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GC-NN SYSTEM ESTIMATING ODOUR QUALITY

JOANNA KOŚMIDER, BEATA KRAJEWSKA

Technical University of Szczecin, Institute of Chemical Engineering and Environmental Protection Processes,
Laboratory for Odour Quality of the Air,
Aleja Piastów 42, 71-065 Szczecin, Poland

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SYSTEM GC-NN OCENIAJĄCY JAKOŚĆ ZAPACHU

Zbadano możliwość wykorzystania chromatografu gazowego (GC) i sieci neuronowych (NN) do rozróżniania próbek ze względu na intensywność (*I*) i hedoniczną jakość (*H*) ich zapachu. Próbki powietrza były aromatyzowane olejkiem cytrynowym z czterema domieszkami. Wytypowano czternaście charakterystycznych punktów chromatogramów i zmierzono ich odległości od podstawy (h_1-h_{14}). Zbiór parametrów h_1-h_{14} (wejścia) i zróżnicowanych indywidualnych sensorycznych ocen *I* i *H* (wyjścia) pełnił funkcję zbioru treningowego dla NN. Potwierdzono możliwość rozróżnienia zapachowej jakości próbek położonych w pobliżu progu wykrywalności różnicy jakości zapachu na poziomie istotności około jedności z wykorzystaniem systemu GC-NN.

Summary

The possibility of applying gas chromatograph to air samples discrimination in regard to odour intensity and hedonic quality was examined. The air samples were aromatised with lemon oil and four admixtures. Fourteen distinctive points of a chromatogram were appointed and the distances from the points to a set basis were measured. The set of h_1-h_{14} parameters (inputs) and varied individual sensory estimations of *I* and *H* (outputs) was used as a training data set for NN. Possibility of discrimination of the odour quality of the samples situated close to the threshold of odour quality difference detectability was confirmed on the level of approximately one.

INTRODUCTION

The Environmental Protection Law legally binding from the 1st October 2001 says (Section II, Air Protection, Art. 86) that a competent minister for the environmental matters may define air quality standards and methods of air quality assessments [7]. The act will appoint admissible frequencies of exceeding of the acceptable odorants level. The acceptable odorants levels are to depend on the degree of the subjectively perceived nuisance. Features of odour quality, primarily odour intensity (weak/strong) and hedonic quality (pleasant/unpleasant) determine the nuisance. At the same time methods of monitoring the odour nuisance will be indicated. Elaboration of objective methods of monitoring is urgent.

Nowadays odour quality assessments are conducted with standardized sensory methods which consist in utilization of a representative group of people opinions. The opinions are

expressed employing standards and verbal, point or graphical scales. Conducting assessments under standard conditions allows for achieving high repeatability and reproducibility of results (e.g. estimations prevailing in the population or medians) [1, 2, 8-10].

Sensory measurements are time-consuming and expensive. They cannot be included in systems of air quality monitoring or permanent examination of raw materials and products quality.

Recently a possibility of applying an electronic nose (EN) becomes more and more feasible. EN is an analyser recognizing odour patterns in a way similar to biological olfaction. It can be applied in alimentary industry, medical diagnostics, crime detection and environmental protection. The analysers are equipped with appropriate sets of several-tens of sensors and data bases – pieces of information on activations of sensors induced by patterns [3]. The studied samples are classified on the basis of similarity of a distribution of sensors activations to the distributions available in a database. Electronic nose determines "what the sample smells like" (what its smell is similar to).

Hitherto attainable electronic noses do not perform any other functions of biological olfaction – they do not answer the question of "how the sample smells". In many cases it would be advantageous to enlarge EN databases with sets of sensory assessments of samples' odour quality, e.g. intensity and hedonic quality.

This paper refers to a first trial of examining the possibility of constructing an instrumental odour quality analyser. It could be applicable not only to environmental protection (monitoring the nuisance of odour appearing in the environment, emissions of odorants monitoring, deodorization efficiency assessments). It would facilitate controlling an odour compositions production in cosmetic and perfume industries, conducting food examinations, etc.

