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Testing Procedure for Performance Evaluation of Electronic Noses for Environmental Odour Monitoring

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Electronic noses capability to simulate human olfaction makes these instruments perfect for direct characterization of odours directly where their presence is lamented. However, the lack of regulation about instrument minimum requirements and standardization limits their widespread diffusion for the determination of the odour impact relevant to a specific industrial activity. This paper aims to propose a testing procedure for verification of electronic nose performance in environmental monitoring. In order to test instrument capability of detecting odour presence, specific tests were defined and carried out to determine instrument lower detection limit towards common environmental odours and the repeatability of responses to a given stimulus.

1. Introduction

Nowadays odours are recognized as air pollutants and in recent years the problem of odour impact has been deeply investigated. Different odour monitoring systems have been developed with the aim of characterizing the odour impact of different industrial activities on the surrounding territories (Capelli et al., 2008, Sironi et al., 2007, Dentoni et al., 2012, Baby et al., 2000). However, although systems capable of reproducing human olfactory systems, commonly named electronic noses represent the most powerful technology for this scope, the absence of standardization has up to now limited their diffusion (Eusebio et al.,2016, Gardner et al., 1996).
In 2016, the European Committee of Normalization (CEN) on Air Quality, the CEN TC/264, has constituted a specific working group WG41 for the definition of a European Standard related to Instrumental Odour Monitoring Systems (IOMS). The group is still working on standardization of performance requirements, and thus on the definition of a suitable experimental procedure for performance verification and validation.
This paper aims to present a methodological approach for testing performance of electronic noses to be applied for environmental odor monitoring at receptors. Given the huge variability of EN systems available on the market, the testing procedure does not concern instrument hardware but focuses only on its performances. This protocol aims to be reproducible in different laboratories and with different instruments, and applicable for monitoring emissions related to different types of industrial activities (waste, water treatment, oil & gas, foundries, etc.).
The research activity presented focuses on the evaluation of instrument performance in detecting odour presence. Specific tests carried out to produce the experimental bases necessary for the definition of the experimental protocol are presented.

2. Definition of the testing procedure

Electronic noses are commonly adopted in the environmental field for the evaluation of the odour impact related to specific industrial activities by means of the continuous monitoring of ambient air. Aspects that should be considered in the assessment of instrument performance in this field, should concern:

- Odour detection, instrument capability of detecting odour presence at different concentrations;
- Odour classification, instrument capability of providing a qualitative odour characterization;

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- Odour quantification, instrument capability of estimating odour concentration by means of a correlation between instrument response and odour concentration.

As already mentioned, this paper aims to propose a methodological approach for the definition of a general testing performance protocol, which can be applicable for different electronic nose technologies involved in the monitoring emissions from various industrial activities.

The instrument capabilities of detecting odours and providing their classification are evaluated through the definition of an experimental protocol. This protocol is structured into different levels, according to the approach proposed by EN 14181:2015, which specifies procedures for establishing quality assurance levels (QAL) for Automated Measuring Systems (AMS) installed on industrial plants for the determination of the flue gas components and other flue gas parameters.

The first two levels of the testing procedure provide the final user with useful information about instrument performance in environmental monitoring by means of specific tests with target compounds representative of common ambient odours. Specific tests allow the evaluation of electronic nose limit of detection, lower detection limit towards those target compounds and repeatability of responses to a given stimulus. These levels are not related to instrument specific applications and therefore raw signals are considered instead of instrument output for performance evaluations.

The third level of the testing procedure is more related to instrument specific application, since it focuses on classification performance evaluation. Thus, the instrument to be tested must be trained for a specific application and its performance is evaluated in terms of classification accuracy, considering the instrument global output. This level of testing specifies methods for instrument evaluation performance on the field during monitoring.

3. Materials and methods

3.1 Electronic noses used for the tests

The electronic nose used for this work is the EOS507c_Ambient, produced by Sacmi s.c. (a detailed description of the instrument design and features is given in Dentoni et al., 2012).

The instrument is equipped with 6 MOS sensors, different in morphology and operating temperature, which respond to VOC presence with electrical resistance variations. The instrument is equipped also with systems for the humidity regulation and "zero air" generation that allows an effective outdoor use, even in the presence of variable weather conditions.

