Comparison "Low Cost Chemical Sensors – Analytical Instruments" for Odour Monitoring in a Municipal Waste Plant

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The gas sensing performances of low cost commercial chemical sensors are compared to the ones of standardized chemical analysers. Real time measurements are performed on the field of three municipal solid waste plants (MSW). Long-term campaigns of several months have been organised during the period 2010-2015. The sensors and the reference analysers have worked simultaneously. The selected sensors are commercial metal oxide semiconductor gas sensors (MOx, Figaro). The sensors-array devices are developed at the ULg laboratory (SAM). Analysers are certified and operated by the official Wallonia public scientific institute (ISSeP). In addition to odour, other target compounds are considered: methane, ammonia, hydrogen sulfide, but also NMHC as limonene, pinene and BTEX The laboratory has a long experience in using chemical sensors for odour in-field measurements, especially for landfills and composting plants. The aim of this study is to evaluate the performances of chemo-resistors array for continuous monitoring of compounds typical of municipal wastes in comparison to reference analysers. It highlights weaknesses and strengths of the two kinds of devices. The obtained results are considered for odour event detection as well as for chemical compound quantification and are discussed to evaluate the efficiency of metal oxide sensors for a low cost gas emissions assessment.

1. Introduction

Since 1995, the ULg SAM laboratory developed and tested low cost chemical sensors arrays for the monitoring of environmental odours in the field (Romain et al. 1997). Our experience shows that, among the chemical sensors, chemo-resistors sensors have interesting properties for our in-field applications and when they have to operate in harsh conditions (Romain et al. 2002). Of course, they are far from being perfect and several limitations (stability, response repeatability, environmental conditions influence, cross-sensitivity, recovery time, LOD…), discussed in several papers, impede their commercial success in the environmental sector in particular for air pollution measurements (Masson et al. 2015; Spinelle et al. 2015). Additionally, today they are confronted to emergent techniques such IMS (ion mobility spectrometer) which seems to be highly efficient for air pollution.

Nevertheless, their low cost is a real advantage for multi-point measurements and development of monitoring networks with high spatial and temporal resolution. Moreover, their cross-sensitivities, typically a drawback for single pollutant sensing, is an advantage for measurement of complex mixtures as malodours. Especially for odour monitoring, a recent Netherland guidance (NTA 9055:2012) gives credibility to sensors-array (usually called e-nose). Stimulated by this first national regulation, a recent European committee is working on a new European standard related to "continuous instrumental odorant monitoring in air". At the same time, the EEA (European Environmental Agency) wants to improve the spatial resolution of measurements for air quality control. Low cost sensors are good candidates for this application in particular for assessment of urban air to give, in real time, air quality information to the people living in cities. For that, metrology tests are recommended in order to compare the low cost sensors with the usual reference analysers (Spinelle et al.

2015). Recently, in October 2014, a 1st Air Quality Joint-Exercise Intercomparison "low cost sensor versus analyser", initiated by the EuNetAir Cost action, was performed in Portugal (Aveiro).

At ULg, in 2010, with the collaboration of the official Wallonia public scientific institute (ISSeP), a long-term study has started in order to compare reference analysers with low cost chemical sensors. The first investigation was performed in municipal waste plants with commercial metal oxide semiconductor gas sensors (MOx, Figaro). The sensors and the reference analysers worked simultaneously for real time measurements. The sensors-array devices are developed at the ULg laboratory (SAM). Analysers are certified and operated by the official wallonia public scientific institute. In addition to the malodours, target compounds are considered. In this paper some results are discussed to evaluate the weaknesses and the strengths of the two technologies.

2. Material and methods

2.1 Field campaigns

In 1998, the Walloon Ministry of Environment decided to organise the monitoring of landfills. The Wallonia Public Scientific Institute (ISSeP) leads this project and the ULg laboratory performs the malodours assessment. Three on the 12 municipal solid waste landfills (MSW-1 to 3) have been selected to start an intercomparison study "sensors-analysers". Long-term campaigns of several months have been organised during the period 2010-2015. The sensors and the reference analysers have worked simultaneously.

The MSW-1 is located at Cour au Bois (coordinates: N50°41' and E4°17'). Two mobile ISSeP laboratories equipped with CH_4, H_2S and NH_3 analysers were installed at the entrance of the site and close to the exploitation cell. The sensors device was installed in each two mobile laboratories (called station) and used the same sampling tubes as for the analysers.

On the MSW-2, located at Habay (coordinates: N49°42' and E5°38'), a network of 5 lab-made sensors devices (called FIDOR) is operational since 2009. This FIDOR installation is described by Nicolas et al, 2012. For the intercomparison, two mobile laboratories from ISSeP equipped with CH_4, H_2S and NH_3, BTEX, limonene and pinene analysers are used. They were installed closer as possible to the two FIDOR devices taking into account the prevailing wind. The locations are shown on the Figure 1.