The subject of our research is a modified electronic nose called GC-NN system. In GC-NN system a gas chromatograph (GC) serves as a set of EN sensors. A neural network (NN) is trained to determine odour quality on the basis of selected features of a chromatogram. Results of sensory-chromatographic analysis of representative samples of polluted air form the training sets.

The process and effects of training a network prepared for assessments of odour intensity of air containing hexane, cyclohexane, cyclohexanol and cyclohexanon were examined before [5-6]. A set of approximately 1500 individual odour intensity assessments of samples of various pollutants concentrations was collected. Pollutants concentrations served as defining variables. Multilayer Perceptrons, with a number of inputs corresponding to the number of pollutants (concentrations as defining variables) and one output (odour intensity as the defined variable), were trained. The results of the research were considered as very promising.

The aim of this paper is preparing GC-NN system for a simultaneous determination of two odour quality features – intensity and hedonic quality (two defined variables). Samples of air containing mixtures of many odorants, including numerous unidentified compounds (volatile citrus oil components and admixtures) were utilized. A typical chromatograms interpretation (qualitative and quantitative analysis) was not conducted. Detector's signals – pieces of information varied in time – were considered as an equivalent of unspecific signals of EN sensors – varied in distance. Heights of selected distinctive points on chromatograms were considered as variables defining odour quality.

PURVIEW AND RESEARCH METHODOLOGY

The survey embraced:

- preparing air samples containing various quantities of citrus oil volatile components and four accessorily added compounds: acetone, ethanol, isopropanol and isoamyl acetate,
- collecting twelve independent sensory estimations of odour intensity and hedonic quality of each sample (defined variables),
- registering chromatograms under steady conditions of incomplete mixture's separation and determining the location of distinctive points (defining variables),
- utilization of results obtained from sensory-chromatographic analysis for NN trainings,
- determining possibilities of NNs within samples discrimination on the basis of odour quality features (odour intensity I, hedonic quality H).

The samples of the aromatised air were collected in foil bags. Air was passed through Rychter washer containing 2 cm^3 of citrus oil (room temperature, flow speed of 6 dm^3/h). The odorants were added with chromatographic syringes. Different amounts of acetone (0-10 μl), ethanol (0-16 μl), isopropanol (0-12 μl) and isoamyl acetate (0-7 μl) were added to the air samples. Some of the samples prepared in a way described above were diluted with pure air (approximately 5 or 20 times).

Sensory-chromatographic analyses of 56 samples were conducted during seven measurement sessions.

A group of twelve panelists took part in sensory estimations. The measurements took place in a well ventilated Laboratory for Odour Quality of the Air. There was at least a 15 minute-break between assessments of succeeding samples.

First three sessions were aimed to train the panelists (the results were not utilised during NN trainings).

Odour intensity was determined by employing n-butanole scale of standards – 10 aqueous solutions of NrB sequential numbers, prepared by gradually diluting the basic solution (standard of $NrB = 1$). Standards' concentrations were a geometric sequence of 20/7 quotient [2].

Individual odour detection threshold of n-butanol had been determined before each determination of a sample's odour intensity. The odour of the standards was successively evaluated, beginning with the most diluted standard ($NrB = 10$). The number ($NrB_{I=0}$) – a mean value of two succeeding standards' numbers (the first sensed and the last still odourless one) – was assigned to the odour detection threshold.

Examination of sample odour was conducted analogically, searching for the first standard which smells as strong as the sample (or stronger). The number (NrB) appointed to the sample was a number of a standard which smells as strong as the sample or a mean of the numbers of two standards indicated as "still fainter" and "already stronger'.

