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Comparison of Evaluation of Air Odour Quality in Vicinity of Petroleum Plant Using a Prototype of Electronic Nose Instrument and Fast GC Technique

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The paper presents the results of investigation on classification of the ambient air samples collected in a vicinity of the LOTOS Group S.A. petroleum plant with respect to odour. The investigations were carried out with an electronic nose prototype and a commercial electronic nose of Fast GC-type – HERACLES II. The prototype was equipped with a set of six semiconductor sensors by FIGARO Co. and a photoionization sensor of PID-type. Classification of the air samples depending on the sampling point with respect to the petroleum plant was performed with linear discriminant function supported with cross-validation method. Analyses with the HERACLES II yielded over 94.2% of correct classifications of the ambient air samples. In case of the electronic nose prototype correct classification was at the level of 67.5%.

1. Introduction

Industry is a sector with wide spectrum of production profiles, various size of production plants and thus of diverse environmental impact, especially on ambient air as far as odours and odour nuisance are concerned (Taylor et al. 2008, Hoffmann et al. 2009, Chang et al. 2014). Special attention is paid to the industrial plants processing big amounts of resources, which are the ones of primary importance for economy but simultaneously have significant impact on neighbouring areas. These plants, typically petroleum and petrochemical plants, can release volatile odorous pollutants to the atmosphere. Potential sources of odours emission include: leaking installations, random failures, storage of fuels and resources, asphalt production and distribution as well as sewage treatment plants (Gostelow et al. 2001, Pearce et al. 2003, Henshaw et al. 2006, Capelli et al. 2008). One of the biggest emitters in the Tri-city Agglomeration (Gdańsk, Sopot, Gdynia) is the LOTOS Group S.A. petroleum plant. Despite monitoring of such compounds as methane, aromatic hydrocarbons from the BTX group and summary non-methane hydrocarbons each year brings an increase in the number of complaints on odour nuisance from the residents of the areas adjacent to the petroleum plant. One of the preventive measures is a collaborative research program for odour nuisance monitoring undertaken by the LOTOS Group S.A. and the Gdańsk University of Technology within a frame of the PBSII/B9/24/2013 scientific project. The consortium decided to work on implementation of the electronic nose as the technique enabling recording of short-term episodes of high concentration of odorants and offering operation in on-line mode. Due to the principle of operation based on holistic analysis the electronic nose instruments can be applied for both detection as well as identification of odour via assigning it to a suitable class of reference odours (Wilson and Baietto 2009, Wilson 2013, Boeker 2014, Gebicki 2016). In a classical approach the electronic nose is comprised of a few or several chemical sensors characterized by defined selectivity with respect to gas components of the analysed sample. In more modern approach the electronic nose can be a combination of parallel-connected chromatographic columns with a suitable detector. In case of this type of device the investigated gas sample is directed to a set (typically two) of chromatographic columns connected in parallel and differing in polarity of a stationary phase. The chromatographic columns separate volatile components, which are then identified by standard chromatographic detectors. In case of the

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electronic nose technique these are short columns for ultra-fast gas chromatography that are employed, which results in short time of analysis equal to 1-2 minutes (Delgado-Rodríguez et al. 2012, Cheng et al. 2013, Xiao et al. 2014). Obtained chromatograms are analysed using data analysis methods; in this case the chromatographic peaks play a role of the sensors.

The authors of this paper would like to present the results of investigation on ambient air odour quality in a vicinity of the biggest industrial facility in the region – Gdańsk petroleum plant LOTOS Group S.A., conducted with an electronic nose of Fast GC-type by Alpha MOS Co. as well as an electronic nose prototype equipped with a set of semiconductor sensors by FIGARO Co. and a photoionization sensor of PID-type. The aim of investigation was comparison of the results obtained with both types of electronic nose instrument as well as verification of usefulness of the electronic nose prototype in this kind of research and its application potentialities in industry.

2. Experimental

2.1 Measurement set-up

The electronic nose prototype consisted 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 with the electronic nose prototype consisted of: a Tedlar bag, 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 1 dm^3/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. The commercial electronic nose of Fast GC-type – HERACLES II was built from two independent chromatographic-detection systems. The main components of these systems were two chromatographic columns characterized by different polarity of a stationary phase and two detectors of FID-type. The measurement set-up consisted of: the HERACLES II device, the Tedlar bag of 5 dm^3 volume and 5 cm^3 syringe. The measurement procedure consisted in sampling of air directly from the Tedlar bag using the syringe. Then 5 cm^3 air sample was supplied to a proportioner. Sorption of the sample occurred behind the proportioner, inside a sorption trap of Tenax. The analytes were released from the trap after it had been heated to 270°C and the stream was directed to two independent chromatographic-detection systems. A single analysis lasted from 90 to 100 s (Gębicki et al. 2014). Surface area of chromatographic peaks was utilized in analysis. Figure 1 presents the electronic nose of Fast GC-type.

