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APPLICATION OF ULTRAFAST GAS CHROMATOGRAPHY TO RECOGNIZE ODOR NUISANCE

Potentialities of ultrafast gas chromatography applied to periodical monitoring of odor nuisance originating from a municipal landfill have been examined. The results of investigation on classification of the atmospheric air samples collected in a vicinity of the landfill during winter and summer season have been presented. The investigation was performed using ultrafast gas chromatography of Fast/Flash GC type – HERACLES II by Alpha MOS. Data analysis employed principal component analysis (PCA) and linear discriminant function (LDA) supported with the cross-validation method. About 77% of the atmospheric air samples collected during winter season and ca. 87% of the samples collected during summer season were classified correctly. Based on a classification of the atmospheric air samples around the landfill, it can be observed that the biggest number of correctly classified samples originated from the directions characterized by odor nuisance. It was the NW direction during winter season and NE direction during summer season.

1. INTRODUCTION

Unfortunately, unpleasant odor (fetor, offensive odor) originating from industrial processes, landfills or sewage treatment plants is not yet monitored in Poland. Each year the institutions dealing with environmental protection collect increasing number of citizens' complaints on odor nuisance in big municipal agglomerations. Between 2006 and 2012, the contribution of the odor nuisance-related complaints increased from 34% to 66%, whereas its number increased more than twofold – from 396 to 869 [1, 2]. The complaints on odor nuisance can be caused by several types of factors including [3]:

- actual odor nuisance,
- too small distance between the source (odor emitter) and human inhabitants,

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- health hazard,
- lack of hermetic isolation or deodorization of odor nuisance sources,
- interest of the inhabitants in environmental protection.

Lack of the legal regulations defining admissible levels of odor/odorants concentrations as well as frequency of their exceeding necessitates a search for other ways of recording and monitoring of this component of atmospheric air. A source of information on the properties of particular odor can be analyses of volatile organic compounds (VOC) performed via instrumental techniques – chromatographic and electronic nose ones [4–7]. The instrumental analysis of gas samples takes advantage of two main approaches. The first one consists in identification of volatile odor compounds using gas chromatography (GC) [8, 9], the second one is based on comprehensive analysis of gas mixture without separation into particular components using electronic nose [10–13]. The electronic nose is defined as an analytical tool intended for fast identification and discrimination of odor substance mixtures thanks to imitation of human sense of smell. This goal is achieved by utilization of different types of chemical sensors, which upon interaction with gas mixture generate characteristic odor profile constituting so called fingerprint of the investigated mixture [14]. Odorant concentrations can also be investigated with the electronic nose instrument based on the technology of ultrafast gas chromatography. This device combines the advantages of gas chromatography with the pros of electronic nose instruments. The electronic nose instruments are equipped with a set of chemical sensors which allow only comparison of volatile fraction of samples without determination of their composition, whereas gas chromatographs enable detailed composition analysis of given sample without determination of volatile fraction profile. Combination of these two techniques during a single analysis makes it possible to obtain information on both composition of investigated samples and volatile fraction profiles. Hence, one acquires complete information on similarity of a given sample to the reference sample [15–17]. HERACLES II system allows research including: comparison of sample odor, fast characteristics of chemical composition of samples, determination of food product expiry date and monitoring of food spoiling processes, monitoring of environmental odor nuisance, evaluation and monitoring of environment based on volatile fractions analysis, quality evaluation and identification of botanic/geographic origin of food products and semi-products as well as identification of forged products.

The main cause of odor nuisance in the Tri-City region (Gdańsk, Sopot, Gdynia) is emission of volatile compounds characterized by unpleasant odor from petroleum plants, phosphorous fertilizer plants, landfills and sewage treatment plants. Due to lack of odorants, concentrations and potential odor nuisance monitoring in this region there is an idea to verify if ultrafast gas chromatography can be successfully utilized to discriminate between the atmospheric air samples collected at the place where people reported odor nuisance and the samples collected at the sites where no complaints were acknowledged.