Odour intensity was calculated as a difference between numbers of the threshold standard and the standard appointed to the sample:

$$I = NrB_{I=0} - NrB$$

Hedonic odour quality of the samples was qualified with an unstructured scale – AB

section. Points A and B were described as "very, very unpleasant odour" and "very, very pleasant odour". The panelists were asked to indicate the point C on the section which would describe sample's location in relation to the ends of the section. The proportion of the sections:

$$H = AC/AB$$

was recognised as a numeral meter of hedonic odour quality.

Chromatographic analysis and sensory estimations of odour quality were conducted simultaneously. Chromatograph *Chromatron GCHF 18.3* and a pillar 2 metres long (diameter of 4 mm) were used. The remaining separation conditions are listed below.

Packing:	*Carbowax 20M* (20%)/*Chromosorb W NAW*,	60-80 mesh.
Temperature:	first isotherm	160°C, 5 min,
	heating	48°C/min,
	second isotherm	210°C, 5 min.
Carrying gas:	nitrogen.	

A typical chromatogram is shown in Figure 1. It was stated that the chosen conditions

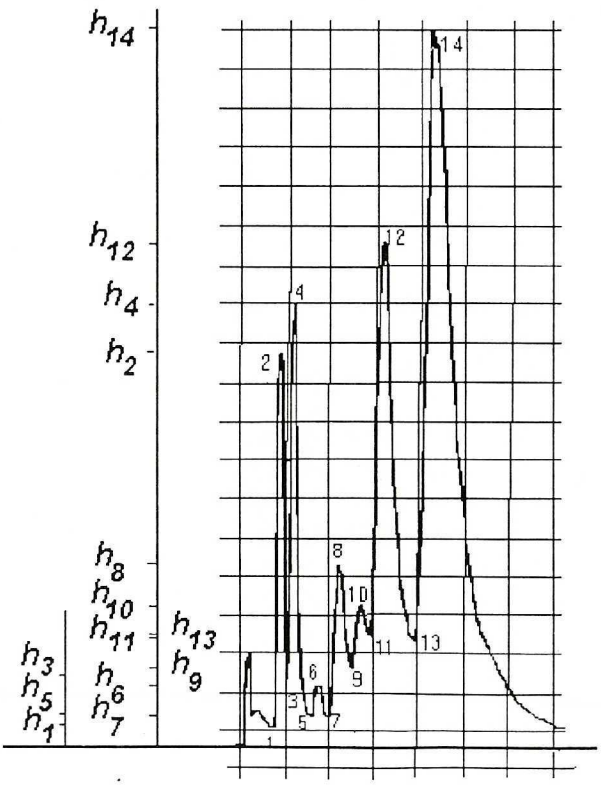

Fig. 1. Chromatogram of an aromatized air sample. Ilustration of the method of determining h_i height of fourteen characteristic points (minimum, maximum)

do not allow for a classical quantitive and qualitative analyses of samples' composition, but allow for achieving the intended aim. The obtained chromatograms can be declared for lines of a specific shape – "fingerprints" of the odorants mixtures. Chromatograms simplified to the shape of a broken line connecting 14 successive extreme points are compared in Figure 2 (example of five samples).

