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Monitoring of Environmental Odors in a Waste Water Treatment Plant and in a Rubbish Dump with a QMB based Gas Sensor Array

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The increasing of complaints about odor emissions near industrial areas and the consequent necessity of methods solving olfactive injuries quarrels, has stimulated the interest in odor measurements techniques.
Environmental monitoring present a series of requirements to be fulfilled such as the reduction of the time required to complete the test, reproducible measurements, real time monitoring.

In this paper we illustrate some property of an electronic nose based on an array Quartz Micro Balances (QMB) chemically sensitized by different types of Metalloporphyrins.

This instrument has been used to monitor the olfactive impact in an industrial area including a wastewater treatment plant, a rubbish dump and a small town. This complex scenario gave the opportunity to evaluate the interactions of many different odor sources in a limited area.

The measurements performed with the QMB array included air, sludge and liquid wastes, and they have been complemented by Gas-chromatographic analysis. The results provided useful insights to model and identify odor sources in order to achieve functional maps for odor tracking in limited areas.

Introduction

Complexity of Environmental monitoring problems is mainly due to different sources of pollution (industrial district, rubbish dump, waste water treatment plant), and to the different targets of monitoring campaigns. Actually there are two main objectives in an environmental air quality monitoring of an area including one of the three citedpolluting elements: to detect the presence of specific volatile compounds and their quantification (Pollution Monitoring), and to monitor the presence of olfactive nuisance due to plants or industries malfunctioning (Olfactive Impact Monitoring).

By the pollution monitoring point of view, although the numerous instrumental controls available to reduce the emission of polluting compounds such as CH_4, CO_2, H_2S, the problem of the contamination monitoring is of primary importance, because of the necessity of more precise systems able to keep the emission concentrations under the security thresholds (Bourgeois W. et al., 2001). At present there are many inadequacies associated with the most common methods used in environmental monitoring. For example, in a waste water treatment plant, a number of techniques are in particular devoted to the measurement of biodegradable organic matter by the 5-day biochemical oxygen demand test (Stuetz R.M. et al., 1999). There is a list of problems related to these techniques: the time required to complete the test (5 days), the difficulty in achieving reproducible measurements, the lack of real time monitoring and control of sewage treatment works, the requirement of constant contact with the wastewater (resulting in instrument fouling, requiring frequent cleaning and re-calibration of the monitoring system). These problems can be summarized as the necessity of a reproducible and non-invasive devices. There is a great quantity of alternative techniques and technologies available for monitoring changes in organic load in wastewater. Biosensors, although very sensitive and selective, have short lifetimes, from a few days to a few months, which limits their application to continuous on-line monitoring. Optical sensors present the advantage of rapidity, versatility, low running-cost, absence of chemicals and limited or absence of sample handling, but they also introduce problems like biofouling of the probe tips, calibration stability and selectivity. The electronic nose, (e-nose) being in principle non-invasive and versatile, has a great potential for real-time and on-line monitoring of wastewater and air quality. Actually air quality has been the primary target of e-nose research projects in environmental monitoring (Keller P.E., 1994; Mouche C., 1999). Indeed, although in most cases annoying atmospheric emissions do not menace public health, they do greatly reduce the quality of life (Schiffman S.S., 1995).

Current methods uses to evaluate odor intensity exploiting the reactions of expert panellists. Sometimes H_2S concentration is used as a stimulant to determine odor strength. More widely used is the evaluation of threshold odor numbers (TON), defined as the number of dilutions at which 50% of panellists can detect no odor. Some experiences in odor environmental monitoring have shown there is not a clear relationship between TON and the concentration of H_2S. These differences could originate from the fact that different sewage receive strong industrial component in their flow and this may account for differences in H_2S emission rates, so H_2S may be an unsuitable surrogate for the determination of odor concentrations. Moreover, methods used for TON determination are time consuming, labour intensive, expensive and subject to large variation between panellists and laboratories.

Another technique for odour impact evaluation is olfactometry: it consists in the evaluation of the olfactive annoyance (in this application) of a mixture by a jury of selected persons (panellists). The olfatcometric analysis, on the contrary of the chemical one, does not provide any identification of substances, but the odor units of the gaseous mixture. This method quantifies the olfactive impact translating this concept from the subjective sensation into an objective number. Electronic nose performs a similar task with a difference between them about the objectivity of the assessors. Indeed, while chemical sensors directly produce an array of number, panellists give an answer that has to be translated in numbers. This translation is

usually done considering the number of dilutions necessary to reach the limit of perception of the panellists, this number is the odor unit for the volume (OU/m3).
The criterion reported in the normative law for the panellists recruitment is based on their sensitivity to normal-butanol. Considering that the mean concentration value of this substances for human is 40 ppb (123 μg/m3), the sensitivity to the normal-butanol of a panellist should be in the range 20÷80 ppb (62÷246 μg/m3). The used unit measures are:1 EROM (European Reference Odour Mass) corresponding to 123 μg/m3 of normalbutanol. 1 OUE (European Odorimetric Unit) consisting in 1 EROM evaporated in 1 m3 of neutral gas in standard conditions.

