



## Comparison of the Measurement Techniques Employed for Evaluation of Ambient Air Odour Quality Influenced by Operation of Industrial Sewage Treatment Plant

Paulina Lewkowska<sup>a</sup>, Hubert Byliński<sup>a</sup>, Wojciech Wojnowski<sup>a</sup>, Tomasz Dymerski<sup>a</sup>, Jacek Gębicki<sup>b\*</sup>, Jacek Namieśnik<sup>a</sup>

<sup>a</sup>Department of Analytical Chemistry, Chemical Faculty, Gdańsk University of Technology, 11/12 G. Narutowicza Str., 80-233 Gdańsk, Poland.

<sup>b</sup>Department of Chemical and Process Engineering, Chemical Faculty, Gdańsk University of Technology, 11/12 G. Narutowicza Str., 80-233 Gdańsk, Poland.  
 jacek.gebicki@pg.gda.pl

The paper presents the results of investigation on ambient air quality evaluation with respect to concentration of odorants in a vicinity of a sewage treatment plant of the LOTOS Group S.A. petroleum plant. The investigation was performed during winter season using a prototype of electronic nose and the Nasal Ranger field olfactometers. The prototype was equipped with a set of six semiconductor sensors by FIGARO Co. and one PID-type sensor. The field olfactometers were used to determine mean concentration of odorants, which amounted from 2.2 to 17.8 ou/m<sup>3</sup> depending on the place of measurement. In case of the investigations with the electronic nose prototype a classification of the ambient air samples with respect to the place of sampling was performed utilizing linear discriminant function supported with a cross-validation method. Correct classification of the ambient air samples was at the level of 83.3%. Moreover, it was shown that discrimination of the ambient air samples differing in concentration of odorants and place of origin was possible with the electronic nose measurements.

### 1. Introduction

Dynamic economic development of many countries contributes to increased amount of pollutants emitted into the environment, which can have a negative effect on living organisms, thus on human health and life. One of the exemplifications of anthropopressure, which can be particularly onerous, are municipal and industrial sewage treatment plants. The main sources of odorants emission from the sewage treatment plants include:

- points of sewage collection (sewerage systems),
- mechanical treatment zones,
- treatment of sediments,
- processing of sediments.

The highest levels of odorants emission originate from the objects where anaerobic conditions occur: preliminary settling tanks, dephosphatation chambers, preliminary mechanical treatment, densification and dehydration of excessive sediments, collection points (Stuetz and Frechen 2001). Complete hermetic insulation of the objects contributing to odour nuisance leads to efficient minimization of odorants emission, however it is connected with significant costs. Nevertheless, it is necessary to apply different methods of deodorization of gases, the aim of which is conversion of the odorants into their odourless form or into the compound characterized by much higher threshold level of odour sensing than the one of the primary odorant. The most frequently utilized methods of deodorization include: biological methods, gas incineration, gas masking, absorption with reaction (Yavuz et al. 2010, Daud et al. 2014, Yan et al. 2014, Alfonsín et al. 2015). Literature survey shows that the odorants present in ambient air, emitted from sewage treatment plants often have negative impact on human yielding such symptoms as: headache, vertigo, nausea, problems with

