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Analysis of Odour Interactions in Model Gas Mixtures using Electronic Nose and Fuzzy Logic

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Measurement and monitoring of air quality in terms of odour nuisance is an important problem. Although the source of these nuisances is different (e.g. wastewater treatment plants, municipal landfills), their common feature is that they are a complex mixture of odorants with different odour thresholds. An additional problem is occurrence of the odour interactions between mixture components. From a practical point of view, it would be most valuable to directly link the odour intensity with the results of analytical air monitoring. This would allow the on-line odour monitoring using electronic noses, which perform a holistic analysis of the gas mixtures composition (like olfactometric methods). The paper presents the possibility of application of fuzzy logic to determine the odour intensity and indicate odour interactions in model, five-component gas mixtures (acetone, α-pinene, formaldehyde, toluene and triethylamine) using electronic nose prototype. As the results of the studies, it was found the electronic nose prototype along with the fuzzy logic pattern recognition system can be successfully used for this application. The results obtained using fuzzy logic are consistent with sensory analysis results in 80%.

1. Introduction

Nowadays, more and more frequent problem of air pollution is the occurrence of odour nuisance. Although the source of these nuisances is different (e.g. wastewater treatment plants, municipal landfills), their common feature is that they are a complex mixture of odorants with different odour thresholds (Fang et al., 2012, Gębicki et al., 2014a). Measurement and monitoring of air quality in terms of odour nuisance is an important problem. At present, odour concentrations are determined by using the standard method EN 13725:2003 „Air Quality - Determination of Odour Concentration by Dynamic Olfactometry". However, from a practical point of view, it would be most valuable to directly link the odour intensity with the results of analytical air monitoring. this solution is best suited to devices called electronic noses. These devices perform a holistic analysis of the gas mixtures composition, without the separation and identification of its individual components (just like olfactometric methods).

One of the advantages of olfactometry is taking into account the interactions (synergy, neutralization, masking) between odour mixture components. Synergism is mutual amplification of two or more stimuli. Masking is usually a substitution of an unpleasant odour with another, more pleasant one. Neutralization, also called compensation, is typically interpreted as activity of additional component of the odorants mixture, which leads to disappearance of odour or to distinct decrease in its intensity.

Previous studies have shown that these interactions can be also described using the electronic nose technique (Szulczyński et al., 2017). In presented studies fuzzy logic was used as the data analysis method. Fuzzy logic turned out to be very useful in engineering applications, where classical logic classifying only according to the truth/false criterion can not effectively cope with many ambiguities and contradictions. It finds many applications, among others in electronic control systems (machines, vehicles and vending machines), data mining tasks or in the construction of expert systems. Therefore, the use of fuzzy logic to analyze the electronic nose data is justified and purposeful.

1.1 Odour interaction theoretical models

Investigations on odour interactions have been carried out for many years, however, they have not led to explanation of the mechanisms of these processes so far. Many theoretical models have been developed over the years. They describe dependence between the odour intensity of air mixture (containing pollutants) and the odour intensity, which would be exemplified if these pollutants were present separately. A multitude of these models engulfs Zwaardemaker, Berglund, Patte and Laffort or U-models. However, the investigated objects are usually mixtures containing two or three types of odorants. Real odorant mixtures are much more complex. Several mathematical models have been developed to predict the quantitative interactions in binary mixtures on the basis of perceived odor intensities of the unmixed components. They are presented in the Table 1.

Table 1: Examples of theoretical models (I – odour intensity; k,α_{AB}, α_U – empirical constants specific to a given pair of substances)

Model	Authors
$I_{AB} = \sqrt{I_A^2 + I_B^2 + 2I_AI_B\cos\alpha_{AB}}$	Zwaardemaker
$I_{AB} = k \cdot (I_A + I_B)$	Berglund, Lindvall
$I_{AB} = I_A + I_B + 2\sqrt{I_AI_B}\cos\alpha_U$	Patte, Laffort

