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Interest of the use of electronic nose for field monitoring of odours in the environment

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1. Introduction

The increasing number of complaints related to malodours generated by agricultural, landfills and wastewater treatment facilities give rise to a growing interest in the measurement of olfactive annoyance. Instrument manufacturers have sought to provide suitable environmental monitoring solutions. Because the need for such devices is generally driven by legislation, compliance with the standardised validation of techniques is often mandatory. So, current standard methods remain the references to measure odour annoyance.
Two procedures are generally proposed: either olfactometry, based on the odour assessment by human panels, or chemical analysis by chromatographic techniques. However, neither of them meet the requirements of on-line monitoring for environmental applications.
New emerging technologies such as electronic noses, based on non-specific sensor arrays, may offer objective and on-line instruments for assessing environment odours. But, despite the recent appearance of commercial devices that can be implemented in the field, a number of limitations can be highlighted, both associated with the technology itself and its application to environmental studies.

2. Basis of the chief odour measurement methods

Olfactometry is the scientific measurement of odour concentration utilising a system of sampling and a regulated methodology to European (EN 13 725) [1] and American (ASTM E679-91) [2] standards. The odour concentration of a gaseous sample is determined by presentation to a panel of observers, with known acuity to odour, in varying dilutions. The procedure aims at determining the dilution at which only half the panel can detect the odour. The odour concentration is then the number of dilutions required for the sample to reach this threshold. It is expressed in multiples of one Odour Unit per m^3 (ou/m^3). This analysis technique provides directly comparable data for different odour types. Although this technique gives the right human sense evaluation and is now based on standard methodology, it remains strongly influenced by subjectivity, is time consuming, labour intensive and expensive. Olfactomery laboratories are often remote from the odour source: it is obviously not appropriate for real-time and continuous operation on site.

Alternatively, chemical analysis of the odorous mixture by gas chromatographic techniques (such as GC-MS) provide the accurate concentration of specific compounds in the sample [3]. Some instruments can be used on-site and for continuous assessment, but analytic methods never provide the global olfactive perception, as most environmental odours are complex mixtures of compounds. Moreover, they do not take into account the interactions between different odorants and interfering background substances, which may lead to synergistic or antagonistic effects.

The electronic nose is a more recent technique based upon a fixed array of non specific gas sensors, each of which responding differently to an odorant and the global pattern of responses being characteristic of that odorant [4].
The hearth of the electronic nose is an array of chemical sensors (metal oxide semiconductors, conductive polymers, quartz microbalances, …). When exposed to a gaseous ambience, these

individual sensors provide individual signals. Subsequently a signal pattern is deduced by analysing these signals par suitable statistical and mathematical methods. The diagnosis is thus based on the "fingerprint" of the gas mixture classified with the help of pattern recognition techniques (artificial neural networks, discriminant function analysis, …).
Before applying such instrument on a real atmosphere for on-line recognition of odours in the environment, it must be trained with typical gas mixtures for this environment. After the training, the system is able to identify one of the learned odours by establishing similarities between the actually observed pattern of signals and the ones previously observed.
Hence, the electronic nose is an analytical instrument that can characterise an odour without reference to its chemical composition. The signal provided is the odour, considered as a whole. That makes this method particularly attractive and shows its great potential.

3. State of the art

Reported developments in complex odour analysis are chiefly focused on quality assessment in the food, drink and perfume industries. So far, fewer attempts have been made to characterise and monitor complex odour in the environment. Although original work carried out with laboratory-based systems and more recent field investigations have shown promising results, the number of trials carried out under realistic environmental conditions is relatively limited.
Some papers review the current status of sensor array technology and discuss its potential application to the assessment of olfactive annoyance in the environment by referring to exhaustive literature surveys [5-8].
Early investigations include the analysis of single substances, but some works deal with more complex odours. In a review of odour measurement techniques for sewage treatment works, Gostelow et al. [9] listed some examples of electronic nose application to environmental odour problems. However, the use of electronic noses to monitor water quality in the field remain still a virtually unexplored domain with only few applications reported so far.