Many experiments have been performed in this field with different electronic noses and an equally number of different tasks.

Baby et al. (Baby R.E. et al., 2000) used the hybrid technology MOSES II e-nose to measure contaminating residues of insecticides and products from leather manufacture that are often offloaded in into streams and rivers. Dewettinck et al (Dewettinck T. et al., 2001) employed an e-nose consisting of 12 metal-oxide sensors to monitor volatile compounds in the effluents of a domestic wastewater treatment plant. In another study by the same group. Bourgeois and Stuetz (Bourgeois W. and Stuetz R.M., 2000) reported the use of a 12 polypirrole conducting polymer sensors array to analyze wastewater sampled sparged with N_2 gas in a temperature-controlled flow-cell. They also examined the use of a real-time sensors and array system for monitoring global organic parameters such as biochemical oxygen demand and total organic carbon.

Gostelow et al. (Gostelow P. et al., 2001) reviewed various sensory, analytical and e-nose methods for monitoring sewage facility emissions. Stuetz et al. (Stuetz R.M. et al., 1998) employed a Neotronics NOSE to investigate the same matter considering also the effects of biofilters and the evaluation of Hydrogen sulphide concentrations.
In the monitoring of indoor air quality, Schreiber and Fitzner (Schreiber F.W. and Fitzner K., 1999, 2000) studied the perception of the quality of indoor air by building inhabitants. Delpha et al. (Delpha C. et al. 2000) investigated the use of an e-nose using metal-oxide TGS sensors for the detection of a leaking refrigerant gas (Forane R134a) in an air-conditioned atmosphere. Sarry and Lumbreras (Sarry F. and Lumbreras M., 2000), investigated the detection of carbon dioxide, Forane R134a, or their mixtures by the means of a five tin-dioxide sensors. Ramalho (Ramalho O., 2000) analyzed the characteristics of indoor paints and their effect on perceived indoor air quality.
In the monitoring of odourous emissions from animal production facilities: Hobbs et al. (Hobbs P.J. et al., 2001) correlated e-nose measurements of pig manure odours to those of a human panel. Four of the principle odourous compounds in pig manure were selected for the study.

Willers et al studied the efficiency of biofiltration of mice cages air with QMB based electronic nose (Willers H. et al., 2004).

Different typologies of metal oxides gas have been used to determine both the concentration and the composition of a mixture of gases containing carbon monoxide, ethanol, methane or isobutene (Negri R.M. and Reich S., 2001), to establish the limit of detection of odours sources in the environment (Nicolas J. and Claude A.C., 2004) and recently in an experiment for the continuous monitoring of odor from a composting plant (Sironi S. et al., 2007).

All these studies obtained good results in terms of potentiality of discrimination and in the correlation with the classical methods results, panel test included.

1.Materials and methods

Arrays of non-specific gas sensor supported by an appropriate method for sample handling and delivery and coupled with multivariate data analysis tools, can be oriented to the classification and quantification of chemical clusters of volatile compounds which is similar, in principle, to the natural olfaction system. These instruments are dubbed ‘electronic noses’ and the results obtainable by with this technology can be viewed as a chemical image or chemical portrait of a given combination of volatile compounds.

The electronic nose instrument was used in this experiment. It is the MERLINO (MOBILE ENVIRONMENTAL LIBRA NOSE), the portable version of a series of prototypes designed and fabricated at the University of Rome Tor Vergata (D’Amico A. et al., 1998). It is based on an array of Thickness Shear Mode Resonators (TSMR) coated by molecular films of metalloporphyrins. The current configuration uses eight sensors. It is worth remarking that the reason for the use of metalloporphyrins as the sensing material for artificial olfaction systems comes from the fact that most of the odorous compounds are excellent ligands for metal ions. Therefore, metal-organic complexes are good candidates for odour sensing, and among them metalloporphyrins are perhaps the richest family offering a wide variety of possibilities to change their structure (Di Natale C. et al., 2007). The metalloporphyrins used in this measurements are tetraphenyporphyrins (TPP) functionalized with different metals and endowed with butyloxyl chains to ensure the necessary porosity to the solid state film (Di Natale et al. 2004):. The molecules used for the experiments here illustrated were: Mn Butyloxy TPP, Co Butyloxy TPP, Cr Butyloxy TPP, Cu Butyloxy TPP, Fe Butyloxy TPP, Sn Butyloxy TPP, Zn Butyloxy TPP, Ru Butyloxy TPP.