concentration and other health hazards (Trincavelli et al. 2009, Capelli et al. 2009). Moreover, emission of odorants has negative influence on plant and animal ecosystems. The level of emission of these compounds to the environment varies in time and strongly depends on sewage quality, rate of biological processes occurring in sewage or different technological solutions applied in sewage treatment plant (Naddeo et al. 2012). Elaboration of an objective method of odour nuisance assessment is one of the activities aimed at environmental protection as well as protection from the effects of odorants emission from municipal and industrial sewage treatment plants. In order to determine emission level of particular odorants released to the atmosphere during operation of sewage treatment plant, or some of its components, suitable measurement techniques should be applied. Their selection often depends on a number of factors, which can influence on the final result of investigation. The tools utilized for evaluation of odorous substances introduced into the environment include electronic nose instruments and field olfactometers (Capelli et al. 2008, Capelli et al. 2010) which allow measurement of concentration level of the odorous substances and emission of odours *in-situ*. Electronic nose is a device, the structure of which was inspired by neurophysiology of human sense of smell. Its main aim is automatic discrimination of the samples of complex matrix and their analysis (Munoz et al. 2010, Wilson 2013, Gebicki et al. 2016). Suitable software, allowing determination of characteristic properties of the sample, enables very fast qualitative analysis of examined odour mixtures. Structure of the electronic nose is analogous to the structure of human sense of smell. The analogy consists not only in application of a matrix of chemical sensors, which are the counterparts of the smell receptors, but also in the way of interpretation of the signal acquired from these sensors. The field olfactometers allow investigation of odorous substances concentration via determination of the value of D/T (Dilution-to-Threshold Ratios) parameter. Due to portability of these devices the results are obtained on-line, a team of panelists describes substance odour in the analysed samples. The results from field test make it possible to identify the sources of odorants and to estimate the total odour emission in particular measurement point. One of the drawbacks of this technique is a necessity of providing an experienced team of panelists, whose sensory sensitivity can deteriorate in time due to different factors, for example varying perception. In case of the field olfactometry there are no defined quality parameters and no criteria as far as accuracy and precision of measurement are concerned. Nevertheless, this technique is frequently applied to ambient air evaluation with respect to odour. The authors of this paper would like to present the results of investigation on ambient air odour quality in a vicinity of the sewage treatment plant of the LOTOS Group S.A. petroleum plant conducted with an electronic nose prototype comprised of a set of semiconductor sensors by FIGARO Co. and a photoionization sensor of PID-type as well as with the field olfactometers by Nasal Ranger Co. The aim of investigation was comparison of the results obtained with both measurement techniques and verification of correct operation of the electronic nose instrument in field conditions.

## 2. Experimental

### 2.1 Measurement set-up

The electronic nose prototype was designed and built of the semiconductor sensors by FIGARO Co. (TGS 823, TGS 826, TGS 832, TGS 2600, TGS 2602, TGS 2603) and one photoionization sensor of PID-type (PPB MiniPID). The measurement set-up utilized in the investigations consisted of: a Tedlar bag of 5 dm<sup>3</sup> volume (SKC Inc., USA), a Tecfluid flow meter, the prototype of electronic nose, a suction pump and a PC class computer. Volumetric flow rate of the air sucked from the Tedlar bag was constant and equal 1 dm<sup>3</sup>/min. Dedicated miniaturized electronic circuit processed the output signal from the sensor set of the prototype. Its task was to convert changes of sensor resistance into voltage signal measurable by analogue-to-digital converter (ADC). The voltage obtained was converted into digital form in the range from 0 to 16 bits. The measurement data were collected and archived. The values of particular sensor signal taken for data analysis originated from the range, where the sensor signal attained steady value.

Four persons took part in the investigations carried out with the Nasal Ranger field olfactometers (St. Croix Sensory, USA). These persons (a team of panelists) were selected from a group of 12 people following a standard procedure elaborated by the St. Croix Sensory, Inc. (St. Croix Sensory 2006). Selected team of panelists was trained with respect to the rules governing the sensory field measurements. Odour concentration Z<sub>ITE</sub> was calculated based on individual D/T values (dilution to sensing threshold) using the Eq(1):

$$Z_{ITE} = \sqrt{Z_{NO} \times Z_{YES}} \quad [\text{ou/m}^3] \quad (1)$$

where:

Z<sub>NO</sub>=D/T+1 - D/T value, where odour is imperceptible, prior to the D/T value, where odour is perceptible,

Z<sub>YES</sub>=D/T+1- D/T value, where odour is perceptible, following to the D/T value, where odour is imperceptible.

