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High Performance Cost Effective Miniature Sensor for Continuous Network Monitoring of H_2S

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H_2S is frequently encountered in the field of odour monitoring because of its high odorous power. Hence, different plants, such as water treatment or composting plants, are expected to monitor their emissions.
A novel high performance cost effective miniature sensor, named Cairclip, has been developed to detect H_2S at the low ppbv level. Based on amperometric detection, it is mainly composed of a dynamic air sampling system, a special filter and a high sensitive electronic circuit containing a data logger.
It is able to detect a minimum of 6 ppbv with a RSD of only 1 % (n=5) and a $T_{10\text{-}90}$ response time shorter than 60s. Analytical performances of Cairclips has been validated with a gas chromatography coupled with flame photoionization detector (GC-FPD) for laboratory experiments and total reduced sulphur compounds analyzer (CTRS) for field analyses. Experiments performed with Cairclips were in agreement with both methods. Hence, average sensitivity of sensors differs of less than 9 % compared to the sensitivity of the GC-FPD. Then, field analyses have been performed in a waste water treatment plant (WWTP) in the south of France using the CTRS and Cairclips. These experiments have permitted to determine, using both methods, reduced sulphur compounds contents in the atmosphere in several measurement points of the site.
In order to confront Cairclip to a standard apparatus of odour generation, three sensors have been exposed to H_2S *via* an olfactometer. The linear correlation observed between concentrations generated and sensors measurements illustrates the potential of such apparatus in the field of olfactory pollutions and more widely in air quality monitoring.

1. Introduction

According to Hudon et al. (2000), from 13 to 20 % of the population in European countries are annoyed by environmental odours. That mainly explains the increasing quantity of papers and rules that are published in the field of odour monitoring (Bokowa et al., 2010).
Following this way, the French law L220-2 (The French Republic, 2010) for the environment mentions that "Is considered as air pollution [...], the introduction by Man, directly or indirectly, or the presence in the atmosphere and enclosed areas of chemical biological or physical agents having prejudicial consequences likely to [...] cause odour nuisance."
The presence of such compounds in the air is mainly due to industrial and agricultural activities such as waste water treatment, storage and fermentation of organic matter (compost, sewage sludge) or

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stockbreeding. Because of their high olfactive power at very low concentrations (few ppbv), compounds such as hydrogen sulfide (H_2S) or methyl mercaptan (CH_3SH) match with this definition. Waste water treatment plants are regularly finger-pointed for their odours emissions and it is today admitted that H_2S is the most prevalent odorant compound that is generated in this kind of industry (Yuwono et al., 2004).

It exists a lot of very accurate analysis systems that are able to provide ponctual informations on olfactive pollution levels but such analytical devices are expensive and not easily transportable. Thus, the monitoring of wide spaces would be either very expensive or statistically realized (Isaac-Ho Tin Noe I. et al., 2010). Another possibility consists in using passive samplers (Llavador-Colomer et al., 2010). In this case, results obtained are reliable but do not permit to highlight brief and intense episodes of pollution. Hence, critical data are automatically lost. More representative spatio-temporal information could be obtained by networking a large number of apparatus on the site of interest. For this purpose, reliable and miniature low-cost devices that are able to performed real time monitoring at the low ppbv level are needed.

We developed reliable and cost-efficient miniature sensors, named Cairclips, which can solve this problem (Pereira Rodrigues et al., 2010). Analytical performances reached with these miniature sensors are not higher than standard apparatus ones, but in most cases, networks of Cairclips give an access to more representative information of pollution than statistical studies or passive samplers for instance.

In its first part, this study details the experiments that have permitted to characterize the performances of sensors. Field analyses performed in an industrial environment are also described. Finally, results illustrating the behavior of sensors versus an olfactometer with dynamic dilution are also presented.