The most universal model was proposed by Zwaardemaker. It depends on vector addition of the odour intensities of mixture components. For example, for a ternary mixture, the model form is as follows:

$$I_{ABC}^2 = I_A^2 + I_B^2 + I_C^2 + 2 \cdot (I_AI_B\cos\alpha_{AB} + I_BI_C\cos\alpha_{BC} + I_AI_C\cos\alpha_{AC}) \quad (1)$$

The interaction coefficient (α) in the Zwaardemaker equation (1) is approximately constant for the given pair of components of the mixture. The literature shows that its value is generally in the range of 102-115° (Yan et al., 2015). Determining interaction coefficients for each pair of compounds is relatively time-consuming.
Another proposed model is the Patte and Laffort model:

$$I_{ABC} = \sqrt{I_A^2 + I_B^2 + I_C^2} \quad (2)$$

It adopts Euclidean additivity of particular components of the mixture when present separately (Laffotrt, Dravnieks, 1982).

1.2 Electronic noses

For many years, scientists have been trying to create devices imitating human senses. Already at the beginning of the 20th century, equivalents of the human sense of sight and hearing were created. Recently, the artificial equivalents of sense of smell and taste have become more and more popular: electronic noses and tongues. E-noses have found a special position in analytical chemistry, where they successfully replace human senses in many areas of human activity: e.g. environmental monitoring (Capelli et al., 2014, Lewkowska et al., 2016) or medical applications (Thaler, Hanson, 2005). Gardner and Bartlett coined the term "electronic nose" in 1988. They later defined it as "an instrument which comprises an array of electronic chemical sensors with partial specificity and appropriate pattern recognition system, capable of recognizing simple or complex odors"(Gardner, Bartlett, 1994). This definition is valid until today. The electronic nose in its construction consists of four main systems: sampling system, detection system, data processing system and pattern recognition system. The description of the systems is shown in the Figure 1.
E-noses in their functioning resemble human sense of smell - sensors are an analogue of the olfactory receptors in the epithelium of the nose. They convert the chemical information into a analytically useful signal. In the next step, this signal is sent to the pattern recognition system, which in the case of a human being is the brain, and in the case of an e-nose the appropriate mathematical-statistical algorithm. The most commonly used data processing methods are: principal component analysis (PCA), partial least square regression (PLS) and artificial neural networks (ANN). The use of artificial neural networks is the most intentional, due to the fact that the architecture of the artificial neural network is intended to reflect the action of the human brain (Wilson, Baietto, 2009).

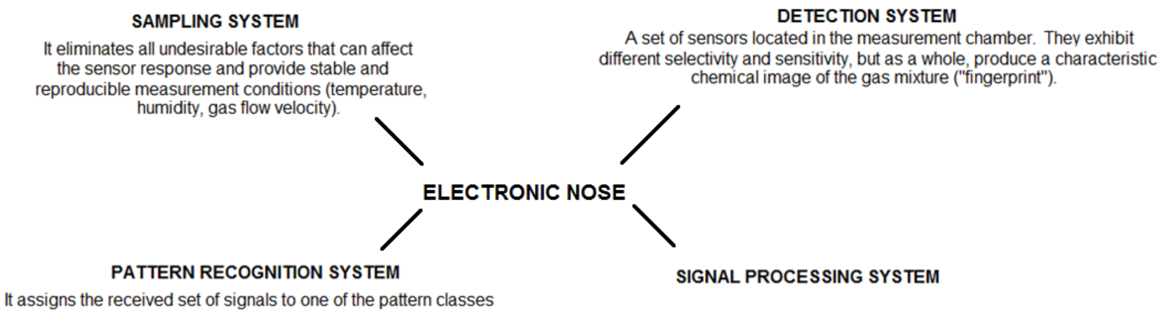

Figure 1: Electronic nose system description.