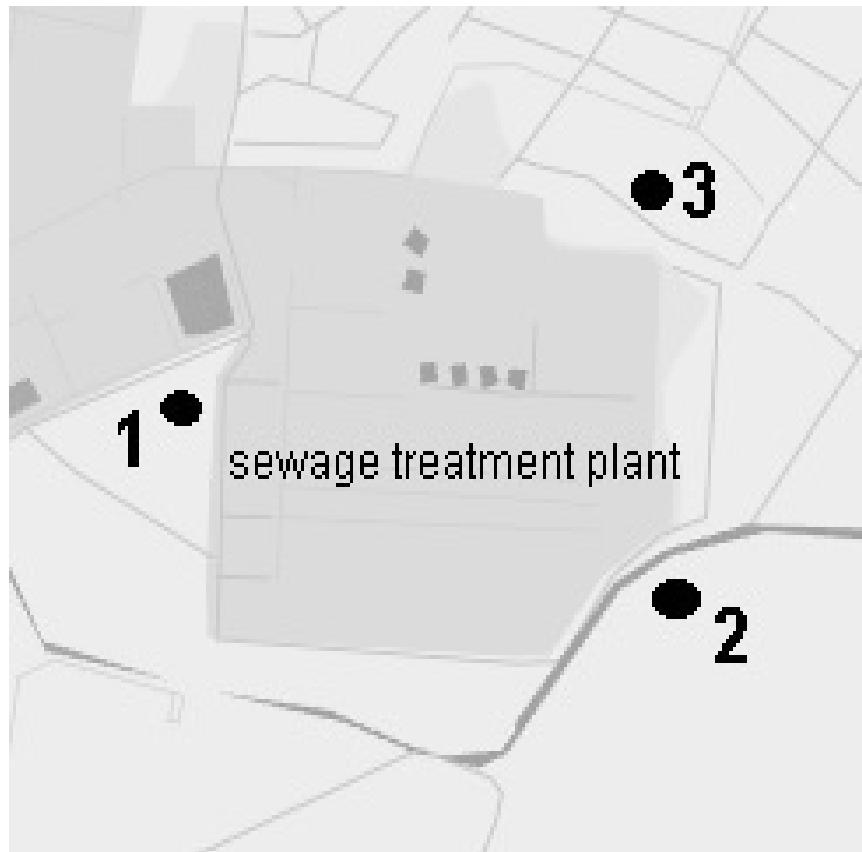
The value of odour concentration  $c_{od}$  [ou/m<sup>3</sup>] was calculated as a geometrical mean of the n set of all individual odour concentrations ( $Z_{ITE}$ ) for a given measurement point using the Eq(2):

$$c_{od} = \sqrt[n]{Z_{ITE1} \times Z_{ITE2} \times Z_{ITE3} \times \dots \times Z_{ITEn}} \quad [\text{ou/m}^3] \quad (2)$$

where:  $Z_{ITEn}$  is the individual odour concentration provided by the panelist.

## 2.2 Methodology of investigation

In case of the investigation carried out with the electronic nose prototype the samples were collected at 3 control points located within 1-kilometre distance from the sewage treatment plant of the LOTOS Group S.A. petroleum plant. Localization and distribution of the air sampling points around the sewage treatment plant is illustrated in Figure 1.



*Figure 1: Map of the sewage treatment plant of the LOTOS Group S.A. petroleum plant with the points of atmospheric air samples collection.*

The samples were collected for 2 months during the winter season. Each day 3 samples were taken from the aforementioned points. There was no atmospheric precipitation during the sampling operation. The samples were collected into the Tedlar bags using a device called Lung sampler. Prior to sampling the bags were blown with nitrogen (in laboratory) and conditioned – blown with the air from the place of the actual samples collection, which were aimed at minimization of changes in the sample composition due to adsorption. The total of 54 atmospheric air samples were collected around the sewage treatment plant.