Figure 1. Location of the sensor devices and the analysers for MSW-2

The wind direction was measured with metrological stations installed on each mobile laboratories and FIDOR. Due to the distinct position of the analysers and the sensors, the data treatment was like a puzzle. Indeed, local effects of the wind disturbed air movement around the sampling probes and the measurements were not comparable. Unfortunately few data of this campaign were interpretable.

The campaign on the MSW-3, located at Monceau-sur-Sambre (coordinates: N50°46' and 4°27') has been carried out during 6 months (2010-2011). Two FID analysers were already running on the landfill before this study. Odour complaints were collected to find out relationships between complaints and instruments responses (FID and sensor-array devices).

2.2 Dynamic olfactometry

Among the different sensorial approaches (Romain 2013), dynamic olfactometry according the EN13725 is considered for this study. Dynamic olfactometry is a sensorial method that determines the odour concentration of an odorous air sample using selected panellists. Odour concentration is expressed in European odour unit per cubic metre ($ou_E/m3$) and represents the number of dilutions with neutral air that is necessary to bring the

concentration of the sample to its odour perception threshold concentration. The analysis was performed using an Odile olfactometer (Odotech, Canada) according to EN 13725:2003 at the laboratory of the University of Liége. The different dilutions of the odour were presented to a panel of 6 trained panellists by a decreasing step sequence in geometric series of factor 1.58. Odour gas is collected in a polymer bag (Nalophan) placed in a sealed-barrel maintained under negative pressure by a vacuum pump. The odours are analysed within 08 hours after the sampling.

2.3 Sensors array and analyzers

All the used sensors-array devices have the same building scheme (Figure 2). The sensors are placed inside a cylindrical chamber made of PTFE and stainless steel. The sensor volume chamber is around 200 ml, may contain up to seven sensors and include a temperature probe and a heater to maintain internal temperature stable (50°C). Relative humidity is also recorded. The chamber inlet and outlet are respectively centered on the inferior and superior sides of the cylinder-forming size, where sensors are forming a circle perpendicular to the gas flow. An adjustable flow pump is placed after the sensor chamber and is regulated to a flow of 250 mL min^{-1}. For continuous monitoring, direct air sampling is preferred to cycling measurements with odorless reference air. The array is composed of 6 metal oxide semiconductor gas sensors (Figaro inc.,Japan) differing in selectivity and sensitivity. For this work, the solid state sensors have been selected for their cross-sensitivities and their commercial recommended applications (TGS822, TGS2620, TGS2180, TGS842, TGS2610, TGS880).The configuration is modular in function of the application (the system is able to host various types of sensors i.e. UST, SGX sensors and additional board for IR sensors and electrochemical cells). Specific software, developed with Labwindows/CVI 2012 (NI instrument, USA), controls the hardware and allows the acquisition of the sensor signals. Sensor conductance is measured every 10 s, averaged on 1minute and recorded in a local memory. The data are either processed online or downloaded for off-line processing (usb external connections).

Mobiles laboratories are equipped with various reference analysers (FID for CH_4, GC-PID for limonene, pinene and BTEX with specific adsorption, chemiluminescence for NH_3 and UV fluorescence for H_2S) regularly calibrated in accordance to the European Air quality directive. The acquisition time is either 10 sec or 30 minutes for NMVOC. The analysers' responses are directly recorded either in ppm or in µg/m³. The air sampling probe is at 2.8 m from the ground.

Figure 2: illustration of the sensors-array device (left) and of the mobile laboratory-installed in MSW-1- (right)

The data sets are analysed with statistical methods (Statistica®, Matlab®, R®).

