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E-noses: Actual Limitations and Perspectives for Environmental Odour Analysis

Jean-Michel Guillot

Ecole des Mines d'Alès, LGEI-Odours and VOCs, 6 avenue de Clavières, 30319 Alès cedex, France
jean-michel.guillot@mines-ales.fr

E-nose applications have been developed for last twenty years for both quality monitoring of industrial processes and measurement in the environment for air pollution. In the first case, calibration is quite easy and measurements are compared to a reference fingerprint. For air pollution studies and especially for odour concentration estimation, the relationship between sensor responses and odour is not obvious. This presentation deals with limitation of e-noses linked to sampling location, calibration procedure, external conditions and instability of studied sources in order to integrate all drawbacks that potentially impact the result. E-noses are very useful tools but unfortunately, they cannot be efficient in all conditions and users must know this aspect. Of course, potentialities are linked to technologies such as metallic oxides, conducting polymer, micro-balance, electrochemical sensors…
New technologies are still in development to offer more sensitivity or more selectivity and if actual limitations are strong for environmental analysis, we can imagine a better situation for the future with typically specific monitoring. In order to improve potential use instrumental odour monitoring including sensors or e-noses, a new working group (WG41) started in 2015 in the frame of CEN/TC264 Air Quality. The objective of this group is to propose a new European standard on this topic: Instrumental odour monitoring. The present paper deals with one aspect of this monitoring approach looking at sensor (e-nose) use for environmental analysis and limitations observed for such an application.

1. Introduction

Actually, eight countries are present in the CEN/TC264/WG41 and approximatively 27 experts but this list can be adapted during the standard elaboration process. Referenced experts (January 2016) are listed in Table 1. Except a standard from Netherlands (NTA 9055, 2012), European countries are developing e-noses without a real frame to determine requirements of these monitoring devices. The standard from Netherlands is dedicated to e-nose for nuisance application and also for safety; it will be helpful for European standard elaboration even if the scope will be different.
This paper is focused on environmental measurement and the objective of WG41 is to work on instrumental odour monitoring in ambient air but also indoor air and gas emissions. The scope will also include the monitoring of the odour removal efficiency of end-of-pipe odour treatment processes and methods of: correlating sensor signal based metrics to the presence and attributes of odour; validating the sensor signal based metrics to the presence and attributes of odour. It is important to note that this future European Standard will not applicable to: measurement of odour concentration in ou_E/m^3; monitoring of hedonic tone; direct assessment of odour annoyance; technical design of the odour sensors or the odour measurement system. E-nose measurement is instrumental, and because sensorial measurement of odours by humans is specific and not reproducible, it is logical to concentrate objectives on technical aspects.
Ideally e-noses or sensors for odour measurement must present different categories of specifications. A non-exhaustive list is presented as requirements for this kind of equipment:

a. To be as efficient as possible comparatively to human nose
    - High sensitivity to odorous compounds
    - High selectivity to these compounds
    - Possibility to be trained

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  - Larger measurement range as possible (from threshold to saturation)

b. To be an efficient measuring technique
  - low sensitivity to external parameters such as:
    - Humidity
    - Temperature
    - Other parameter around the device: wind, atmospheric pressure…
  - Stability in operating conditions
  - Stability even if submitted to cycles (Off/On).
  - Repeatability
  - Easy maintenance (including availability of components)
  - Drift correction (if necessary)

c. To be used on large applications (large panel of environments)
  - Easiness of calibration
  - Fast response time
  - Recovery
  - Easiness of manipulation
    - Autonomy (power, data storage…)
    - Portability (low weight and low dimensions…)
    - Robustness

Each line of the previous list can induce a limitation of e-nose use but everything is made to minimize the impact these parameters on output data.