Analysis of the data obtained with the electronic nose prototype was performed employing free R software being a part of Free Software Foundation (Free Software Foundation, Boston, MA, USA). In case of the investigation carried out with the Nasal Ranger field olfactometers the measurements were performed at the same time and in the same control points, where the air was sampled into the Tedlar bags. The total of 216 measurements were performed with the Nasal Ranger field olfactometers. An exemplary measurement with the field olfactometer is shown in Phot. 1.



*Phot. 1: Application of field olfactometer for measurement of ambient air with respect to odorants concentration in a vicinity of the sewage treatment plant of the LOTOS Group S.A. petroleum plant.*

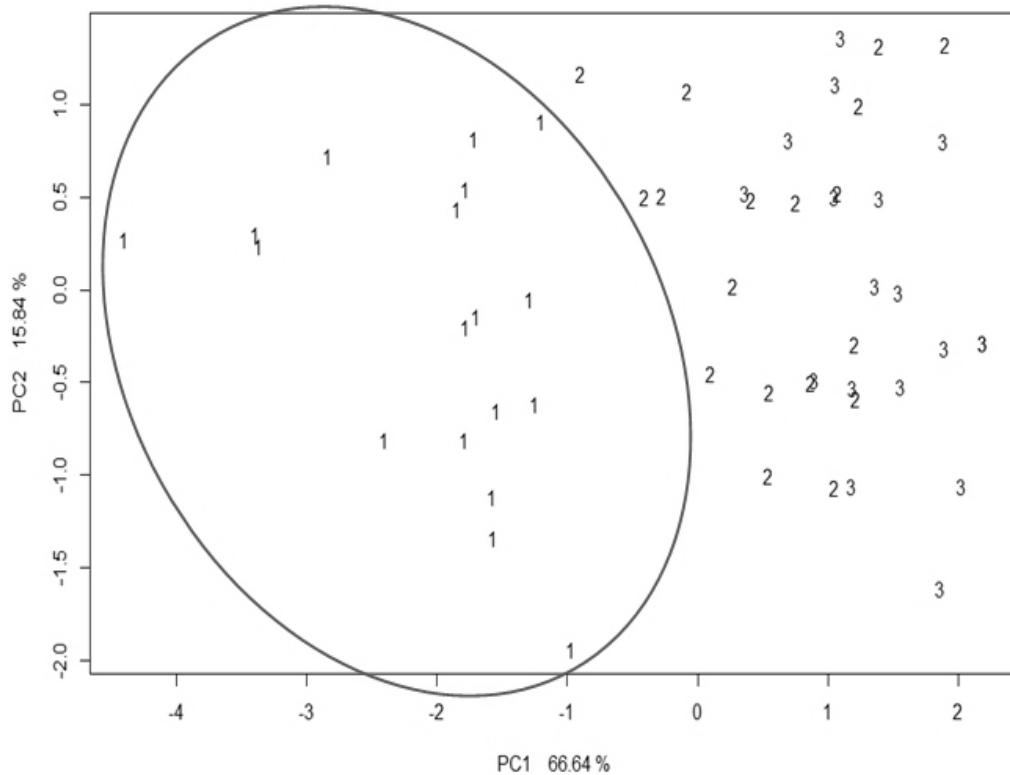
### 3. Results and discussion

Table 1 presents mean odorants concentrations in the ambient air samples collected in a vicinity of the sewage treatment plant of the LOTOS Group S.A. petroleum plant. It can be noticed that the odorants concentrations determined for the point 1 (P1) are the highest and their mean value is 17.8 ou/m<sup>3</sup>. It is possible that apart from the odorants emitted from the sewage treatment plant there was additional input connected with emission of odorants from the petroleum plant nearby. At the remaining measurement points P2 and P3 the mean odorants concentrations were 3.2 and 2.2 ou/m<sup>3</sup>, respectively, which is within the detection abilities of the field olfactometer (1.7 ou/m<sup>3</sup>). Low values of odorants concentrations at the control points P2 and P3 could be caused by wind direction, which was north-east during the measurement, thus moving air masses towards the control point P1.