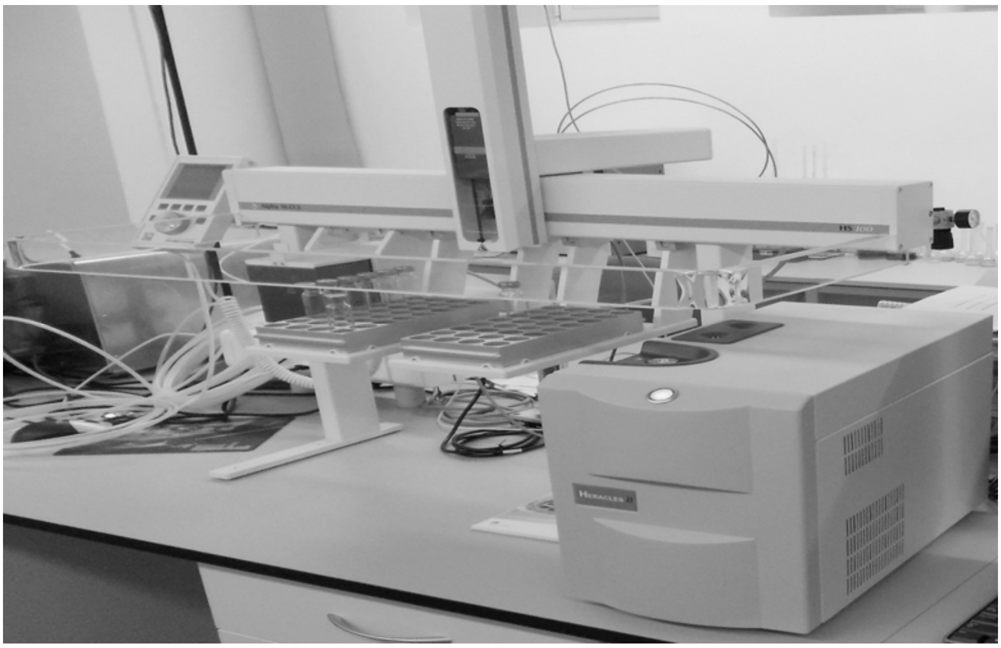

Figure 1: Electronic nose of Fast GC-type - HERACLES II.

2.2 Methodology of investigation

The ambient air samples collected in a vicinity of the LOTOS Group S.A. petroleum plant were used for investigation of air quality with respect to odour. They were collected at 5 control points localized in the places where the petroleum plant was conducting continuous monitoring. Localization and distribution of the ambient air sampling points around the petroleum plant are illustrated in Figure 2.

Figure 2: Localization of each sampling point.

The samples were collected during the winter season. Each day 5 samples were taken from the aforementioned points. There was no atmospheric precipitation during the sampling operation. The samples were collected into the Tedlar bags (SKC Inc., USA) of 5 dm^3 volume using a device called Lung sampler. The total of 120 atmospheric air samples were collected around the petroleum plant and analysed.

Discrimination and classification of the ambient air samples with respect to odour nuisance were performed with linear discriminant analysis (LDA) and principal component analysis (PCA) employing free R software being a part of Free Software Foundation (Free Software Foundation, Boston, MA, USA).

3. Results and discussion

Figure 3 presents the PCA results for the samples of ambient air collected in a vicinity of the LOTOS Group S.A. petroleum plant when the measurements were carried out with the electronic nose prototype. Three 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 petroleum plant the odours could be emitted from the sewage treatment plant located nearby. The second cluster represents the point P2 and the third cluster corresponds to the remaining sampling points. Application of PCA makes it possible to discriminate the ambient air samples collected from different locations and differing in odour.

Table 1 presents a matrix with the results of cross-validation supported LDA classification of the ambient air samples collected around the petroleum plant when the investigations were carried out with the electronic nose prototype. 67.5% of the samples collected from selected control points were correctly classified. The biggest number of correctly classified samples was 23 and they originated from the point P1. In the remaining cases the number of correctly classified samples were as follows: 21 for the point P2, 14 for the point P3, 13 for the point P4 and 10 for the point P5. Only in case of the control point P1 correctness of classification was 95.8%.