Table 1: European experts for work group (WG41) on Instrumental odour monitoring

Referenced experts by national standardization offices (January.2016)		Country
Ton van Harreveld	(convenor of WG41)	Netherlands
Nicolet Baas	(secretariat)	Netherlands
André van Boheemen		Netherlands
Bianca Milan		Netherlands
Benjamin Bergmans		Belgium
Ilse Bilsen		Belgium
Julien Delva		Belgium
Kurt Haerens		Belgium
Anne-Claude Romain		Belgium
Arne Oxbøl		Denmark
Jacob Mønster		Denmark
Jean-Michel Guillot		France
Mathieu Huet		France
Franz-Bernd Frechen		Germany
Thomas Hübert		Germany
Gerhard Kahr		Germany
Sascha Nehr		Germany
Ivano Battaglia		Italy
Laura Capelli		Italy
Pierluigi Barbieri		Italy
Silvia Rivilli		Italy
Andrea Rossi		Italy
Emanuele Vassallo		Italy
Tiziano Zarra		Italy
Carlos Diaz		Spain
Stuart Lee		UK
John Saffell		UK

But First of all, it must be considered that the response profile could be different as expected. Figure 1 shows an ideal response profile.

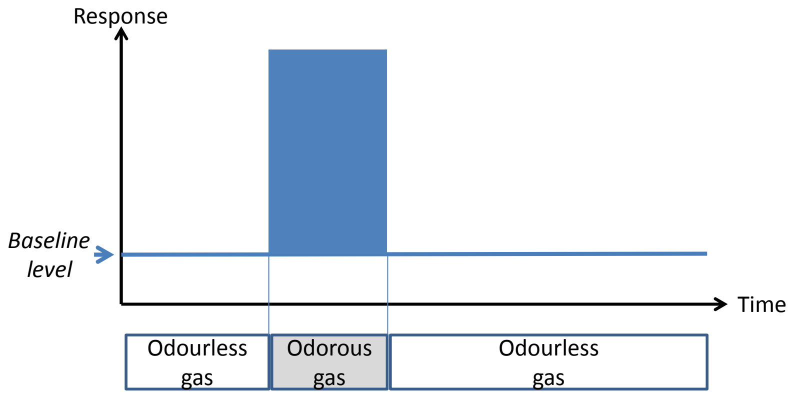

Figure 1: Ideal immediate response profile where the intensity of response is linked to concentration.

It is obvious to see in Figure 1 that even if response time is ideal, the response level (intensity) must have a proportional value with the concentration in a defined range (detection limit, saturation).
The response time is one point and the recovery time is a second one. As shown in Figure 2, a more realistic profile differs a lot from Figure 1 profile. If response time is variable between sensors and technologies, the recovery time is generally more problematic. If the recovery time is low, the sensor is quickly able to detect a new odorous gas exposure with a correct response. If the signal takes time to return to baseline level, a new odorous gas exposure could give a response with high uncertainty. That's the reason why, users have to keep in mind the type of response profile of their analytical device to interpret correctly the output signals.

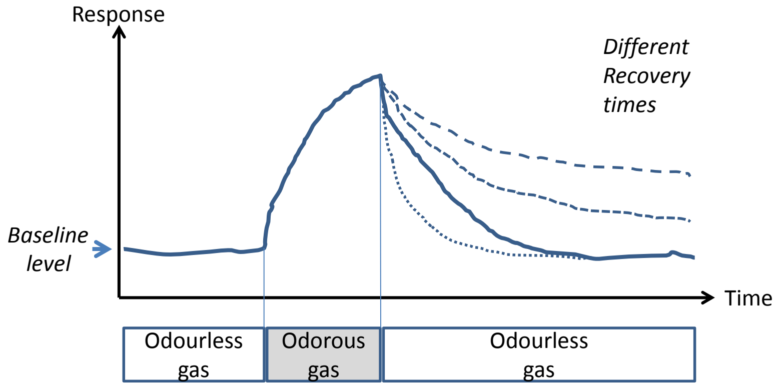

Figure 2: Realistic response profile with different recovery times (adapted from Arshak et al., 2004)

Globally, it can be considered that limitations are mainly due to 3 factors Romain and Nicolas (2010):