1.3 Fuzzy logic

Very interesting approach in the field of e-nose data analysis is fuzzy logic. L. Zadech introduced the basis of fuzzy sets theory. Classical logic system is based on the two values, mostly represented by 0 and 1, or true and false. The boundary between them is unambiguously defined and unchanging. Fuzzy logic is an extension of the classical approach to approach closer to human brain. It introduces additional values between standard 0 and 1. this action is called blurring. It gives the opportunity to come up with values between this interval (eg, almost false, half truth). In the case of non-fuzzy sets, the membership function is rectangular. It is set to 0 (no membership in the set) or one (membership in the set). In case of fuzzy sets, other membership functions, such as trapezoid, triangular, gaussian, sigmoidal are used. In this work, trapezoid functions were used.
Fuzzy logic allows a fuzzy description of real systems and is an alternative to describing systems using classical binary logic. From this point on, the methods developed on the basis of the theory are of great interest. Their development goes hand in hand with the growing number of applications of fuzzy logic in practice. It is also used in electronic nose data analysis algorithms. The proposed scheme of using fuzzy logic to estimate the odour intensity using e-nose is presented in the Figure 2.

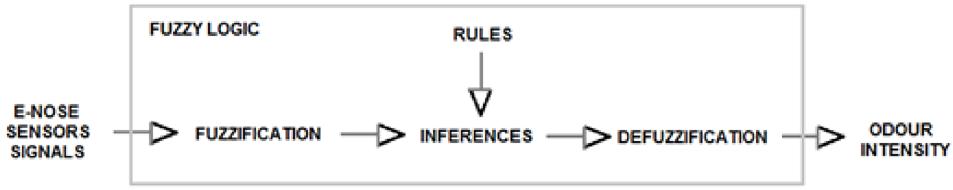

Figure 2: Scheme of using electronic nose combined with fuzzy logic to estimate the odour intensity

An example of defined fuzzy set for the e-nose sensor signal values and a set of applied rules based on conjunctive operations was described by Szulczyński et al. (2018).

2. Experimental

2.1 Reagents and chemicals

For determining the usefulness of the fuzzy logic algorithms to determine the odour interactions using the electronic nose, 32 aqueous five-components solutions of odorous compounds: acetone, *α*-pinene, formaldehyde, toluene and triethylamine were prepared. Concentrations of compounds used in mixtures preparation are presented in Table 2. Solutions were prepared to perform sensory and electronic nose analysis. The chemicals (Sigma-Aldrich) were of analytical reagent grade.

Table 2: Concentrations of compounds used in mixtures preparation

Mixture component	Concentration A [ppm v/v]	Concentration B [ppm v/v]
acetone	200	400
α-pinene	0.1	0.2
formaldehyde	200	400
toluene	0.5	1.0
triethylamine	1.0	2.0

Solutions were prepared by mixing five components using all 32 concentration combinations (2^5). The concentrations of substances have been selected in such a way that their odour intensity values are between 0.4 and 1.4. The odour intensity of prepared samples was determined in three ways:

- using a sensory panel (sensory analysis),
- using an electronic nose combined with fuzzy logic,
- using theoretical model (2).

For easier interpretation of the results, the prepared samples were coded as shown in the Figure 3.

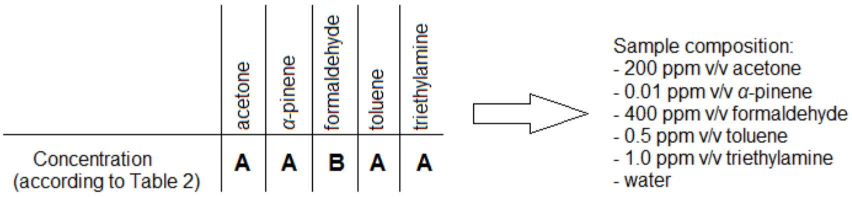

Figure 3: Coding scheme for sample names

2.2 Sensory and electronic nose analysis

Sensory evaluation of odor intensity of prepared mixtures was carried out by 4 persons, selected according to the procedure described by Gębicki et al. (2014b). Each member of the panel was responsible for assigning the appropriate odour intensity value to a given sample using a 7-step scale described in German Standard VDI 3940.Electronic nose analysis were carried out using an e-nose prototype equipped with eight sensors (Table 3).

Table 3: Types of chemical sensors used to build an electronic nose prototype.