2. Materials and methods

2.1 Apparatus

The analyses of reduced sulphur compounds by gas chromatography (GC), especially H_2S, have been performed with a CHROMA-S (Chromatotech, Houston, TX - USA) doted of a MXT-624 column, (Øi 0.53 mm, length 30 m, stationary phase thickness 3 µm, Restek, Bellefonte, PA - USA) and equipped with a flame photometric detector (FPD). Total reduced sulphur compounds analyses have been realized by UV fluorescence spectroscopy with an AF22M-TRS (CTRS) from Environnement SA (Poissy – France). The odour measurements have been carried out with an olfactometer with dynamic dilution (ODILE™) from Odotech (Montréal – Québec– Canada).

2.2 Generation of gas test atmosphere

Unless otherwise specified, H_2S gas concentration has been generated using a permeation device VE3M (Environnement SA, Poissy - France) doted of a certified permeation tube Dynacal® from VICI Metronics (Poulsbo, WA - USA).

2.3 Sensors (Cairclip)

The miniature detectors presented in this study (Figure 1a) are based on amperometric technology.

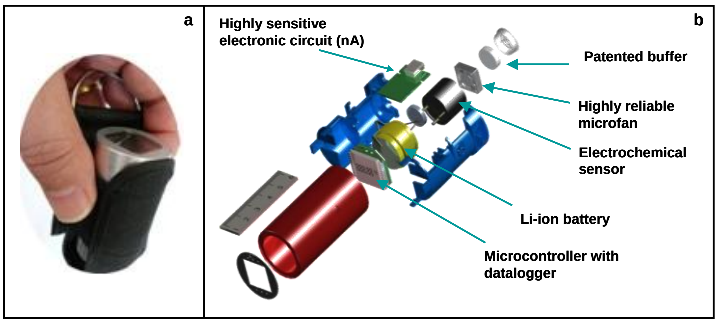

Figure 1: a) Photography of a sensor and b) schematic representation of its main components

With the aim to maintain a constant air flow through the sensor, they have been doted of a dynamic air sampler (microfan). Associated with a patented buffer, a highly sensitive electronic circuit and a microcontroller, they are able to provide low level accurate representative measurements (*Figure 1b)*.

3. Results and discussion

3.1 Cairclips analytical performances

Before performing field measurement campaigns, sensors have been characterized in laboratory with an accurate permeation device doted of a certified H_2S permeation tube. As shown in Figure 3 a stable and reliable signal was obtained when sensors were exposed to dynamic hydrogen sulphide concentrations.

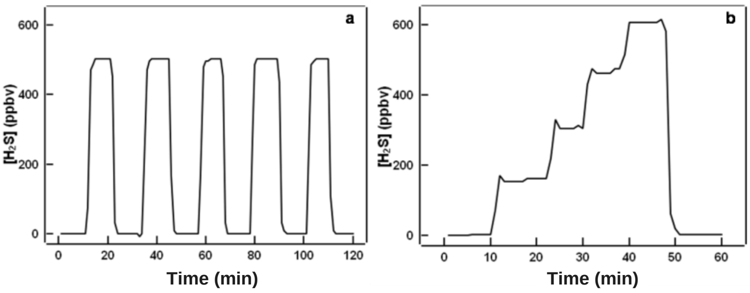

Figure 2: Graphic representation of the signal of a sensor exposed to a concentration of H_2S of a) 500 ppbv, b) 0, 150, 300, 450 and 600 ppbv. Gas generation has been performed with a permeation device VE3M.

A detection limit of 6±2 ppbv has been reached with an excellent repeatability illustrated by a relative standard deviation of only 1 % at 50% of the range (Table 1). Moreover, considering 5 successive exposures of 5 min at a concentration level of 500 ppbv, a variation of the signal of only 1% was observed demonstrating the excellent reproducibility of measurements.

Table 1: Analytical performances of sensors

Range (ppbv)	Detection limit (ppbv)	Zero repeatability (ppbv)[1]	Repeatability at 50% of the range (%)[1]	Reproducibility at 50% of the range (%)[1]
0 - 1000	6	±2	1	1

[1]n = 5

In their USB version, Cairclips are able to perform continuous measurements for 36 hours minimum without needing any time of charge; whereas associated to a long-term battery and a solar panel, the expected life of this device is 1 year without requiring any calibration step.
As all detectors, the signal of Cairclips can be biased in presence of interfering gases. Reduced sulphur compounds can react but it is mainly species of the class of mercaptans, otherwise highly odorous (few ppb), that are generally encountered. It is worthy to note that in the field of H_2S monitoring, these compounds are very often, that is not to say always, problematic when the analytical method does not include a separating system.