The paper presents the results of investigation on classification of atmospheric air samples collected in a vicinity of the municipal landfill with respect to odorants concentrations.

2. MEASUREMENT SET-UP

The measurement set-up consisted of three main elements: 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. The main elements of these systems were two chromatographic columns characterized by different polarity of stationary phase (non-polar MXT-5 and medium-polarity MXT-1701) and two detectors of the FID type. The length of each column was 2 m. Surface area of chromatographic peaks was utilized in analysis. A single analysis lasted 90 s.

2.1. RESEARCH METHODOLOGY

Investigation of air quality with respect to odor nuisance was performed with the air samples collected within 2 km distance around the landfill along four directions (NE-60°, SE-120°, SW-240° and NW-300°). Localization of the air sampling points around the landfill is illustrated in Fig. 1.

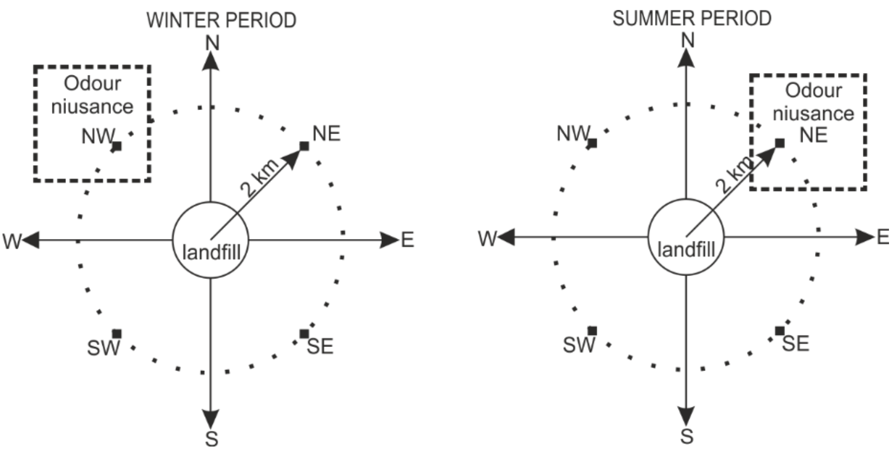

Fig. 1. Map of the municipal landfill with the points of collection of atmospheric air samples