3.2 Target compounds and sample preparation

The first and second level of testing involve the choice of target compounds representative of common emission types in the environmental field to be considered for the evaluation of lower detection limit and response repeatability. These compounds should guarantee reproducibility of the procedure in different laboratories and with different instruments. Target compounds selected and methods for the creation of the gas samples to be given to the electronic nose for tests are reported in Table 1.

Table 1: Details about target compounds and sample preparation method

Compound	Family	Aggregation State	Sample Preparation Method
Acetone	Ketones	Liquid (>99%, Sigma-Aldrich)	Dilution from headspace: 30 mL liquid in 7 L air, stored at 25 °C and 60 % RH for 1 h, then separation of the headspace in another 7 L bag
Dymethildisulfide	Sulphur compounds	Liquid (>99%, Sigma-Aldrich)	
Ethanol	Alcohols	Liquid (>99%, Sigma-Aldrich)	
Limonene	Terpenes	Liquid (~90%, Sigma-Aldrich)	
Ammonia	Nitrogen compounds	Gas (Bottle, certified 19 ppm, Sapio)	Dilution from bottle at 19 ppm
Hydrogen sulphide	Sulphur compounds	Gas (Bottle, certified 649 ppb, Sapio)	Dilution from bottle at 649 ppb

3.3 Experimental protocol

As explained in section 2, the experimental protocol is structured into three different levels, which involve specific tests for the evaluation of the instrument performance in detecting odours and providing a classification.

The experimental activity presented in this article limits to the deep investigation of the first two levels of the procedure, focusing on the evaluation of the instrument Limit Of Detection (LOD) and the Lower Detection Limit (LDL) towards target compounds, and the repeatability of responses to a given stimulus.

Since the first two levels of the protocol are not related to a specific instrument application, instrument responses are processed considering raw signals (i.e. resistance ratios for MOS sensors) and not considering the instrument global output. The resistance ratio $^{R_0}/_R$ is defined as the ratio between the resistance value at time zero R_0 and the resistance value R recorded at the end of the measure, when sensor signal reaches a plateau.

Definition of Limit Of Detection (LOD)

The LOD is the instrument air threshold that represents the neutral condition for environmental monitoring, i.e. the condition where no odour is perceived. It is defined as the sum of the mean value C_m and three times the standard deviation s_r of the responses obtained for a relevant (at least 30) number of ambient air samples, as reported in Eq(1) (Devore, 2011):

$$LOD = C_m + 3 \cdot s_r \qquad (1)$$

The LOD is determined for each sensor and results obtained are compared with signal noise to be sure that they are distinguishable from the instrument background signal.

Determination of Lower Detection Limit (LDL)

The LDL represents the lowest concentration of the target compound at which the instrument is able to detect its presence. For LDL determination, target compounds are presented to the instrument at increasing concentrations (Figure 2). Samples of target compounds, prepared as reported in section 3.2, were analyzed by dynamic olfactometry to determine their odour concentration and define dilution factors to be applied to present to the electronic nose concentrations around the supposed LDL concentration. The values obtained for each sensor are compared with the LOD already calculated to determine the LDL (Figure 3).

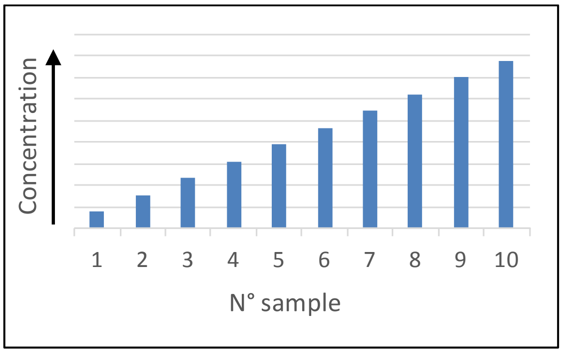

Figure 1: sample concentrations for LDL evaluation

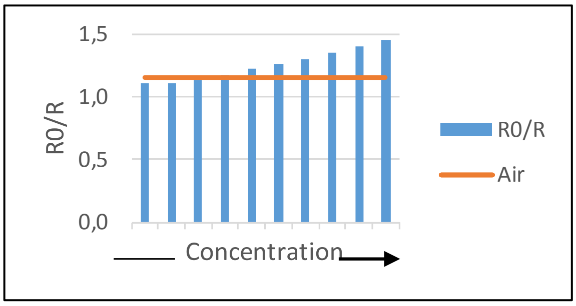

Figure 2: Example of LDL evaluation

If no odour is perceived by the instrument, a sample at higher concentration is presented to the electronic nose for LDL evaluation, while, if the instrument detects odour presence at the beginning of the analysis, the substance training will be stopped and a sample at lower concentration will be analysed in order to provide a more accurate estimation of the LDL.

