real-time concentration evaluated by gas chromatography

Moreover, above the high selectivity and sensitivity of measurement, the stability of the sensor's response towards rapid changes of humidity was insured thanks to a "buffer" filter placed at the gas inlet. This point is very important as this phenomenon frequently occur during measurements performed in the field.

Experiments in the field

First tests in the field obtained with 30 Cairboxes were then performed in the WWTP described in **Figure 2**. An example of the results obtained (here on 26th May 2010) is shown in **Figure 4**. Our results show that all CairHaz were able to precisely monitor H_2S (and CH_3SH) concentrations with level peaks above 200 ppb in the morning that day, stating that odorous compounds are still present in the field after water treatment.

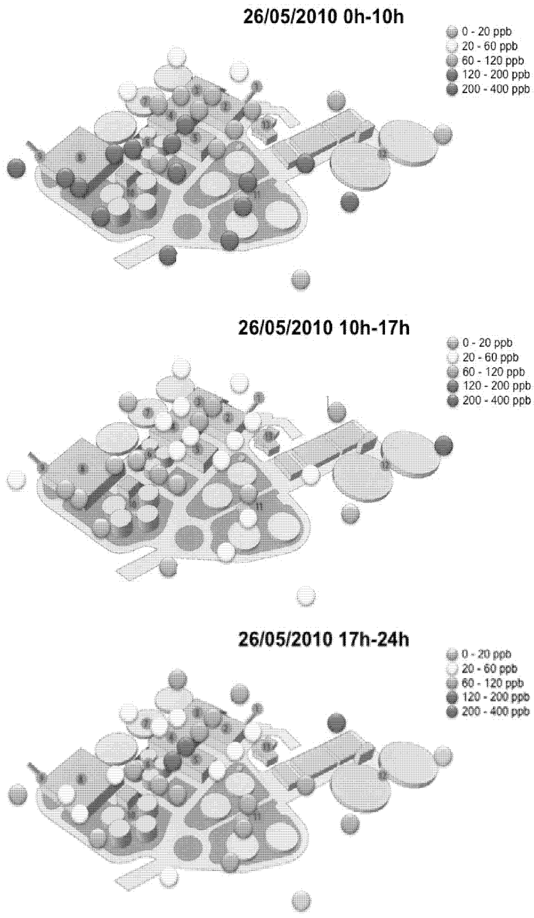

Figure 4: Results obtained in the field (WWTP in the South of France, 26/05/2010)

Conclusion

The overall results from this study demonstrate the high performances of the CairHaz for the selective, accurate and sensitive monitoring of low-level gases concentrations without any recalibration. Therefore, gas pollutant detection is now feasible by using miniaturized and low-cost sensors and is now accessible for industrial applications by installing arrays of devices in way to map pollutant levels in extended areas. Further experiments should now be done to optimize the positioning of the Cairbox in the field to be able to make efficient alarms when odor level is above critical values. Moreover, software enabling real-time mapping of H_2S concentrations, as well as a forecasting of odor evolution depending on wind direction in the WWTP, is on progress.

Reference

Bokowa A. 2010. The review of the odour legislation. Proceeding of WEF2010 conference. 492-510

Ebeling D, Patel V, Findlay M, Stetter J. 2009. Electrochemical ozone sensor and instrument with characterization of the electrode and gas flow effect. Sens. Act. B, 137, 129-133

Yuwono A.S. and Schulze Lammers P. 2004. Odor Pollution in the Environment and the Detection Instrumentation. Agricultural Engineering International: the CIGR Journal of Scientific Research and Development. 2004. Vol. IV, 1-33