- Conditions in analyzed air (typically environmental atmosphere)
- Properties of sensors (nature and type of sensors)
- Signal processing efficiency (data analysis)

All these limitations are described in paragraphs 2, 3 and 4, but if we consider odour and relationship with chemical compounds, the first limitation is absolutely the high difficulty to correlate a signal (generally electric) due to the presence of compounds (odorant or not) and odour perceived by human nose. With rigorous calibration, some examples of acceptable correlation can be found but such a result is obtained when chemical composition is relatively stable in diversity of compounds and when sensors are mainly analyzing concentration variation or composition variation in a defined range of potential mixture evolution. A sensor or an array of sensor cannot give right data for unknown compounds and so, that's why it is necessary to keep in mind this limitation. Correlatively to this aspect, odour unit per cubic meter (OU_E/m^3) is the measurement unit for olfactometry and then for sensorial analysis. After calibration and in some limited cases, the output data (signal) can be changed to this unit but in that case it must cited as equivalent odour unit (eq. OU_E/m^3). A better correspondence between chemical compounds and sensorial perception could be reached with the

development of olfactory sensors. These sensors are made with olfactory receptors, odorant binding proteins and olfactory epithelium for the detection compounds (Shankaran et al., 2012).
Another fundamental thing for environmental odours is the fact that the exposed area can be very large. In that case and even if a relative proximity to sources is preferred to be sure to detect something, it is necessary to increase the number of measurement points. The cost of a complex e-nose limits the use of tenth of devices that's why for air quality measurement; a low-cost sensor approach is also in development (Mead et al, 2013; Pereira-Rodrigues et al., 2010). The objective is to amplify measurement points to cover a large area.

2. Conditions in analyzed air

Sensors are generally sensitive to variations of temperature and humidity but also atmospheric pressure, oxygen proportion… So to obtain the better signal stability, it is possible to limit the effect of these parameters with water vapour elimination and heating to maintain the same temperature of sensors. It is also possible to study the impact and to measure influent factors and then to correct the signal to give the better appropriate response.
An example of chemo-resistive gas sensor (CRGS) impacted by fluctuations in the ambient humidity and temperature is given by Hossein-Babaei and Ghafarinia (2010). In that case, the drift compensation to correct condition impacts was developed. The measured ambient humidity and temperature are the inputs to the system and the contaminant concentration is the output. Then, an artificial neural network was designed and trained to determine the contamination level at different ambient conditions.
Even if a compensation of this influence can be corrected, it is clearly more and more complex if the number of sensors increases and if each sensor presents a different behaviour. The uncertainty has to be verified for each global system to be sure that humidity and temperature variations are enough corrected, in the range of normal use, to give an acceptable response.
After laboratory development, all sensors and e-noses must be tested in real (external) conditions for environmental application. The field tests allow verifying the effectiveness of this electronic nose for the continuous detection of odours in ambient air and its stability to variable atmospheric conditions as shown by Dentoni et al. (2012).

3. Properties of sensors

A lot of sensors are used for gas measurement and some types are selected for odorous compounds. At the beginning of e-noses, conductive sensors were mainly used then piezo-electric sensors were also considered for odorant measurement. A shown in the following, not-classifying and not-limitative list, sensors can be distinguished as:

- Conductive sensors
  - metal-oxide semiconductor (MOS),
  - conductive polymers (CP),
- Piezo electric sensors
  - quartz crystal microbalance (QCM),
  - surface acoustic waves (SAW)
- Other sensors
  - metal- oxide semiconductor field-effect transistor (MOSFET)
  - chemo-resistive gas sensor (CRGS)
  - electrochemical sensors
  - optical sensors
  - biological sensors
  - …

The lack of sensitivity and selectivity is often cited for sensors and e-noses comparatively to human nose (Shankaran et al., 2012). To improve sensitivity and to give selectivity, biological component can be adapted on sensors. For example, a biosensor system composed with an array of five SAW resonators coated with three types of odorant-binding proteins (OBPs) has been developed (Di Pietrantonio et al., 2015). This "bio-electronic nose" showed detection limits at 0.48 ppm and 0.74 ppm for octenol, and carvone respectively. Such detection limits are considered as low and this sensitivity is completed by discrimination between octenol and carvone molecules. So applications could be assessment of food contamination by moulds, or indoor air quality in buildings.