3.2 Field analysis

Beforehand the deployment of sensors on field, Cairclips have been calibrated in laboratory with the permeation device. This calibration has been then validated by comparing signals obtained with 5 cairclips to measurements performed with a GC-FPD (Figure 3).

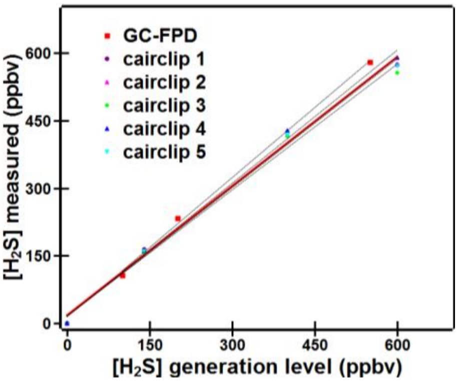

Figure 3: Comparison of signals measured with 5 Cairclips for a H_2S concentration of 0, 140, 400 and, 600 ppbv and the measurements performed with the GC-FPD exposed to 0, 100, 200 and 550 ppbv of H_2S. Others parameters as Figure 2.

Considering the sensitivity of the sensors, a RSD of only 2 % was obtained, demonstration of their excellent reproducibility. Moreover, when the sensitivity of the GC-FPD is compared to the average sensitivity of cairclips, a difference of only 9 % was observed. These results have permitted to validate the calibration of the sensors.
Because of its size and its mechanism, the GC-FPD cannot be transferred on site, especially under severe conditions. A CTRS has thus been transported instead of the GC-PFD and employed as the comparison/reference method in parallel of the Cairclips. Prior to field campaign, the signal of the CTRS has been compared to the one of the chromatograph (Figure 4).

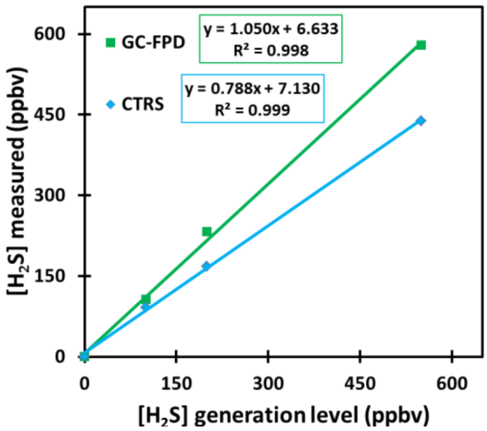

Figure 4: Comparison of signals measured with the GC-FPD and the CTRS exposed to 0, 100, 200 and 550 ppbv of H_2S. Others parameters as Figure 2.

It is worthy to note that contrarily to the comparison Cairclips/GC-FPD, there was a divergence between the CTRS and the GC-FPD. This difference resulted from a drift of the sensitivity of the analyser which did not affect its linearity.
CTRS has been then successively positioned on different places of a WWTP of the south of France conjointly to 2 Cairclips. Results are presented Figure 5.

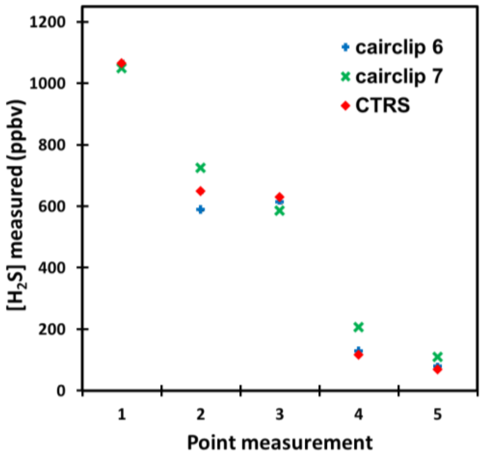

Figure 5: Comparison of field analyses performed with 2 Cairclips of the network and the CTRS

Measurements performed with the Cairclips are in agreement with data provided by the CTRS. These excellent results have thus permitted to validate Cairclip technology, under real condition, for the monitoring of a relatively wide range of H_2S. It is also interesting to note that differences observed in laboratory have not occurred on field. That could be due to the presence of other reduced sulphur compounds that have not the same response either if they are measured with the Cairclips or with the CTRS.