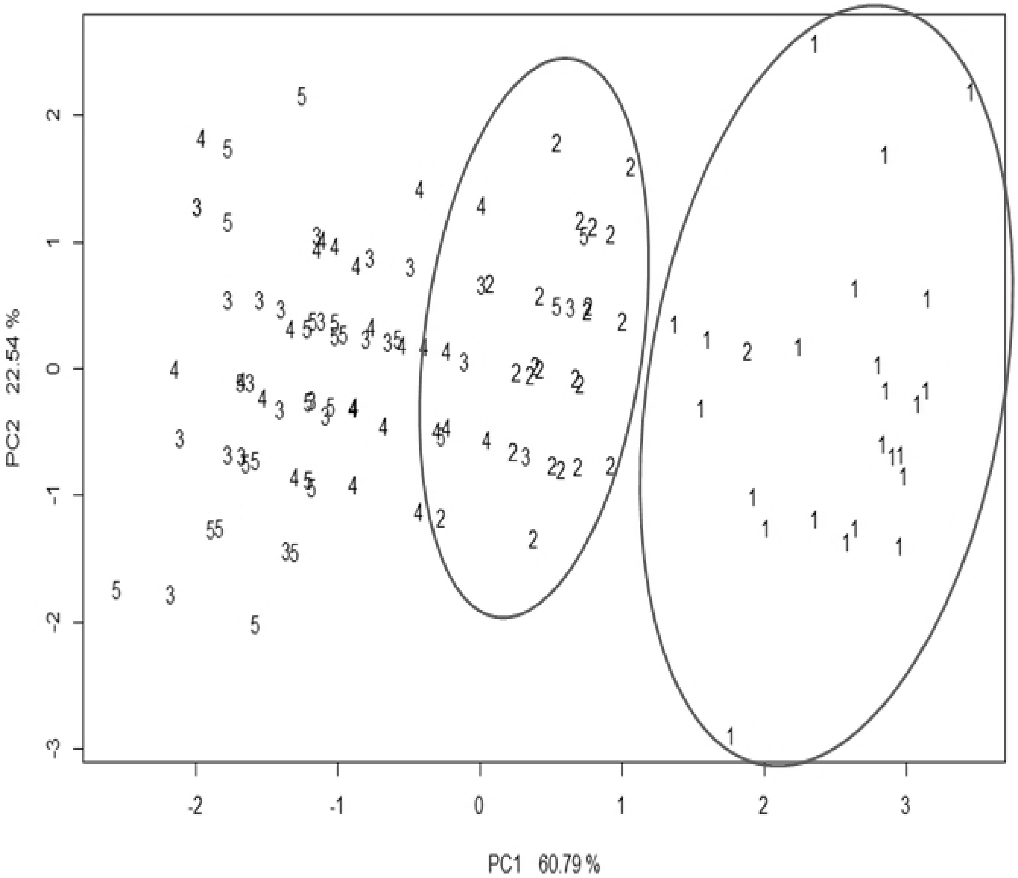

Figure 3: PCA result for the samples of ambient air collected at 5 control points localized around the LOTOS Group S.A. petroleum plant. Measurements were carried out with the electronic nose prototype.

Table.1 Cross-validation supported LDA classification of the ambient air samples collected around the LOTOS Group S.A. petroleum plant. Measurement data for classification were obtained with the electronic nose prototype.

	P1	P2	P3	P4	P5
P1	23	3	0	0	0
P2	1	21	2	0	1
P3	0	0	14	5	8
P4	0	0	3	13	5
P5	0	0	5	6	10

Figure 4 illustrates the PCA results for the samples of ambient air collected in a vicinity of the petroleum plant when the measurements were carried out with the electronic nose of Fast GC-type – HERACLES II. Also in this case on the two-dimensional plane there are three characteristic clusters of points corresponding to the sampling locations. However, separation of these three clusters is more distinct as compared to Figure 3. It is the evidence of better sample discrimination ability with respect to odour comparing to the electronic nose prototype.

Table 2 shows a matrix with correct classifications of the ambient air samples collected around the petroleum plant when the investigations were carried out with the electronic nose of Fast GC-type – HERACLES II. The classification was carried out with the LDA classifier and the cross-validation method. 94.2% of the samples collected from the control points were correctly classified. The biggest number of correctly classified samples was 24 and they came from the point P1. In the remaining cases the number of correctly classified samples were as follows: 24 for the point P2, 22 for the point P3, 21 for the point P4 and 22 for the point P5. Only in case of the control point P1 correctness of classification was 100%.