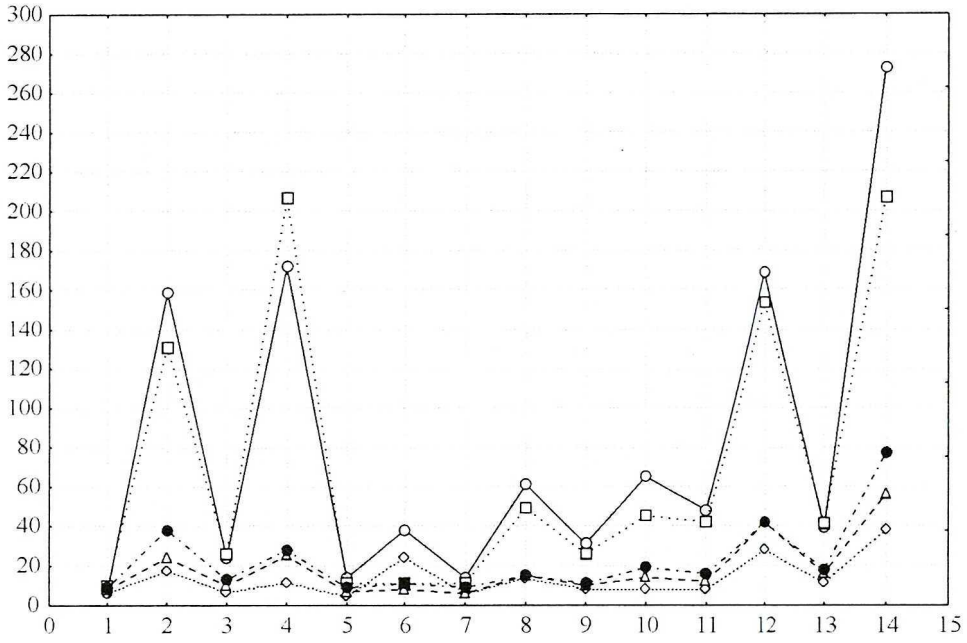

Fig. 2. Broken lines connecting fourteen characteristic points on chromatograms of five selected samples

Training sets consist of:

- fourteen defining variables h_1-h_{14}, i.e. the location of characteristic extreme points on chromatograms (see Figure 2: distances of the extreme 1–14 points from the basis),
- two defined variables, i.e. the results of sensory evaluations of both odour features (individual estimations of *I1* and *H1* of each samples) were applied during the trainings of the neural network prepared for determining odour intensity (*I2*) and hedonic quality (*H2*).

Network architecture and training algorithms were selected using *Intelligent Problem Solver,* available in *Statistica Neural Network* (StatSoft) program.

RESULTS

The results of sensory examinations of odour quality of 56 samples by twelve panelists are presented in Figure 3. The samples were lined up incrementally according to medians of individual hedonic quality assessments of odour. It ascertains that levels of both features are not intercorrelated. Moreover, it shows that the examined samples were characterised with a very low range of sensory features variability. Odour intensity of the examined samples was