4. Typical user needs

In the field of environmental monitoring and more particularly of water quality, the typical needs of the final user of electronic nose require both qualitative (classification) and quantitative (regression) approaches.
On a qualitative point of view, different annoyance odours must be discriminated and the identity of unknown samples must be predicted using previously calibrated learning model.
A range of data processing techniques may be used to analyse sensor array data, but due to the large number of variables (i.e. number of sensors) and samples, pattern recognition techniques (such as multivariate statistics and artificial neural networks) are employed to reduce the dimensionality of the sensor array data. The relationships between the samples can then be compared and correlated using simple scatter plots. The choice of analysis technique is dependent on the amount and nature of information available and the type of information required from the analysis.
Figure 1 could refer to a typical result of a Discriminant Function Analysis (DFA) concerning observations made on a landfill site with an electronic nose. Three types of odour tonalities can be perceived : either the fresh refuse one, or the odour of landfill gas, or the one of the leachates. The scatter plot of the observations in the plane of the two calculated roots shows the clustering into the three expected groups. The model so calibrated by DFA can further be used by the landfill manager to classify a new observation. For example, the emergence of an odour identified as "leachates" can let suspect a problem of the leachate treatment system.

[Image Number 1]
Figure 1 : Possible scatter plot of electronic nose observations on a landfill site in the plane of the two first roots of a discriminant function analysis.

This ability of an electronic nose to rapidly discriminate between slight variations in complex mixtures makes the techniques ideal for on-line process diagnostics and screening across a wide range of application areas.

Quantitative approaches imply regression procedures by correlating sensor responses with some quantitative parameter obtained either by another instrument or by human perception. In some cases, reasonable fits are obtained when the sensor responses are compared with odour concentration resulting from olfactometry measurements. However, this approach is impeded by the subjectivity of the olfactive evaluation, the non-linear relation between the perceived intensity of an odour and its concentration, as well as by adaptation phenomena perception) as a result of extended exposure to that odour [8]. This complicates the elaboration of quantitative models. Moreover, the model so calibrated is often site specific and its validity over long periods of time must be demonstrated before sensor array systems can be used for quantitative analysis.
In the field of water quality, the overall electronic nose output is often compared with classical water characterisation variables, such as volatile suspended solids [10] or global organic parameters (biochemical oxygen demand and total organic carbon) [11]. Studies generally conclude that a number of different wastewater quality relationships could be formulated from the electronic nose analysis of a sewage liquid. In all cases, the principal advantages put forward by the authors to justify an electronic nose with respect to traditional analytical methods are the rapidity of the response and the non-invasive nature of the measurement.
The model obtained by regression could be used as on-line monitoring tool of a process. For example, figure 2 highlights a "stress" episode in a composting process, caused by the absence of aeration of the compost pile. A specific indicator is constructed by relating the sensor signals to the four families of compounds emitted during that "stress" phase (nitrogen compounds, carboxylic acids, ammonia and chlorinated compounds). It is constructed by a canonical correlation analysis. The figure shows the time evolution of that combination of the sensor signals applied to the whole data set obtained by the continuous signal monitoring for 11 days. The root value exhibits a peak during the "stress" period.
Of course such global odour indicator could be calculated for other environmental process, such as waste water treatment and it could be monitored as global process control variable.

[Image Number 2]
Figure 2 : Global odour signal obtained from the response of a sensor array to detect a stress episode of a composting process.

More generally, the purposes of continuous, in situ monitoring of odorous emissions with electronic nose could be :
-to predict the raise of malodour in the background before it becomes an annoyance for the surrounding,
-to use the odour as a process variable, aiming at a better understanding of the odour release and relating this emission to the process phase, or the problem, which caused the emission,
-to control in real time odour abatement techniques, such as the atomisation of neutralising agents.

Simple sensory early warning devices which can detect sudden changes in a process stream present obviously a great interest.

5. Applications related to water quality

The use of electronic noses to monitor water quality in the field may concern the agricultural and industrial effluents allowed to seep into the ground water or to flow into streams or rivers [6]. The electronic nose can be used in these applications by collecting samples of the effluent. Boreholes can also be employed to collect samples to test groundwater contamination.
A very promising area is the detection of hydrophobic and highly volatile organic compounds (VOC's) in water systems [8]. The recent developments in on-line detection of oils and petroleum hydrocarbons [12] have arisen from the recent advances in sensor technology as well as from progresses in computing and pattern recognition.
Studies aim also at the real-time control of wastewater treatment plants [13] or at the quality test of potable water [14].

A specific obstacle when dealing with liquid samples is to generate or collect a headspace gas that can be reliably and safely measured by the sensor array. With parameters such as flow, temperature or suspended solids constantly changing, the major difficulty lies in drawing a headspace sample that is representative of the liquid phase [8].
But several applications concern also the monitoring of the odours emitted in the air from wastewater [9]. Odour abatement and control is indeed a major issue facing municipal sewage treatment facilities.