The measurement consists of a frequency shift, registered respect to a reference value (filtered dry air), of each of the eight sensors as the response to a sample fluxed into the measure chamber.

Two different sampling protocols were used during this measurements campaign: one for the outdoor measurements and the other to collect and measure the wastewater and sludge from plant processes.

To perform outdoor meaurements, we continuously sampled air from outside, moving the e-nose around the industrial district, from the plant to the town. During the pathway inside the monitored area a series of stop at selected points were planned to carry oit some cleaning cycles of the sensors, in order to obtain different reference values to evaluate in the final data elaboration.

In the measurements performed to monitor the treatment processes inside the wastewater treatment plant, four wastewater sources were taken into account and sampled: the inlet of the plant, the output of the grit removal, the homogenizer and the nitrification processes. Moreover some some tests have been executed to monitor the efficiency of dewatering processes, collecting samples from the three parallel dewatering processes (filter press, belt press filter, centrifuge), and from the final output of the entire operation. All these sample of wastewater and sludges were collected in glass vials and measured after 15 minutes at the temperature of 30°C.

Results

Promising results were obtained in the three different scenarios: the first refers to a great Wastewater Treatment Plant, whose dewatering and treatment processes have been monitored, and the industrial district served by this plant, in which the impact on the quality air has been evaluated; the second consists of an industrial site formed by a tannery and its treatment plant; the third considered the effects of a large rubbish dump on the surrounding area.

Wastewater treatment Plant

E-nose Data have been analyzed with the Principal Components Analysis (PCA) and with the Partial Least Square (PLS) techniques. Model illustrates the effectiveness of this instrument for the identification of different odour sources inside an industrial district (see Figure 1) and the possibility to identify and compare the olfactive impact of the different industrial processes taking palce in the area surrounding the plant (see Figure 2). In particular in Figure 1 it is possible to trace on the plane of the first two Principal Components (PCs) the same pathway followed in the series measurements carried out around the industrial district. Moreover, from the same data set, it is possible to distinguish different clusters, grouping the measurements relative to the sampling points closer to an uniform odor source (considering each industrial site as a specific odor source different one to each other).

In Figure 2 we represent with a color scale the intensities calculated adding all the mean df registered for the set of measurements collected for each of the nine selected points inside the area. It is worth remarking that the town and the wastewater treatment plant are the two points with the lowest olfactive intensities, which could certify in some way the correct functioning of the plant. Nonetheless on the basis of collected data it is possible to confirm that odors from the plant are not present inside the town.

Liquids and sludge headspace monitoring for the different treatment phases can give a useful contribution to the evaluation of the efficiency of dewatering processes. Actually, in many plants, different parallel processes are used to obtain the same result, and it is interesting to test the effectiveness of the processes (in this case filter press, belt press filter, centrifuge). The e-nose showed to be able to estimate this efficiency on line and the evaluation of olfactive intensities calculated for the three processes and for the final result (dewatered sludge) confirms the value of the final product of the treatment, ‘less water less odour’, and seems to indicate the filter press process as the most efficient of the three.

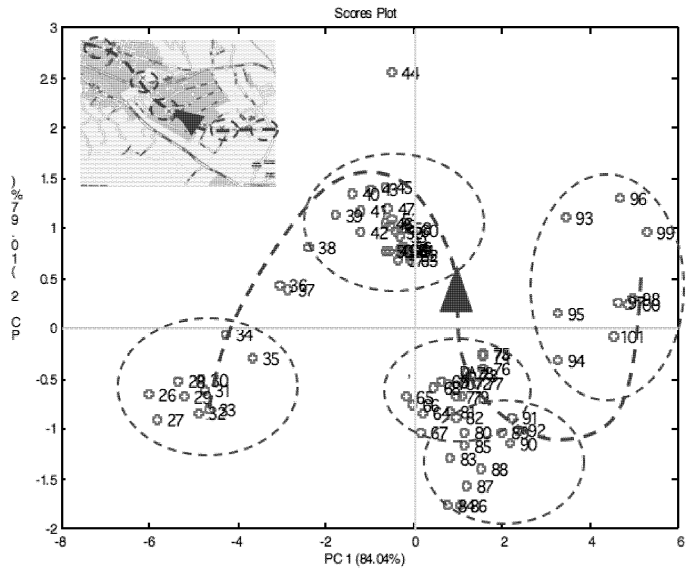

Figure 1.
Characterization of the different odour sources present in an industrial district, obtained tracking on the score plot of the first two PCs of the PCA model built on the e-nose data, the same pathway followed during the measurements (reported in the map on the right corner of the plane).