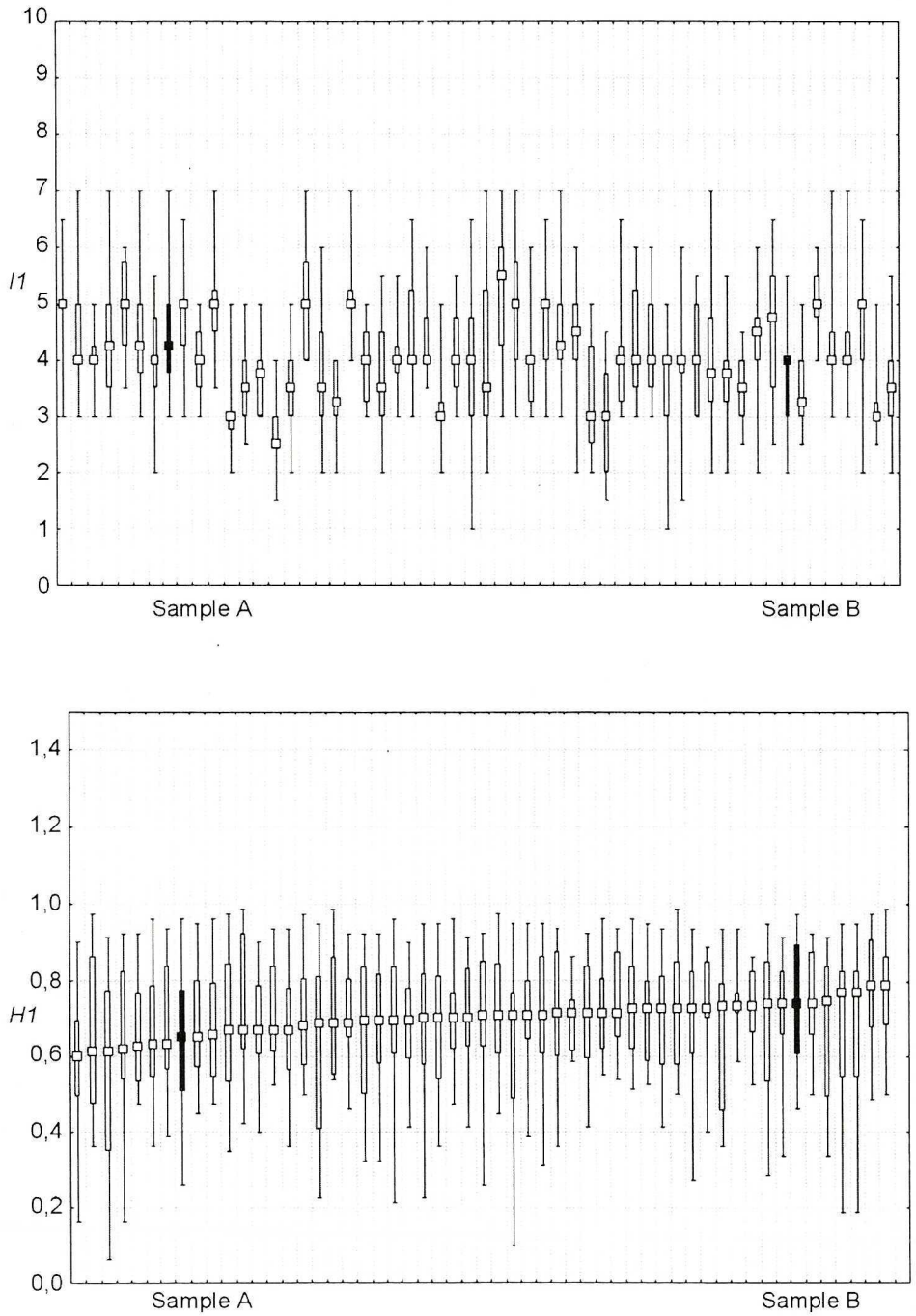

Fig. 3. Results of sensory estimations of samples odour intensity (*I1*) and hedonic quality (*H1*) arranged according to ascending median values $H1_{med}$

within the range of $I1_{med}$ = 2.5–5.5 and hedonic quality within a lower range of $H1_{med}$ = 0.6–0.8.

Taking into account a small precision of sensory evaluations (panelists' smell sensitivity variation) one should not expect a high level of differences significance between opinions on particular samples. Two samples A and B were selected out of a 56-sample set in order to obtain the least difference between values of individual hedonic quality medians and retain the possibility to discriminate the samples on a level of differences significance not lower than 0.86. A sample of values: $H1A_{med}$ = 0.65 and $H1B_{med}$ = 0.74 corresponds to this premise. A difference between sets of individual hedonic quality evaluations of the samples' odour was found on the level of significance of 0.86. Odour intensity of the same samples equalled $I1A_{med}$ = 4.25 and $I1B_{med}$ = 4.0. The difference between them was found on the level of significance of 0.96.

Taking account of the foregoing statements it was adjudged useful to check whether the collected sensory-chromatographic measurements results allow for an artificial neural network training to such a degree that it is able to discriminate two A and B samples on the basis of their chromatograms (h_1-h_{14} parameters, heights of 1–14 points).