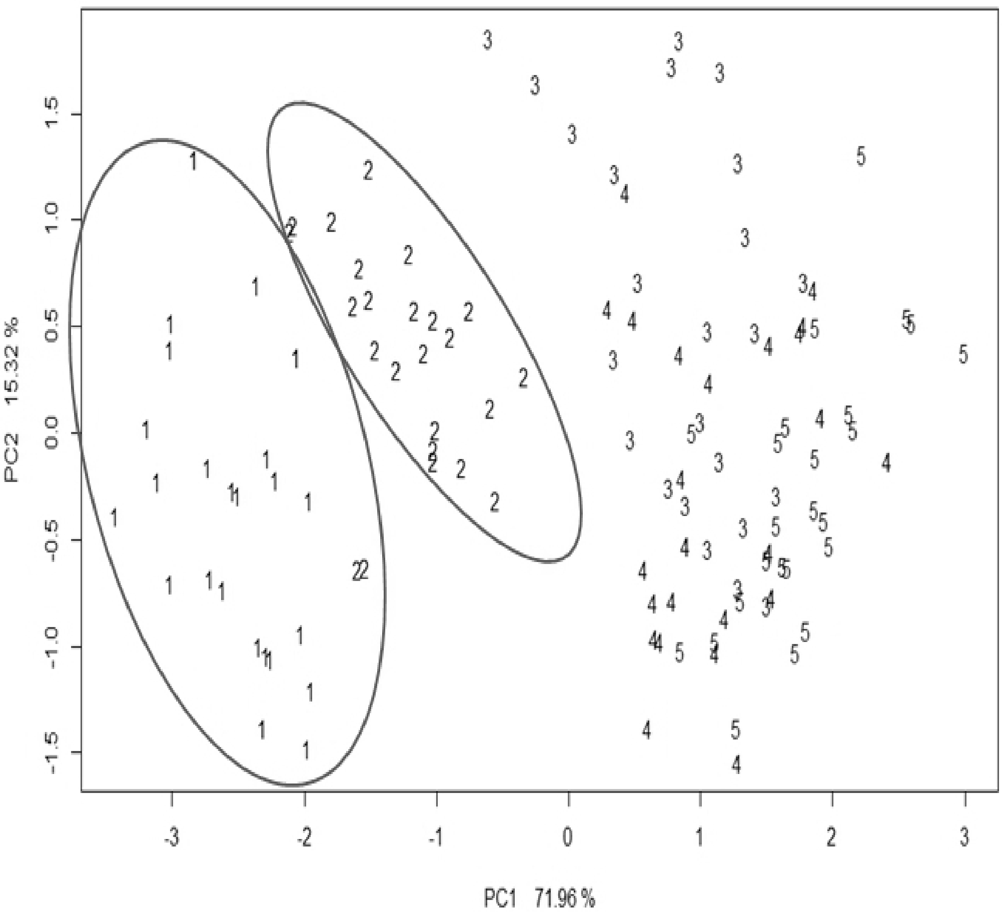

Figure 4: PCA result for the samples of ambient air collected at 5 control points localized around the LOTOS Group S.A. petroleum plant. Measurements were carried out with the electronic nose of Fast GC-type – HERACLES II.

Table. 2 Cross-validation supported LDA classification of the ambient air samples collected around the LOTOS Group S.A. petroleum plant. Measurement data for classification were obtained with the electronic nose HERACLES II.

	P1	P2	P3	P4	P5
P1	24	0	0	0	0
P2	0	24	0	0	0
P3	0	0	22	1	0
P4	0	0	2	21	2
P5	0	0	0	2	22

4. Conclusions

The aim of investigation was discrimination and classification of the ambient air samples collected at 5 control points localized around the LOTOS Group S.A. petroleum plant. The investigation was focused on possibility of differentiation of the air samples containing odorants. Analyses were 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 commercial electronic nose of Fast GC-type – HERACLES II by Alpha MOS.
Based on classification of the ambient air samples collected in a vicinity of the petroleum plant it was observed that the biggest number of correctly classified samples originated from the control point P1, which according to the sampling personnel was characterized by odour nuisance. In case of the cross-validation supported LDA classification this value was equal 67.5% for the measurements performed with the electronic nose prototype and 94.2% for the measurements carried out with the electronic nose of Fast GC-type – HERACLES II. The investigations revealed superior detection abilities and correctness of classification of the ambient air samples in case of the electronic nose of Fast GC-type – HERACLES II. Nevertheless, the measurements performed with the electronic nose prototype were promising and showed its application potential in the investigated field. It should be emphasized that the data analysis of the prototype electronic nose downloaded the information from the sensors 7. In the case of a commercial electronic nose, the data downloaded from the first 15 chromatographic peaks from the two columns. If, treat each chromatographic peak (area) as a signal from a single sensor, then you can understand the advantage of the ability of the electronic nose detection built of chromatographic columns.

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