Electronic nose performance optimization for continuous odour monitoring in ambient air

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Abstract

Industrial plants with odour emissions affect the quality of air and are often cause of public complaints by the people living surrounding the plant. For this reason, the control of odour represent a key issue. The starting point for an effective odour control it's their objective quantification. The electronic nose represent the odour measurement technique with probably the greatest potential, but currently there is not a universally recognized procedure of their application for the continuous monitoring of environmental odours.The aim of this paper is to present and describe a novel procedure to training electronic noses in order to maximize their capability of operating a qualitative classification and estimating the odour concentration of ambient air. This novel approach will reduce the uncertainty and increase the reliability of the continuous odour measures. The research is carried out through a real case study application in a big liquid waste treatment plant (LWTP). The seedOA system, patented by the SEED group of the University of Salerno, was used as e.nose device. The characterization of the odour concentrations from the different treatment units and the identification of the principal odour sources is discussed.

Keywords: air quality, dynamic olfactometry, liquid waste treatment plant, multisensory array system, public complaints.

1. Introduction

Offensive odour emitted in ambient air from different types of industrial plants are among the main causes of conflict by the community living surrounding the plants and of complaints at the local authorities (Zarra *et al.*, 2008; Belgiorno *et al.*, 2012). A prolonged exposure to odours causes a variety of undesiderable reactions in people, including unease, headaches, respiratory problems, nausea or vomiting (Zarra *et al.*, 2008). The particular and complex nature of the volatile substances, its variability on the time, the strong influence from atmospheric conditions and the subjectivity of smell perception are elements which delayed their regulamentations (Zarra *et al.*, 2008). Nowadays the available techniques for ambient odour measurements are classifiable in analytical, sensorial and sensor-instrumental (Belgiorno *et al.*, 2012; Zarra *et al.*, 2014). Analytical measurements allow the characterization of odours in terms of chemical composition (GC-MS, colorimetric methods). Sensory measurements, such as dynamic olfactometry standardized by EN13725:2003, provide for using human nose as sensor, with a view to defining and measuring the effects of the odours on a panel of qualified examiners. Sensor-instrumental techniques allows defining information about the chemical composition and the smell propriety of the investigated odour. Between this last instrumental class, the Electronic Nose (e.nose) appears as the one with the most suitable potential. In fact, the use of the e.nose technology allows having a continuous and real time (or "near real time") monitoring of odours (Romain *et al.*, 2010; Munoz *et al.*, 2010). According to Gardner and Bartlett (1994) an e.nose system consists of an array of non-specific gas sensors, a signal collecting unit and a pattern recognition software. The 'heart' of the E.Nose technologies is their measurement chamber with inside the sensor array, designed to detect and discriminate complex odour mixtures (Rock *et al.*, 2008). Different numbers of sensors are used to create the characteristic response called "fingerprint". Moreover different types of sensors are available in the commercially market using a range of materials, including metal oxides, conducting polymers, surface acoustic wave devices and catalytic metals (Rock *et al.*, 2008; Munoz *et al.*, 2010). The principal steps implemented to use e.nose technologies consists of an initial training phase and a subsequent on site measurement application. The training of the e.nose represents the most important phase of the whole process (Romain *et al.*, 2010; Giuliani *et al.*, 2012). The goal of the training phase is to create the site-specific 'odour measurement model' (OMM) that are robust, repeatable and reliable. For its definition, different statistical techniques can be used, in order to process the sampled data. A qualitative and a quantitative OMM were usually elaborated. The qualitative OMM have the objective to discriminate the different odour classes (e.g. odour sources) into a spatial domain. While the quantitative OMM have the finality to define the correlation equation between the electrical signal data,