Determination of repeatability

Repeatability represents the degree of agreement between instrument responses to a given stimulus. It can be estimated considering a repeated series of tests carried out under the same conditions. For this purpose, samples of target compounds at fixed concentration are presented to the instrument (Figure 4).

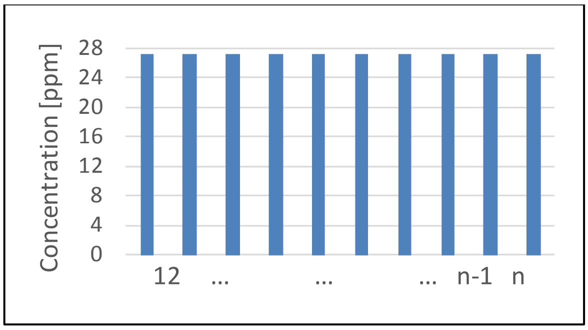

Figure 3: sample concentrations for repeatability evaluation

The repeatability is calculated as reported in Eq(2), using the t-student statistical distribution at a defined confidence interval (Devore, 2011):

$$r = \sqrt{2} \cdot s_r \cdot \mathrm{t} \qquad (2)$$

where s_r is the standard deviation and t is the student variable associated with the confidence interval, in general set at 95%.
The standard deviation is calculated as reported in Eq(3) (Devore, 2011):

$$s_r = \sqrt{\frac{(C_i - C_m)^2}{N-1}} \qquad (3)$$

where C_i is the value of the i-th measurement, C_m the average value of the measures and N the number of repetitions. It is suggested to repeat tests for three consecutive averaging time periods to obtain a robust estimation of repeatability (Spinelle et al., 2013).
Since the repeatability is directly proportional to the error made on the repeated measures, the lower the repeatability, the better (and therefore reliable) the ability of the instrument to recognize a specific compound will be.

4. Results and discussion

4.1 Limit Of Detection (LOD)

57 samples of ambient air taken at the Politecnico di Milano were analysed in 'air training' mode and signals recorded were processed as reported in section 3.3 to obtain a good estimate of (LOD).
In *Table 2* mean value, standard deviation and LOD per single sensor are reported.

Table 2: Limit of Detection (LOD)

	R_0/R_1	R_0/R_2	R_0/R_3	R_0/R_4	R_0/R_5	R_0/R_6
Mean	1.0911	1.1758	1.0423	1.0981	1.0485	1.3874
s_r	0.0574	0.0905	0.0365	0.1538	0.0371	0.2256
LOD	1.2633	1.4473	1.1519	1.5595	1.1598	2.0643

4.2 Lower Detection Limit (LDL)

The lower detection limit was estimated for target compounds by analysing odour samples prepared according to procedure described in section 3.2, in 'substance training' mode. This instrument mode allows the analysis of sample at 10 different concentrations, from 10% to 100% of its concentration. For each concentration level, values of resistance ratios recorded were compared with the limit of detection and the lowest concentration that allows at least one sensor to exceed the air threshold value was recorded as the LDL towards the examined compound.

In order to test instrument performance in odour detection, LDL calculated towards the target compounds were compared with their odour threshold OT (i.e. the lowest odour concentration of the compound perceivable by the human smell). This comparison provides useful information about instrument capability of estimating odour impact. Indeed, the higher the correspondence between the LDL and the OT, the more performing the instrument will be during environmental monitoring in the detection of odours responsible for olfactory nuisance.

Table 3 reports the LDL determined for target compounds tested and their odour threshold OT.