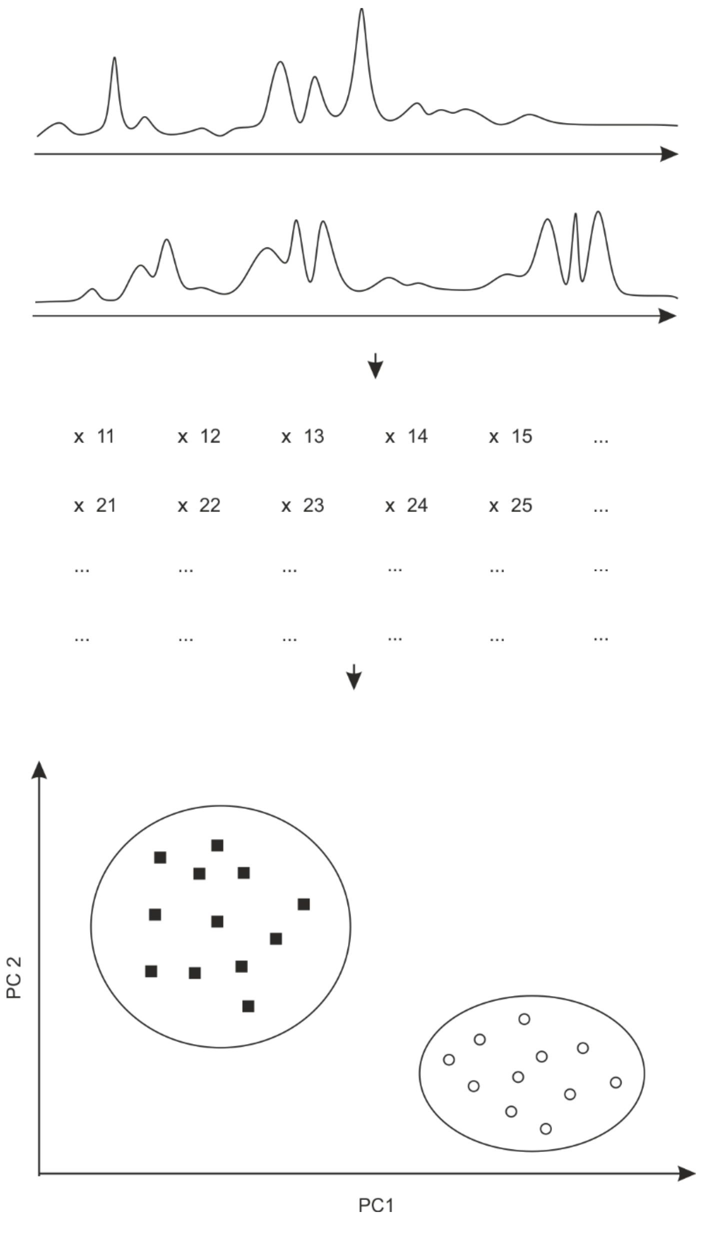

Fig. 2. Schematic procedure of visual evaluation
of data analysis using ultrafast gas chromatography

The samples were collected during two periods: winter (the turn of January and February) and summer (the turn of August and September) ones. Each day 4 samples were collected along the aforementioned directions and within the aforementioned distance from the landfill. Selection of the sampling periods was connected with the complaints (on odor nuisance) of the inhabitants of the housing estates neighbouring with the landfill along the NW direction during winter season and along the NE direction during summer season. The atmospheric air samples collected along the other directions (depending on sampling period) were treated as the reference samples as no complaints on odor nuisance were acknowledged in these directions. There was no precipitation during the sampling periods. The samples were collected into the Tedlar bags (SKC Inc., USA) of 5 dm^3 volume using a device called lung sampler, which was designed and built in the Department of Analytical Chemistry of Gdańsk University of Technology. The total of 60 atmospheric air samples were collected around the landfill (4 collection points×5 days×3 repetitions).

Table 1

Organic compounds detected around the municipal landfill

Group	Compound	Group	Compound
Aromatic hydrocarbons	benzene	Halogenated hydrocarbon	1-chloro dodecane
	toluene	Organic acids	acetic acid
	ethylbenzene		butyric acid
	propylbenzene	Aldehydes	nonanal
	butylbenzene		decanal
	styrene		undecanal
	o-xylene		dodecanal
	m-xylene		benzaldehyde
	p-xylene	Ether	caprylic ether
	p-cymene	Ester	ethyl acetate
	1,3,5-trimethylbenzene	Alcohol	1-butanol
	1,2,4-trimethylbenzene	Terpenes	α-pinene
Ketones	2-butanone		camphene
	acetophenone		D-limonene
Aliphatic hydrocarbons	butane		3-caren
	nonane	Organic sulfur	dimethyl disulfide
	undecane	Amine	dimethylamine
	dodecane		
	tridecane		
	pentadecane		

Classification of the atmospheric air samples with respect to the sampling points (thus different odor nuisance) utilized the linear discriminant analysis (LDA) method. The goal of the LDA is to extract from the training set the suitable subsets which are characterized by desired feature. In the next step, new data (testing set which does not belong to the training set) are assigned to particular subsets. Additional application of the cross-validation method allows treating the entire data set as the training set and testing set, thus classification takes less time as there is no need to work on two sets. The principle of cross-validation method in LDA classification has been described in the previous papers [18, 19]. Principal component analysis was utilized for visual evaluation of an ability of discrimination between the air samples originating from the places with odor nuisance and the places without it. The method of principal component analysis allows analysis of multidimensional data due to reduction of their multidimensionality. It is possible due to the fact that the PCA algorithm analyses distribution of data variation. Then it finds new, mutually perpendicular directions in space, which allow maximum exemplification of this variation. The undisputed advantage of the PCA method is a possibility of visualization of results using two- and three-dimensional plots, the axes of which are the principal components found by the algorithm. These plots show clusters representing the objects of similar properties. Classification of the atmospheric air samples with respect to their odor nuisance was performed using LDA employing free R software being a part of Free Software Foundation (Boston, MA, USA). Figure 2 shows schematically how visual plots allowing discrimination between the samples are obtained through the statistic-chemometric analysis from chromatographic data (surface area of peaks) via creation of vector matrix. Table 1 lists the compounds that were detected around the municipal landfill.