3. Results and discussions

3.1 Field calibration: Sensor signals-Chemical concentrations

Traditionally, sensors calibration is performed in the laboratory in controlled conditions with certified gases. For sensors with cross-sensitives such as the chemo-resistors, the calibration curve found in the lab gives bad results when applied in in-field conditions. The complexity of the compounds mixture encountered in ambient air as well as the influence of meteorological conditions explain this unsuccessful results. Another approach could be to use external reference analysers for field calibration of the sensors in their real conditions of operation. In this work, one of the goals was to check if there is a trend, if possible linear, between the sensors conductance and the chemical concentration given by the analysers. Examples of such relationships (data from MSW-1) are shown on figure.3.a and 3.b.
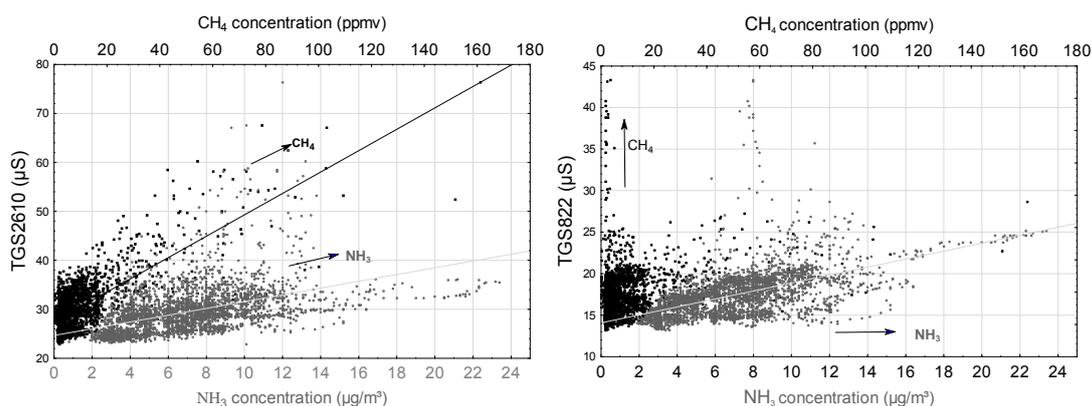
Figure 3. Examples of field calibration of "TGS 2610-TGS 822" with NH₃ and CH₄ (MSW-1, 4weeks)
TGS2610 (µS) = 27,45 + 0,30* CH4(ppm) (r² = 0,50); TGS2610 (µS) = 24,66 + 0,69* NH3 (µg/m³) (r² = 0,22)
TGS822 (µS) = 17,04 + 0,05* CH4(ppm) ; (r² = 0,04); TGS822 (µS) = 14,08 + 0,48* NH3 (µg/m³) ; (r² = 0,29)
(The linear calibration functions are here only given for the interpretation and not for quantification. For quantification, validation and uncertainties calculations would be mandatory)

Even with high data dispersion, a rather good correlation is obtained for TGS2610/NH₃ and TGS2610/CH₄ with a better result for CH₄. For TGS822, the relationship with CH₄ is bad and the higher sensor responses (above 30 µS) are not explained by CH₄. Unfortunately, the trends are not always so clear. Often, it looks more like a scattering plot. Using sensors with broad-sensitivity restrains inevitably a perfect quantification of single pollutant in complex air. However, sensitivities differences are highlighted and those cross-sensitivities have to be interpreted as beneficial for measurement of complex ambient air using sensor arrays. In that case, MLR or PLS models could be developed.

3.2 Correlation between target compounds

The chemical concentrations given by the reference analyzers are compared for each location and for each target compound. A simple linear regression is applied to highlight potential relationships between the target compounds. The results are rather surprising. For instance, for the MSW-1 landfill and the two locations there are no linear correlations between CH₄, NH₃, H₂S (Table 1 and Figure 4). Methane is usually considered as a tracer compound but the results point out that it can explain only a minority of the gas emissions and odour events (Table 1 and Figure 4).

Dataset : MSW1-station1- 4 weeks 3447 data for each variable	Mean	Std	R²		
			CH₄ ppm	NH₃ µg/m³	H₂S µg/m³
CH₄ (ppm)	2.9	4.9	1	0.03	0.06
NH₃ (µg/m³)	6.9	3,1	/	1	0.1
H₂S (µg/m³)	2	0.7	/	/	1
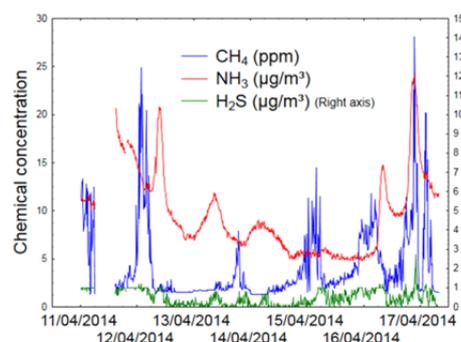
Table 1 and Figure 4: illustration of relationships between CH₄, NH₃, H₂S

For the MSW-2, the results are similar with the logical exception of the pair Benzene/Toluene for which R^2 is equal to 0.86.

These observations confirm that the measurement of a single key compound is not sufficient for real time assessment of landfill emissions. For the detection of all the events, several analyzers are needed and it involves a costly monitoring. Another solution could be using a sensing device with broad sensitivities. If the aim is not to accurately quantify single compounds, low cost sensors-array could be an interesting alternative.