Table 3: Odour threshold and Lower Detection Limit of target compounds

Compound	OT	LDL	
	[ppm/ou/m^3]	[ppm]	[ou/m^{-3}]
Acetone	29	3.9	0.1
Ammonia	0.042	7.6	180
Ethanol	2.7	3.2	1.2
Limonene	0.072	0.176	2.4
Hydrogen sulphide	0.00025	0.195	780
Dymethildisulfide	0.56	1.56	2.8

The instrument LDL towards ethanol, limonene and dymethildisulfide are comparable with their OT. This in turn means that the IOMS sensitivity is similar to odour human perception, which is of course a desirable requirement for environmental odour monitoring. Conversely, the tested electronic nose is not able to detect ammonia and hydrogen sulphide at the same concentrations of humans. It might be useful to equip the detection system with sensors more sensible towards those compounds for monitoring emissions characterized by high concentrations of those compounds. In the case of odour monitoring, also correlate detection is an opportunity, but this requires separate verification.

Instrument LDL towards acetone, instead, is considerably lower than acetone OT. This very high sensitivity towards this compound might lead the instrument to overestimate the odour impact. In such cases, it is required to define signal correction factors to improve the correlation of the LDL with the human perception.

4.3 Repeatability

Repeatability was estimated, as described in section 3.3, for acetone, ethanol and ammonia, considering a 95% confidence interval (t=1.812). 10 repeatability tests were carried out for each compound, considering concentrations above the LDL to be sure that the instrument was able to perceive odours. Table 4 reports concentrations selected for the repeatability tests, whose results are reported in Table 5.

Table 4: Compounds concentration considered for repeatability tests

Compound	Concentration [ppm]
Acetone	27
Ethanol	10
Ammonia	25

Table 5: Results of repeatability tests

Compound		R_0/R_1	R_0/R_2	R_0/R_3	R_0/R_4	R_0/R_5	R_0/R_6
	Mean	1.2332	1.6516	1.2519	1.1984	1.2642	5.2814
Acetone	s_r	0.0931	0.1589	0.0620	0.1057	0.0844	2.0266
	r	0.2387	0.4071	0.1588	0.2708	0.2163	5.1934
	Mean	2.4245	1.5111	1.7451	1.1907	3.4849	1.7754
Ammonia	s_r	0.4265	0.1849	0.1301	0.0605	0.8243	0.8287
	r	1.0928	0.4737	0.3334	0.1550	2.1124	2.1236
	Mean	1.3415	1.7246	1.3081	1.3613	1.3360	5.2239
Ethanol	s_r	0.0237	0.0287	2.4473	0.0141	0.0157	0.2778
	r	0.0606	0.0737	6.2714	0.0362	0.0402	0.7120

The repeatability values determined are different for each sensor. This is due to the different nature of sensors installed on the instrument. In general, all sensors show a good repeatability towards the compounds tested, excepted for sensor 6 for acetone and sensor 3 for ethanol.

5. Conclusion

This paper proposes a methodological approach for the definition of a performance evaluation procedure for electronic noses to be applied for environmental odor monitoring at receptors. The experimental activity focused on the evaluation of instrument performance in detecting odour presence, by means of specific tests with target compounds representative of common odours in the environmental field. In particular, this work focused on the definition of the LOD and the LDL towards target compounds, and repeatability of responses to a given stimulus.

Ideally, an instrument for environmental odour monitoring should perceive odours like human nose does in order to provide an accurate estimation of the odour impact. Therefore, the higher the correlation between OT and instrument LDL, the best the instrument performance will be. The LDL determined towards target compounds provide information about electronic nose detection system capability to perceive common compounds responsible for odour annoyance in the environmental field, which can be used in the selection of the instrument to be installed at receptor based on the specific application. On the other hand, the evaluation of response repeatability provides useful information to monitor instrument performance in the field, since an increase of the repeatability value might point out instrument aging and might suggest maintenance work on the instrument (e.g. sensors substitution).

As a general rule, for environmental odour monitoring, which implies the analysis of complex mixtures, validation of the instrument in the application becomes the crucial step for requirements testing. However, preliminary testing with target odours still remains an important step to gain information about the instrument functioning under repeatability conditions as well as to test a wide range of possible different conditions (e.g., of temperature and humidity) the instrument might be subjected to during on field application.

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