Independently to the sensor type, drift or stability variation is a real drawback for sensor arrays. The variation (drift) is generally a decrease of response over time and to limit such a drawback, several approaches can be discussed:

- The replacement of sensors: It could be acted to replace a sensor after a small decrease of efficiency but in that case, it needs high maintenance on equipment and of course, the cost of such an approach is unacceptable.
- The frequent recalibration: Such an approach needs a lot of time and this repetition is laborious with an impact on cost.
- Manufacturing repeatability.

Of course Drift correction (Padilla et al.,2010) is also a way to limit this drawback, such correction can be linked to signal processing.

4. Signal processing efficiency

Without signal treatment, output data of sensors can be plotted (bar chart…) but the first level of response cannot give enough information about odour discrimination…So output values are mathematically treated. This signal processing includes both feature extraction and pattern recognition techniques, and is mainly based by methodologies or ways as:

- Multivariate data analyses (MDA): principal component analysis (PCA), canonical discriminate analysis (CDA), featured within (FW) and cluster analysis (CA)
- Or Network analyses: artificial neural network (ANN) and radial basis function (RBF)

As the other limitations, signal processing is in development but the improvement is not specific to environmental applications. That’s the reason why, limitations due to other factors i.e. conditions in analyzed air and properties of sensors are more important for environmental applications.
As mentioned by Capelli et al. (2014), future challenges for e-nose environmental monitoring shall concentrate on the adjustment of the instrument for outdoor applications as a priority. One important goal is to produce e-noses able to tolerate the real environmental variability.

5. Conclusions

Sensors and e-noses are still in evolution. New technologies are emerging with more precision that indicates the importance of such equipment for the next future. If quality control can easily use such devices, typically to verify a product quality in an industrial process, the application on environmental odour is less easy. Depending on the application, some drawbacks limit a real efficiency to follow outdoor odorous pollution. These drawbacks can be lack of sensitivity, perturbations with extreme weather conditions and/or other atmospheric pollutants, low number of monitoring points to have a sufficient mapping of the studied area, insufficient correction of drift, low maintenance and of course a combination of some of these non-limitative drawbacks.
The environmental application in ambient air must be therefore well prepared to minimize all potential perturbations and then to invest in an efficient monitoring system. Measurement at the emission is generally less difficult due to more stable conditions (temperature, humidity, known emitted compounds) but these conditions can also be too aggressive for the equipment.
It does not exist measurement equipment applicable for all situations but it is possible to propose adapted solutions in larges cases selecting measurement points (emission or ambient air), their number, and technology of sensors that must be adapted to conditions and able to detect compounds. Of course the solution must integrate the “soft part” with corrections after calibration, drift parameters. This part needs time development and adaptation but is not technically limited comparatively to raw data collection. In addition to these “hard” and “soft” aspects, the cost is the factor that allows a large distribution or not. This cost must include a global overview of the equipment with investment, regular maintenance, replacement of sensors, energy consumption (power mains, battery, and renewable source such as solar panel), signal transmission (wired or wireless communication), data recording and treatment and finally presentation of measurement results. This last point can be limited to the control center of the studied site/area or can include dissemination of information on a website or a mobile application.
On the pure technical part, the emergence of micro-sensors or nano-sensors will probably change the point of view about e-noses. With a real increase of sensitivity and with a high number of nano-sensors on the same device, these new devices will be more similar to human nose. The probable architecture will be composed by

the receptor module (with nano-sensors) and the brain module (signal processing, data recording…). It is easy to imagine replacing the receptor module after a defined period of measurement.
Finally, with a total freedom for future development of monitoring devices, the work of WG41 will be helpful to have a standard on instrumental odour monitoring and their minimum requirements on essential criteria.

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