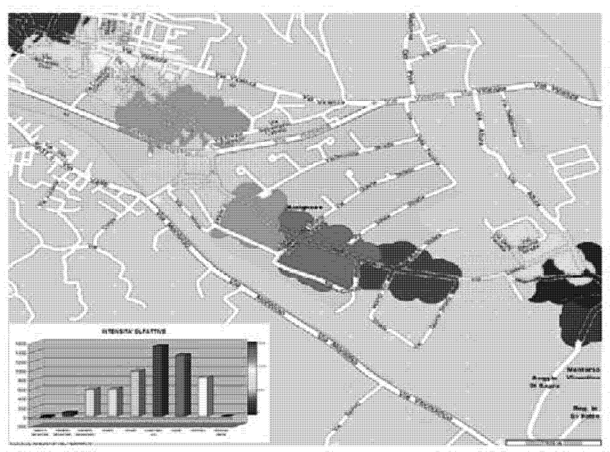

Figure 2.
Olfactive intensity map of the industrial area (lowest intensities in the town and in treatment plant).

Industrial site (tannery and treatment plant)

In this case the activities of an industrial site formed by a tannery and its wastewater treatment plant was monitored. The measurements campaign carried out in this area was very similar to the first one reported, and also in the small town closed to the industrial area it was performed an air quality evaluation. We obtained three main results: the correct discrimination of the odors of the different parts inside the industrial site (tannery and treatment plant) (see Figure 3); the elaboration of a model to analyze e-nose data and detect the possible presence of tannery characteristic odor outside its proper site; and the elaboration of an olfactive intensity pattern of the monitored area.

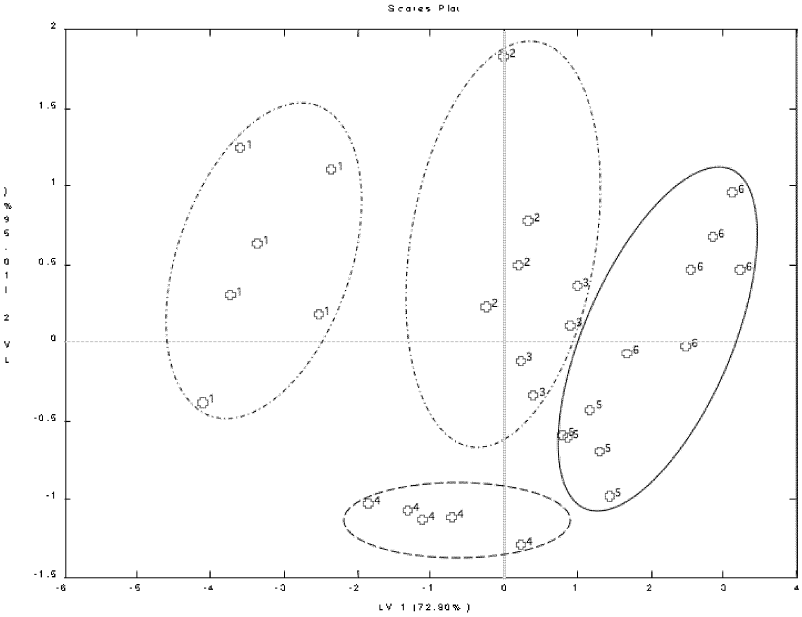

Figure 3. *Characterization of the different odour sources present in an industrial site. Each point in the scoreplot of the first two Latent Variables of the PLS-DA model built on the collected data, is representative of a part of the industry (1: tannery, 2: wastewater treatment processes, 3: sludges treatment processes) of the street in front of the industrial site (4) and of the the town (5, 6).*

Rubbish dump

The monitoring of a large rubbish dump serving a large population was the last site monitored with the electronic nose. In this case, the area under monitoring was too large because of the huge extension of the areas for tip collecting. The e-nose was shown to be able to discriminate the characteristic odors of several different areas (the collecting zone, the incinerator and the built-up area close to the rubbish dump (3km)). Moreover, the measurments by GC-MS of air sampled in this area confirmed a common pattern of VOCs, with some particular concentration of specific compounds characteristic for each of the three areas.

Conclusions

To conclude, we can translate in a question the objectives cited in the introduction: is the electronic nose, with its non-invasive and versatile character, and its potential for real-time and on-line monitoring of wastewater and air quality, a good instrument for environmental monitoring?

We have seen that by means of the models built on e-nose data it is possible to discriminate the presence of a particular odor inside a limited area and to obtain odor characterization and intensity maps. Moreover the experimental set-up has shown a good reproducibility. In particular, the registered patterns are referred to different days with different weather conditions: we can observe the influence of the wind in the magnitude of the intensities, but not in the pattern profile.

This technology is promising in this field of application and further experiments should be conducted in parallel with other instruments to monitor all the useful parameters to understand better what the e-nose really 'smell' and classify.

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