Figure 1. Investigated LWTP and odour emission sources

acquired trough the sensor array, and a measure of the 'odour characteristics'. In the actually application of the e.nose in the environmental fields, the e.nose data metrics are usually related to the Odour Concentration (OU/m^3) measured with dynamic olfactometry, according to EN 13725:2003. Nowadays there are no regulations or guidelines that standardize the odour measurement in ambient air with this type of instruments. In May 2015, a new CEN/TC264 'Air Quality' standardization working group (WG41) started to define a new European standard for the use of instrumental odour monitoring in ambient air, indoor air and gas emissions, but there are still at work (Guillot, 2016). Likewise there are actually no universally adopted and approved procedure that deals and regulates the training phase and the performance and the requirement of an e.nose to consider it available for environmental ambient odour measurements. The define of key points in order to guarantee a efficient and reliable measure with the e.nose is therefore a critical issue in which the scientific community are involved. The present work illustrate a novel procedure to training electronic noses in order to maximize their capability of operating a qualitative classification and estimating the odour concentration of ambient air. The proposed procedure optimizes the performance of the e.nose system studying their best sensor array selection. The aim of the research is to reduce the uncertainty and increase the reliability of the continuous odour measures. To perform the study, analyses were conducted at a real large liquid waste treatment plant (LWTP).

2. Materials and methods

2.1. Experimental setup and program

Research activities were carried out at a real liquid waste treatment plant (LWTP), located in the municipality of Buccino, in the province of Salerno (Campania Region, IT). The LWTP has a design capacity of 60.000 p.e. (population equivalent) and an average daily flow rate of 6.600 m^3/d. The plant includes different treatment lines and are based on an activated-sludge process. To test the experimental hypothesis, six odour emission sources have been monitored in the LWTP, four of which related to the waste-wastewater treatment line (P1, waste influent; P2, equalization basin; P3, primary sedimentation; P4, aeration basin) and two to the sludge treatment line (P5, sludge thickening; P6, sludge dewatering by belt press) (Figure 1). In addition, in order to create the 'blank' point in the e.nose measurement model, non-odour samples were collected in one place of the plant area (Romain *et al.*, 2010; Giuliani *et al.*, 2012). Monitoring activities were carried out trough a weekly sampling campaigns over a period of 2 months. A total of nine sample were taken for each investigated sources over the monitoring period. Air samples were carried out according to EN 13725:2003, using the 'lung' technique. Nalophan® sampling bags with 10 liters volume were used for the sampling. Each collected samples were analysed with dynamic olfactometry to calculate the odour concentration (OU_E/m^3) and with the e.nose system to create the qualitative and quantitative 'odour measurement model' (OMM).

2.2. Odour concentration characterization

Odour concentration was carried out by dynamic olfactometry according to EN 13725:2003 at the Olfactometric Laboratory of the SEED (Sanitary Environmental Engineering Division) research centre of the University of Salerno, using an olfactometer model TO8 by ECOMA, based on the ''yes/no'' method, relying on a panel composed of four trained persons. All the measurements were conducted within 14 h after sampling, according to Zarra *et al*. (2012) studies to reduce the variability of the mixture and increase the reliability.

2.3. Electronic nose and data analysis

The seedOA (Sanitary Environmental Electronic Device for Odour Application) multisensor system, designed and implemented by the SEED research group of the University of Salerno (IT), was used as e.nose technologies. The seedOA consists in a set of 12 metal oxides non-specific gas sensors (MOS, Figaro, USA Inc.), 2 specific gas sensors (TGS825 for H_2S and TGS826 for NH_3) and 2 internal conditions sensors (humidity and temperature), placed on two different levels of a innovative measurement chamber (code®) (Viccione *et al*. 2012) patented by the SEED research group. The code® chamber is composed of a hollow cylinder having a volume of 300 cm^3 and a central cylindrical diffuser for the flow homogenization and regulation. The design and architecture of the seedAO reflect the human nose, with the two levels that represent the two nostrils (in which are located the same types of senors in a symmetrical manner) and the processing system that interprets the brain.

Figure 2 shows the scheme of the sensors and their location within the code® measurement chamber of the seedOA. All samples were analyzed according to the procedure proposed by Giuliani *et al*. (2012) with a cycle type "odour – non-odour", a running time of 10 minutes per sample and the extraction of the registered data set relating to only the last one minute of the 10-minute analysis. The measurements provided by the device are electrical resistance (R) (KΩ), recorded every 2 seconds. The supervised Linear Discriminant Analysis (LDA) processing techniques was applied to create the qualitative OMM. While the Partial Least Squares (PLS) method was used to develop the quantitative OMM, correlating the acquired fingerprint with the olfactometric data, determined by dynamic olfactometry. All statistical analysis were carried out using the software Statistica© (StatSoft srl, It).