*Table 1. Concentration of odorants at each measurement point [ou/m<sup>3</sup>] in a vicinity of the sewage treatment plant of the LOTOS Group S.A. petroleum plant.*

	P1	P2	P3
concentration	17.8	3.2	2.2

Figure 2 presents the PCA results for the ambient air samples collected in a vicinity of the sewage treatment plant of the LOTOS Group S.A. petroleum plant when the measurements were performed with the electronic nose prototype. Two characteristic clusters of points corresponding to the sampling locations can be distinguished on a two-dimensional plane. One cluster is associated with the samples collected at the point P1 where apart from emission from the sewage treatment plant the odours could be emitted from the petroleum plant located nearby. The second cluster represents the sampling points P2 and P3 where the odorants concentrations were at low level. Application of PCA makes it possible to discriminate the ambient air samples collected from different locations around the sewage treatment plant and differing in odour.



*Figure 2: PCA result for the ambient air samples collected from 3 control points localized in a vicinity of the sewage treatment plant of the LOTOS Group S.A. petroleum plant. Measurements were carried out with the electronic nose prototype.*

Table 2 presents a matrix with the results of cross-validation supported linear discriminant analysis (LDA) classification of the ambient air samples collected around the sewage treatment plant of the LOTOS Group S.A. petroleum plant when the investigations were carried out with the electronic nose prototype. 83.3% of the samples collected from selected control points were correctly classified. The biggest number of correctly classified samples was 18 and they originated from the point P1. In the remaining cases the number of correctly classified samples were as follows: 13 for the point P2, 14 for the point P3. Only in case of the control point P1 correctness of LDA classification was at the level of 100%.

*Table. 2 Cross-validation supported LDA classification of the ambient air samples collected in a vicinity of the sewage treatment plant of the LOTOS Group S.A. petroleum plant. Measurement data for classification were obtained with the electronic nose prototype.*

	P1	P2	P3
P1	18	0	0
P2	0	13	4
P3	0	5	14

Correct classification of the ambient air samples collected from the control point P1, which simultaneously correlates with the highest odorants concentrations determined with the field olfactometers, is the evidence of detection abilities of the electronic nose prototype. The prototype and applied data analysis methods allowed discrimination of the air samples characterized by different concentration of odorants. Analogous investigations of the ambient air samples collected around a municipal landfill performed with an electronic nose prototype equipped only with the semiconductor sensors (without the PID-type sensor) yielded correct classification of the air samples at the level of barely 40% (Gębicki et al. 2014). Application of the PID-type sensor in new version of the prototype resulted in improvement of detection properties and provided classification at the level of 83.3%.

#### 4. Conclusions

The aim of investigation was comparison of the results of ambient air measurement in a vicinity of the sewage treatment plant of the LOTOS Group S.A. petroleum plant obtained with field olfactometry and electronic nose techniques. Moreover, correctness of the electronic nose prototype operation in field conditions was evaluated and verified. The investigation was performed with the electronic nose prototype containing the semiconductor sensors by FIGARO Co. and the photoionization sensor of PID-type as well as with the Nasal Ranger field olfactometers. The investigations carried out with the electronic nose prototype revealed ability of discrimination of the ambient air samples differing in concentration of the odorants. Correctness of classification of the ambient air samples performed using the LDA method was at the level of 83.3%. It was observed that the biggest number of correctly classified samples originated from the control point P1, which according to the field olfactometry investigation was characterized by the highest concentration of odours. High correctness of ambient air samples classification and ability of sample discrimination with respect to odorants concentration make the electronic nose-type instruments suitable for air quality evaluation as far as odour is concerned. Note, however, that the main factor to differentiate between air samples using electronic nose is its intensity odours. Research has shown that logarithms signals of semiconductor sensors are proportional to the intensity of the odours (Gebicki et al. 2015). In the case of comparable intensity to distinguish between samples of odour atmospheric air with the semiconductor sensor only, it would not be possible, because of the high value of the detection limit.

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