Sensor type	Manufacturer / Model	Target gases
Photoionization	ION Science / MiniPID	VOCs
Electrochemical	Figaro / FECS44-100	ammonia
Electrochemical	Figaro / FECS50-100	hydrogen sulphide
Metal Oxide Semiconductor	Figaro / TGS2600	air contaminants
Metal Oxide Semiconductor	Figaro / TGS2602	VOCs and odorous gases
Metal Oxide Semiconductor	Figaro / TGS2603	air contaminants (triethylamine, mercaptanes, etc.)
Metal Oxide Semiconductor	Figaro / TGS823	organic solvent vapours
Metal Oxide Semiconductor	Figaro / TGS8100	air contaminants (hydrogen, ethanol, etc.)

E-nose experimental setup is presented in Figure 4. Synthetic air flow through a system at a constant flow rate of 300 cm^3min^{-1} (controlled by a mass flow controller). The dynamic headspace analysis of prepared samples was conducted. By changing the position of the valve V1, the air flowed through the sample to the measurement chamber. The electronic nose worked in the stop-flow mode: the sample flow time was 60 seconds. After closing V2 valve, the gaseous sample was stopped in the sensors chamber for 30 seconds. After this time the purified air was returned to the measurement chamber for regeneration of the sensors. Signals from the sensors were recorded using an ADC (Simex SIAi-8). Data analysis and other calculations were performed using RStudio Desktop (v. 1.0.143) software.

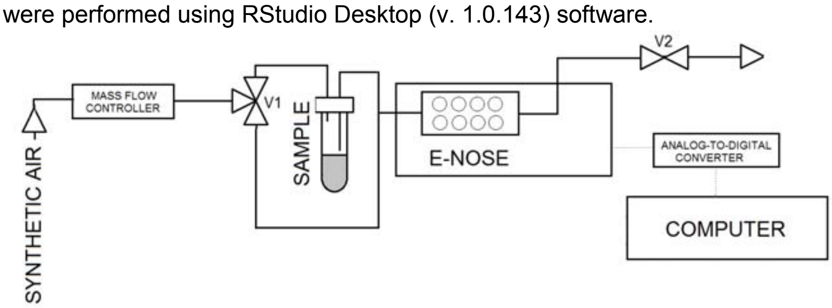

Figure 4: Electronic nose experimental setup

3. Results and discussion

In Figure 5 are presented odour intensity values of tested samples determined using: theoretical model (2), sensory analysis and electronic nose combined with fuzzy logic. Values which are statistically different from the theoretical are marked with a darker color. A statistical U Manna-Whitney test was utilized to find the measurement points, which differed statistically from the theoretical values.