6. Specific problems for environmental applications

Much of the original works concerning environmental applications has used sensor arrays in laboratory-based conditions. However, in order to understand the effects of environmental parameters on localised odour pollution, it is necessary to translate these laboratory-based experiences into formats that can be applied to making measurements under variable conditions [15]. Effectively, although new sensor materials and designs are continuously being reported, the major limitation of currently available sensors remains their sensitivity to changes in temperature, humidity and flow rate.
The solutions to this obstacle is generally to work under fixed experimental conditions, i.e., to incorporate the effects of variations in ambient temperature and humidity into the design of instruments, through the use the sample pre-treatment systems. That was demonstrated for headspace pre-treatment in on-line wastewater monitoring [13]. However, when considering the practical application of a sensor array, this can make the overall instrument more complex and expensive and can also affect its portability or limit sample throughput.
A second approach is to measure these parameters and calibrate the sensors under varying humidity levels in order to compensate for changes in subsequent data analysis [16]. Yet, the method has still to be validated for real-life environmental applications where pollutants must be analysed rapidly in ever changing background conditions and in the presence of interfering compounds.
Alternatively, the development of a classification model under a wide range of operating and meteorological conditions makes those conditions "neutral" for the odour recognition [17]. It is an effective but sometimes fastidious solution.

Sensor drift is an other serious impairment of chemical sensors. They alter over time and so have poor repeatability since they produce different responses for the same odour. That is particularly troublesome for electronic noses for which the sensor signals can drift during the learning phase, requiring the repeated exposure to the same type of odour.
Consequences of sensor drift on the classification results exclude the possibility of further odour identification [18]. Though drift correction algorithms could be applied for each individual sensor, the usual way to counteract the global drift for a sensor array is to correct the whole pattern, using multivariate methods. First the main direction of the drift is determined in the first components space of a multivariate method, such as PCA. The drift component can then be removed from the sample gas data, correcting thus the final score plot of PCA [19].

Moreover, the combination of multiple sensors, cross-selectivity and pattern recognition analysis make the usual techniques of instrument calibration difficult to apply to electronics noses. As a result of this issue there are, to date, no international standards which directly refer to electronic nose measurement.

An additional problem occurs in cases in which the concentration of volatiles is low, which is often the case in the environment: the limit of detection of the sensors and the limits of recognition of the electronic nose are reached. A possible solution to such problem should be to improve the sample uptake, for example, by pre-concentrating the analytes prior to investigation [20].

Other requirements of field monitoring include low cost, low maintenance, small size, low response time and low power consumption where autonomous, portable instruments are concerned.

7. Trends and future works

Electronic nose technology exhibits several possibilities for environmental monitoring. There is a true potential for sensor array in this area, provided that some conditions were respected. With the technology used so far, it is unrealistic to envisage a universal electronic nose, able to cope with any odour type. Specific data processing and sometimes specific instruments must be designed for each application. In the field of water quality, sewage odour profiles are specific for individual treatment works and for different unit processes within a work. These different sewage odour compositions induce a scatter of the observations, which must be removed prior trying to find relationship with odour concentration determined by other methods [21].

Results to date have mainly been based on the assessment of environmental odours measured near emission sources. This is due to the constraints of using commercial chemical sensors which exhibit a limit of detection often higher than the threshold of smell (generally in the order of 1 ppmv). So, environmental monitoring by electronic nose must be envisaged only in the surroundings of the emission.

Potential applications in odour assessment by electronic noses are numerous, but, before these specific applications can become a reality, a number of challenges still need to be overcome.
Programmes of experimental work should be undertaken to properly assess various characteristics of electronic nose performance, including drift, comparability of sensors before and after replacement, environmental influence, sensitivity and signal to noise ratio.

There aren't so far any possible comparison between different electronic nose results. Even an instrument whose sensors were replaced isn't any more the same as the original one: the learning phase must be started again. In the frame of environmental applications, that particularly exclude the possibility to use the electronic nose to test the compliance with standards.

So, it is necessary to develop calibration procedures and to realize suitable calibration artefacts. Any new "calibration standards" will need to consist of generic mixtures that reflect the gas components typically found in the environment, and which have a significant effect on the various detector responses. It is also essential to validate the quantitative assessment of sensor array responses against other methods, such as olfactometry measurements to confirm comparisons with human perception.

There is therefore a need to develop internationally acceptable methodologies for the harmonization of electronic nose characterisation and performance testing. This requirement can be best met through the development of standardised procedures and protocols that enable quantitative and objective comparisons to be made between different types of instrument. These procedures could then form the basis of future international standards in this area.

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