3.3 Event detection

Dynamic plots of sensors response and compounds concentration show that an array is able to detect the same events than the different analysers (Figure 5). Moreover, the array detects additional true events not explained by analysers but by the presence of pollutants not measured by them. The sensors response time

doesn't seem to be a problem but the detection limit of the sensors is a clear limitation and should be improved by the producers. For instance, for one of the studies, the sensors were not responsive to NH_3 below 9 µg/m³ and to CH_4 below 10 ppmv. The danger is to generate false negatives information to the operator. Moreover, an event detection algorithm should also consider humidity and probably O_3 variations. Another remark is that the recovery time of the sensors is longer than the analysers' one and can, in some cases, induce the loss of emission events.
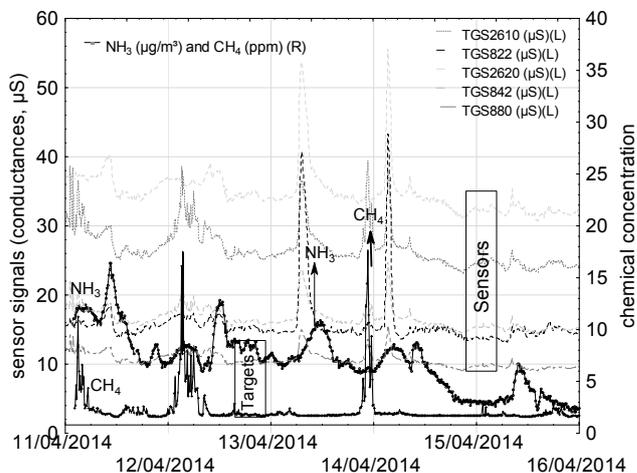

Figure 5: Events detection with sensors and validation for NH_3 and CH_4 (730 data)

3.3 Odour monitoring

After calibration of sensors-array devices with odour concentration measured by dynamic olfactometry (model developed by PLS) and/or with a recognition model with validated odour-non odour data set (e.g. by calculation of the Mahalanobis distance from the odourless class), an odour concentration indicator is generated (Nicolas et al. 2012). Dynamic measurement of this odour indicator (resulting of the integration of all the sensors signals) gives powerful information on the "global" emission of the landfill, especially events generating odours. As example, Figure 6 presents the odour evolution in parallel with the target compounds. The correlation coefficients between the odour indicator and the chemical concentration are surprisingly good (0.87 for H_2S and 0.92 for CH_4, odourless compound but often considered as a biogas marker). In this example, the correlation is below 0.1 for the other pollutants. For MSW-2, the R^2 is equal to 0.30 for H_2S, 0.30 for CH_4 and 0.59 for NH_3. These results are explained by the locations of the station and by the difference in the landfills process.
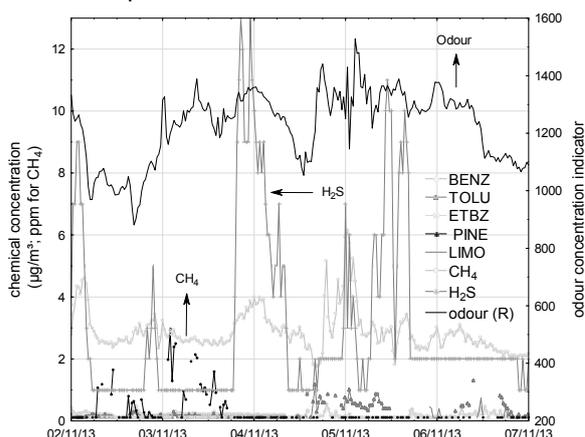

Figure 6: Time series of odour and chemical concentration (750 data, MSW-2)

In MSW-3, complaints have been collected. During the period of the study, 17 complaints among 28 were validated. They have been compared to the FID measurements and to the odour concentration given by the sensor-array device, in a range of time of 2 hours before and after the complaint. The devices were able to predict 11 complaints on 17 -but false positive were also observed- while the FID do not detect the incoming complaints.

4. Conclusions

Several issues are pointed out and can motivate to go ahead with low cost sensors for environmental monitoring. For event detection and risk assessment, sensors-arrays could probably replace costly analysers even if the measurement uncertainty is higher. Moreover, one sensor device gives more apparent pollution events (and malfunctioning process) than several analysers together. For accurate measurements of single pollutants concentration, analysers are definitively preferred considering the current sensors performances. Odour assessment should take the benefit of the cross-sensitivities of some sensors (for instance metal oxides, TGS) –comparisons with the chemical concentration given by the analysers demonstrated that monitoring of some key compounds is not enough to detect all the odour events-. An additional comment on the use of sensor-array device called e-nose: odour concentration values given by commercial e-nose must be considered as an indication more than an accurate value expressed in ou/m³. Major concerns are to identify what we are allowed to do with sensors ("what") and to define which features -with their accuracy- are authorized to be given to the final users ("how").

Reference

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