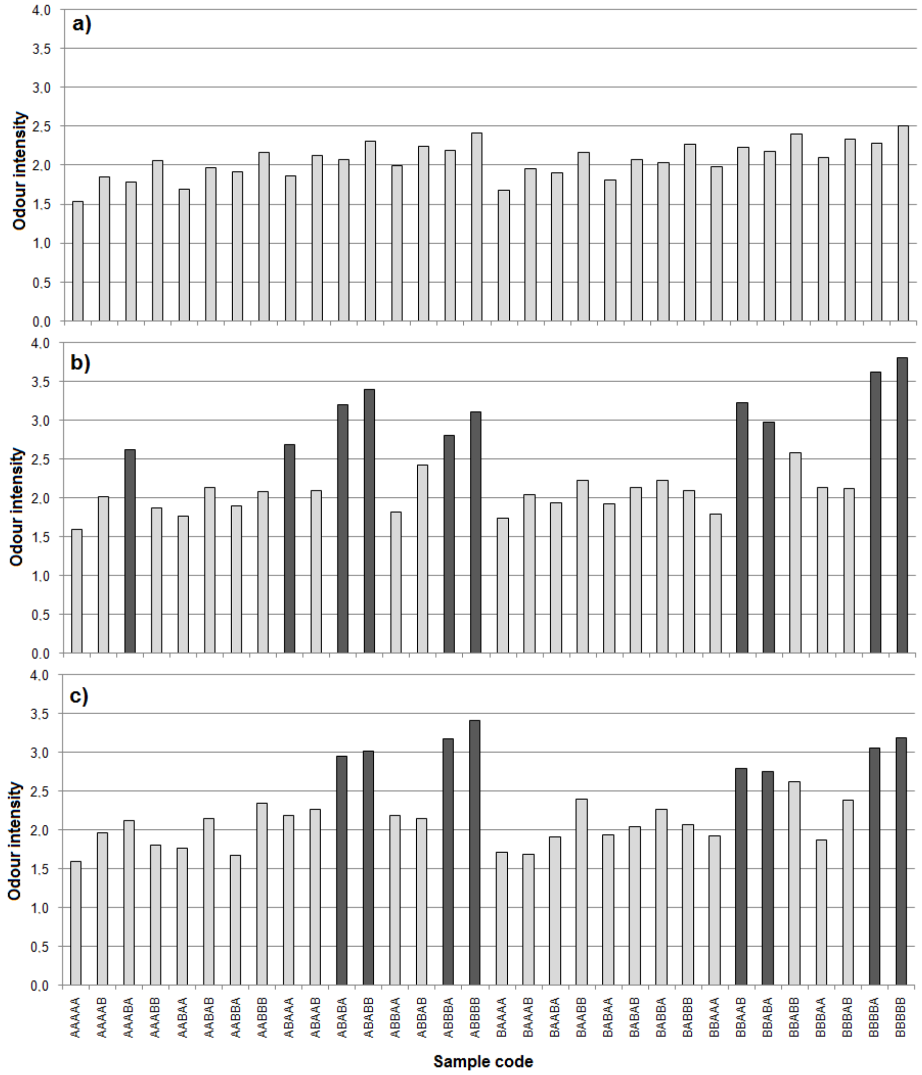

Figure 5: Odour intensities of tested samples determined using (a) theoretical model, (b) sensory panel and (c) electronic nose combined with fuzzy logic.

As a result of the conducted studies, it was found that both: the sensory panel and the electronic nose analysis were found odour intensity values statistically different from the theoretically predicted. This fact indicates the presence of odour interactions in the tested five-component gas mixtures and the imperfections of predicting the odour interactions by used theoretical model (2). Both: sensory and e-nose tests have been found to enhance the perceived odour intensity (synergy effect). It should be noted that the odour interactions were observed only in the case of samples with a higher concentration of α-pinene and toluene. This may be due to the characteristic, pleasant smell of toluene and the pine, resinous scent of α-pinene, which makes the smell feel more pleasant. Similar results were also observed in previous studies (Szulczyński et al., 2017). The results obtained using the sensory panel indicate the presence of 10 distinctive values, which is about 31% of tested samples. However, results obtained using an electronic nose combined with fuzzy logic are consistent with sensory panel sensations in 80% (8 interactions indicated by e-nose system/10 interactions indicated by sensory panel). Correlation between sensory analysis results and electronic nose measured values are is presented in Figure 6.

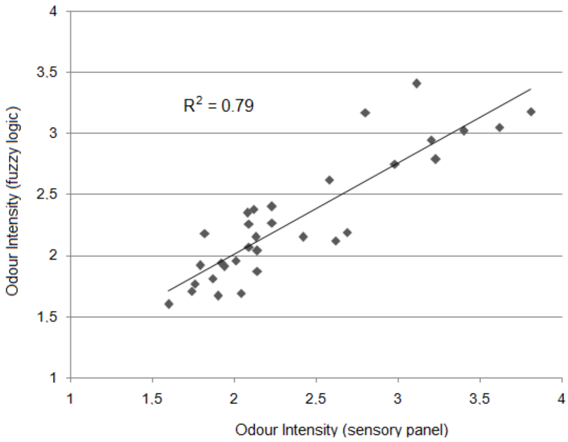

Figure 6: Correlation plot of obtained results

4. Conclusions

Correlation coefficient for this two groups of results is equal to 0.79, which indicates a very good positive correlation between the obtained results. Such a high value of coverage of the results allows to conclude that using the electronic nose to determine odour interactions in the tested five-components gas mixtures together with fuzzy logic is justified and purposeful. This fact gives possibility to use electronic noses as devices that can replace traditional olfactometers in the future, mainly due to the significantly shorter analysis time and automated measurement capabilities.

Acknowledgments

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