3. RESULTS AND DISCUSSION

Figure 3 presents the PCA results for the atmospheric air samples collected in a vicinity of the landfill during winter season.

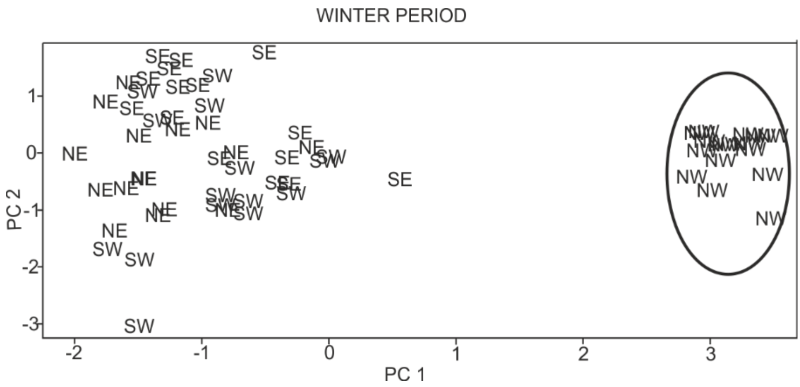

Fig. 3. PCA result for the atmospheric air samples collected during winter season from four directions localized in a vicinity of the municipal landfill

It can be seen that on the two-dimensional plane there are two point clusters attributed to the places of air sampling. One cluster corresponds to the samples collected from the NW direction, being a source of odor nuisance complaints. The other one represents the remaining directions, from which the atmospheric air samples had been collected. This cluster corresponds to the air samples collected from the places, where no complaints on odor nuisance were acknowledged. Hence, application of PCA allows discrimination of the samples collected from various places differing in odor nuisance.

Table 2 presents a matrix with the results of cross-validation supported LDA of the atmospheric air samples collected in a vicinity of the landfill during winter season. 76.7% of the samples from the selected directions were classified correctly. The biggest number of correctly classified samples was equal to 15 and originated from the NW direction. In the remaining cases the following number of samples were classified correctly: 11 from the SE direction, 10 from the NE as well as from the SW direction. As far as the NW direction is concerned, characterized by odor nuisance complaints, correct classification amounted 100%. In the case of LDA classification performed exclusively on the training set (without cross-validation method), the correct classification level was 88.3%.

Table 2

LDA classification of the samples of atmospheric air[a]

Cross-validation method – 76.7%				
	NE	SE	SW	NW
NE	10	2	1	2
SE	3	11	1	0
SW	0	1	10	4
NW	0	0	0	15
Without cross-validation method – 88.3%				
	NE	SE	SW	NW
NE	12	2	1	0
SE	1	14	0	0
SW	0	1	12	2
NW	0	0	0	15

[a]Samples collected in a vicinity of the municipal landfill during winter season. Measurement data for classification were obtained with the electronic nose HERACLES II.

Figure 4 presents the PCA results for the atmospheric air samples collected in a vicinity of the landfill during summer season. Also in this case, the two-dimensional plane reveals two distinct point clusters attributed to the places of samples collection. One of the clusters corresponds to the samples collected from the NE direction, where odor nuisance complaints were recorded during that season. The other cluster represents the remaining directions of the atmospheric air samples collection. This region corresponds to the air samples collected from the places, where no complaints on odor nuisance were recorded.