2.4. *Optimization procedures and studies*

To increase the performance of the seedOA system, the optimization of their sensor array was studied. Nine types of e.nose array configurations (C1 – C9) were investigated and compared:

- *C1:* all the sensors array of the measurement chamber;
- *C2:* only the sensors array located at the first level;
- *C3:* only the sensors array located at the second level;
- *C4:* only the specific gas sensors (referring to NH_3 and H_2S);
- *C5 – C9:* couple of identical sensors or sensors referred to the same target gas, located of both levels:
    - *C5:* sensors for alcohol and organic solvent vapors (TGS822);
    - *C6:* sensors for methane (TGS842, TGS2611);
    - *C7:* sensors for alcohol and water vapors (TGS880);
    - *C8:* sensors for volatile organic compounds (TGS2620);
    - *C9:* sensors for air contaminants (TGS2602).

For each investigated configurations the corrisponding data sets were extracted from the complete acquired database and processed with the LDA and PLS techniques.

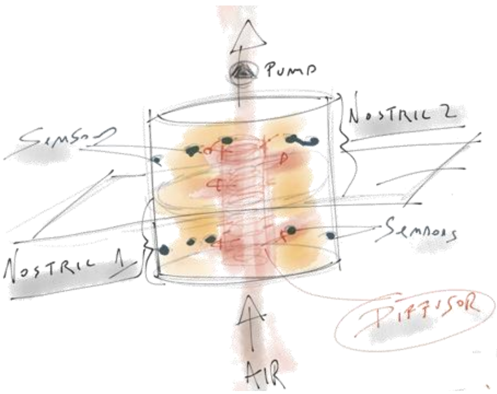
3. Results and discussions

3.1. *Odour concentration characterization*

Figure 3 reports the results of the olfactometric analysis at each investigated source at the LWTP plant, over the whole monitored period in terms of Box-Whisker diagrams. The results show that the highest odour concentration (Cod) among the investigated sources were detected at the liquid waste-wastewater receiving unit (P1, 92’682 OU_E/m^3), while the lowest were measured at the aeration basin (P4, 38 OU_E/m^3). The largest variability of the determined odour concentrations was recognized at the receiving unit, related to the different type of treated waste (e.g. leachate from landfill, sludges from dairy waste, leachate from refuse derived fuel plants). The preliminary units (P1, P2) of the waste/wastewater treatment line presents the highest average odour concentrations, while the secondary treatments of the waste/wastewater treatment line shown the lowest average values in terms of Cod. Between the sludge treatments, the thickening show the highest average Cod values. These results are in line with literature studies that identify influent liquid waste thank as one of the most relevant units in LWTPs in terms of odour concentrations (Belgiorno *et al*., 2012; Zarra *et al*, 2016).

3.1. *Optimization studies*

Table 1 highlights the accuracy percentages of correct classification for each investigated odour class (source), for each analyzed seedOA array configuration applying the LDA technique. The classification of each observation is carried out based on the Mahalanobis distance between the observation and the centroid of each group. The results show the existence of a different accurancy in terms of odour source classification in considering different array configuration..



code® LEVEL	TARGET GAS	MODEL N.
I, II	Alcohol and organic solvent vapors	TGS822
I, II	Alcohol and water vapors	TGS880
I, II	Methane gas	TGS842
I, II	Volatile Organic Compound	TGS2620
I, II	Methane	TGS2611
I, II	Air contaminants	TGS2602
II	Ammonia (specific)	TGS826
II	Hydrogen Sulfide (specific)	TGS825
I	LP gas (e.g. propane and butane)	TGS2610
I	Water Vapor Detection	TGS2180

Figure 2. Sensors scheme and location in the code® measurement chamber of the seedOA