In order to increase our knowledge of these new devices, we thought that it could be interesting to expose Cairclips to variable quantities of H_2S generated by an olfactometer which is a reference apparatus in the field of odours pollutions.
The results are presented Figure 6.

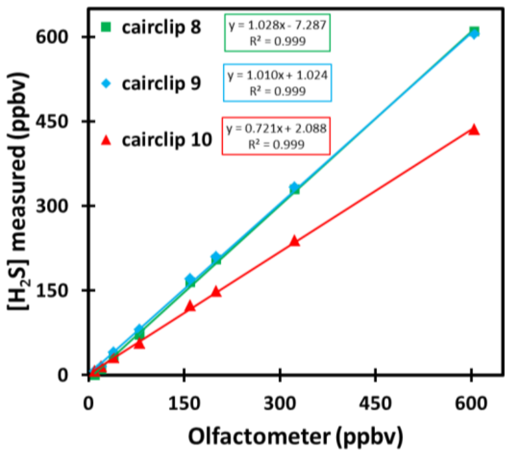

Figure 6: Comparison of signals measured with 3 different Cairclips exposed to increasing quantities of H_2S (0 to 605 ppbv) generated by an olfactometer.

2 of the 3 sensors have behaved as expected with a correlation coefficient of 0.999 and a sensitivity of 1.028 and 1.010 instead of 1.000 attesting to the quality of measurements performed with the cairclips. Regarding the difference observed with the 3rd cairclips, it has been found that it was only due to a calibration coefficient underestimated.

4. Conclusion

In this study, the potential of cairclips for the monitoring of low concentration levels of H_2S has been demonstrated. It has been shown that these sensors are able to detect hydrogen sulphide at the low ppbv level (6 ppbv). Moreover, the analyses performed in a WWTP in the south of France have confirmed the reliability of cairclips under real conditions.

These results let us envisage a lot of applications such as the management of industrial processes in function of gas emissions with the assistance of cairclips. The deployment in waste water treatment plants, composting facilities or livestock buildings of H_2S sensors, and of the recently developed NH_3 sensor, could permit to enhance the knowledge of processes in order to optimize them. Moreover, results obtained during the exposition of cairclips to H_2S generated with an olfactometer have shown their promising potential as complementary tools to studies that can be performed by smell jury.

References

Bokowa A.H., 2010, The review of the odour legislation, Chemical Engineering Transactions, 23, 31-36, DOI: 10.3303/CET1023006.

Hudon G., Guy C., Hermia J., 2000, Measurement of Odor Intensity by an Electronic Nose, J. Air Waste Manage. Assoc. 50, 1750-1758.

Isaac-Ho Tin Noe I., Siino F., Bara C., Urvoy Y., Haaser C., Tripathi A., Ait Hamou L., Mailliard T., 2010, Tool for Predicting and Monitoring the Impact of Wastewater Treatment Plants on Odour, Chemical Engineering Transactions, 23, 267-272, DOI: 10.3303/CET1023045.

Llavador-Colomer F., Espinos-Morato H., Campos-Candel A., Mantilla-Iglesias E., 2010, Estimation of Hydrogen Sulphide Emissions at Several Wastewater Treatment Plants Through Experimental Measurements by Using Passive Samplers, Chemical Engineering Transactions, 23, 213-218, DOI: 10.3303/CET1023036.

Pereira-Rodrigues N., Guillot J.M., Fanlo J.L., Renner C., Aubert B., 2010, Miniature and Low-cost Devices for the Precise and Reliable Monitoring of Low Concentrations of H_2S in Changing Environments, Chemical Engineering Transactions, 23, 237-242, DOI: 10.3303/CET1023040.

The French Republic, 2010. Environmental legislation (in French), Article 220-1.

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, 6, 1-33.