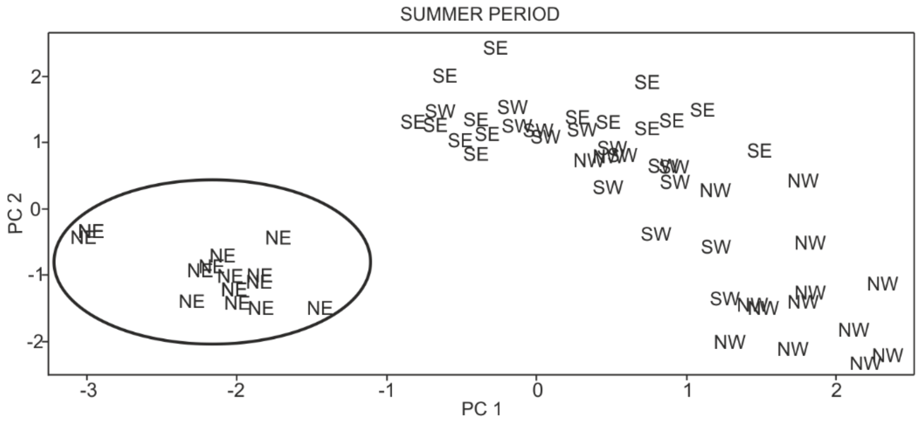

Fig. 4. PCA result for the atmospheric air samples collected during summer season from four directions localized in a vicinity of the municipal landfill

Table 3

LDA classification of the samples of atmospheric air[a]

Cross-validation method – 86.7%				
	NE	SE	SW	NW
NE	15	0	0	0
SE	1	12	2	0
SW	0	1	12	2
NW	0	1	1	13
Without cross-validation method – 95.0%				
	NE	SE	SW	NW
NE	15	0	0	0
SE	1	14	0	0
SW	0	0	14	1
NW	0	0	1	14

[a]Samples collected in a vicinity of the municipal landfill during summer season. Measurement data for classification were obtained with the electronic nose HERACLES II.

Table 3 presents a matrix of correctly classified atmospheric air samples collected in a vicinity of the landfill during summer season. The classification was performed with the cross-validation supported LDA. 86.7% of the samples from the selected directions were classified correctly. The biggest number of correctly classified samples was equal to 15 and originated from the NE direction. In the remaining cases the following number of samples were classified correctly: 13 from the NW direction, 12 from the SE as well as from the SW direction. As far as the NE direction is concerned, characterized by odor nuisance complaints, correct classification amounted 100%. In the case of LDA classification performed exclusively on the training set (without cross-validation method) the correct classification level was 95.0%.

The possibility of receiving a higher odor nuisance values of correctly classified atmospheric air samples using the LDA method during the summer is associated with such parameters as temperature and relative humidity. In this period, these values are higher than in winter. It also causes the development of chemical and biological processes and ultimately contributes to the release of more amount of odor compounds. Moreover, the differentiation of atmospheric air samples and efficient working of the electronic nose is easier to obtain.

4. CONCLUSIONS

Based on a classification of the atmospheric air samples around the landfill, it can be observed that the biggest number of correctly classified samples originated from the directions characterized by odor nuisance. It was the NW direction during winter season and NE direction during summer season. Moreover, it was observed that during the winter season there was lower number of correctly classified samples as compared to the summer season. In the case of cross-validation supported LDA, this number was 76.7% during winter season and 86.7% during summer season. The ability of discrimination of the atmospheric air samples collected in a vicinity of the landfill from respective direction is a basis of the electronic nose instrument training and thus creating a database for correct interpretation of the obtained results. Commercially available electronic nose HERACLES II would be a perfect tool for such task, especially for periodical monitoring. We hope the content of the paper is valuable as far as scientific and application aspects are concerned and that it may somehow contribute to broader implementation of the electronic nose technique in this field.

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