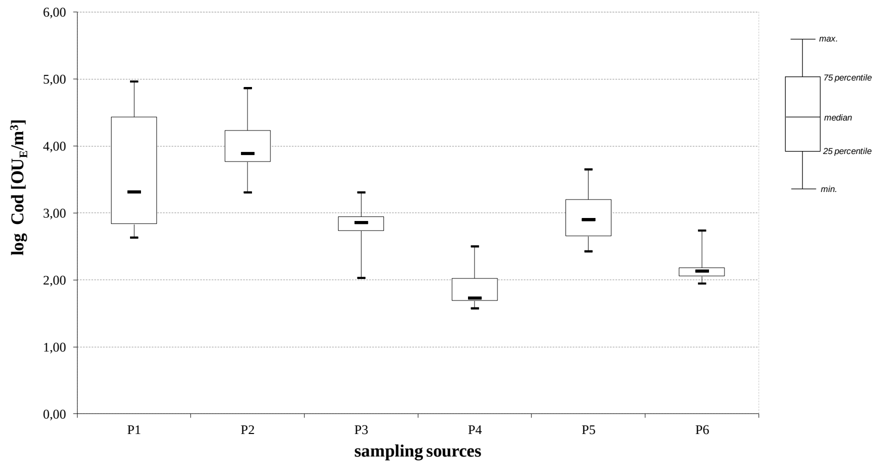


Figure 3. Box-Whisker diagrams on measured odour concentrations at LWTP investigated sources

The importance of the proposed procedure to investigate the most suitable sensor array configuration to ensure the highest accurancy of the used e.nose is thus demonstrated. For the analyzed case study, the configuration C1 (all sensors array) represents the one that provides the most robust classification odour model, with a percentage of 93,30%. While the configuration that gives the lowest reliability are the configuration that use only the TGS2602 sensors (63,67%). The odour sources related to the preliminary treatments of the waste/wastewater treatment line and their referred to the sludge treatments shown the highest average values of the percentage of correct classification in all investigated configurations. This odour sources are the only that reachs an accuracy percentage of 100%, but not in every analysed configuration. It can be seen how more higher the detected odour concentration on the sources is and more reliable is the attribution of their observation to its odour class (higher percentage of correct classification). The results of the quantitative PLS model applied on the acquired data in the different investigated configurations are reported in Table 2 as forecast probability indexes (R^2). Likewise to the application to the LDA model, the PLS application shows different values of the confidence level between the odour concentrations determined by olfactometric measurement and predicted by the PLS model, analyzing different array configurations. The highest correlation coefficient is calculated even in this case considering the entire array of sensors (C1) (R^2 = 0,94).

Table 1. Qualitative classification rates with LDA model in the investigated sensor array configurations

Sampling source	% correct classification								
	type of array configuration								
	C1	*C2*	*C3*	*C4*	*C5*	*C6*	*C7*	*C8*	*C9*
P1	100,00	77,78	100,00	77,78	77,78	44,44	77,78	77,78	77,78
P2	100,00	100,00	77,78	55,56	100,00	100,00	100,00	100,00	55,56
P3	77,78	55,56	55,56	44,44	22,22	44,44	00,00	00,00	00,00
P4	55,56	44,44	55,56	22,22	11,11	11,11	00,00	22,22	00,00
P5	88,89	44,44	100,00	55,56	44,44	44,44	22,22	77,78	44,44
P6	100,00	77,78	77,78	77,78	100,00	55,56	11,11	11,11	44,44
odourless	100,00	100,00	100,00	96,43	22,22	100,00	100,00	100,00	93,55
All data	**93,30**	**80,00**	**85,55**	**73,91**	**71,26**	**73,02**	**65,96**	**72,14**	**63,67**

Table 2. Correlation coefficients of odour concentrations measured by dynamic olfactometry and predicted by PLS model applications in the various investigated seedOA sensors array configurations

Correlation coefficients	*type of array configuration*								
	C1	*C2*	*C3*	*C4*	*C5*	*C6*	*C7*	*C8*	*C9*
R^2	0,94	0,81	0,84	0,67	0,75	0,68	0,66	0,69	0,61

4. Conclusions

The definition of a optimized procedure for the training of a multisensor array system improving their performance trough the optimization of the sensor array selection is analyzed and discussed. The results of the investigations show the existence of different accuracy in terms of odour source classification and correlation coefficients of odour concentrations measured by dynamic olfactometry and predicted by PLS model applications in considering different sensors array configuration. The importance of the analysis of the most suitable sensor array configuration to optimize the e.nose performance to maximize their ability to recognize odours qualitatively and quantitatively in ambient air is thus demonstrated in the present work. For the investigated LWWTP the optimum array configuration was identified as there considering the entire sensors array for both qualitative and quantitative OMM. Research highlights the importance to have e.nose technologies that allows the possibility to change and select their array of sensors for the specific analyzed case study, to increase their reliability and repeatability. Likewise the research confirm the impossibility to define standard option for the e.nose technologies that represents the optimal measurement conditions in every case.

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