Tab. 1. An excerpt of a set consisting of individual odour intensity and hedonic quality evaluations (defined variables: $I1$ and $H1$) and adequate parameters of chromatograms (defined variables: h_1-h_{14})

No.	Defining variables; h [mm] (inputs)														Defined variables (outputs)	
	h_1	h_2	h_3	h_4	h_5	h_6	h_7	h_8	h_9	h_{10}	h_{11}	h_{12}	h_{13}	h_{14}	$I1_{med}$	$H1_{med}$
1	7	86	16	47	9	140	28	52	26	27	24	118	32	154	4,5	0,663
2	7	86	16	47	9	140	28	52	26	27	24	118	32	154	6,0	0,763
3	7	86	16	47	9	140	28	52	26	27	24	118	32	154	3,0	0,863
4	7	86	16	47	9	140	28	52	26	27	24	118	32	154	4,5	0,375
5	7	86	16	47	9	140	28	52	26	27	24	118	32	154	4,5	0,288
6	7	86	16	47	9	140	28	52	26	27	24	118	32	154	4,0	0,713
7	7	86	16	47	9	140	28	52	26	27	24	118	32	154	4,0	0,788
8	7	86	16	47	9	140	28	52	26	27	24	118	32	154	4,0	0,838
9	7	86	16	47	9	140	28	52	26	27	24	118	32	154	5,0	0,500
10	7	86	16	47	9	140	28	52	26	27	24	118	32	154	4,5	0,950
11	7	86	16	47	9	140	28	52	26	27	24	118	32	154	2,0	0,863
12	7	86	16	47	9	140	28	52	26	27	24	118	32	154	5,0	0,563
13	7	7	7	44	8	8	6	31	16	21	18	87	22	110	3,0	0,938
14	7	7	7	44	8	8	6	31	16	21	18	87	22	110	3,5	0,363
15	7	7	7	44	8	8	6	31	16	21	18	87	22	110	4,0	0,850
. . .																
634	6	18	8	12	5	5	5	12	8	12	11	38	14	81	5,5	0,563
635	6	18	8	12	5	5	5	12	8	12	11	38	14	81	3,5	0,463
636	6	18	8	12	5	5	5	12	8	12	11	38	14	81	3,0	0,863
637	6	9	6	7	4	12	6	10	7	7	7	23	10	33	2,5	0,938
638	6	9	6	7	4	12	6	10	7	7	7	23	10	33	3,0	0,763
639	6	9	6	7	4	12	6	10	7	7	7	23	10	33	3,0	0,675
640	6	9	6	7	4	12	6	10	7	7	7	23	10	33	4,0	0,775
641	6	9	6	7	4	12	6	10	7	7	7	23	10	33	1,5	0,400
642	6	9	6	7	4	12	6	10	7	7	7	23	10	33	2,5	0,363
643	6	9	6	7	4	12	6	10	7	7	7	23	10	33	2,5	0,638
644	6	9	6	7	4	12	6	10	7	7	7	23	10	33	3,0	0,500
645	6	9	6	7	4	12	6	10	7	7	7	23	10	33	2,0	0,625
646	6	9	6	7	4	12	6	10	7	7	7	23	10	33	2,5	0,888
647	6	9	6	7	4	12	6	10	7	7	7	23	10	33	2,5	0,663
648	6	9	6	7	4	12	6	10	7	7	7	23	10	33	3,0	0,788
649	9	104	23	132	14	38	15	41	24	49	38	102	29	191	4,3	0,650
650	9	21	11	23	7	11	8	14	10	14	12	31	14	56	4,0	0,738

A set of individual odour intensity and hedonic quality evaluations (defined variables: *I1* i *H1*) of 56 samples and the adequate h_1-h_{14} parameters (defined variables) were applied for training the networks. An excerpt of the set is presented in Table 1.

Neural networks trainings were conducted by employing a set consisting of 648 training patterns (individual evaluations of 54 samples). The tests were performed by applying medians of sensory evaluations and 14 characteristic points of samples A and B chromatogram. Twelve neural networks were generated and tested. The prevailing network types were Radial Basis Function (RBF) and GRNN with two or three hidden layers. Two examples of the generated neural networks are shown in Figure 4.

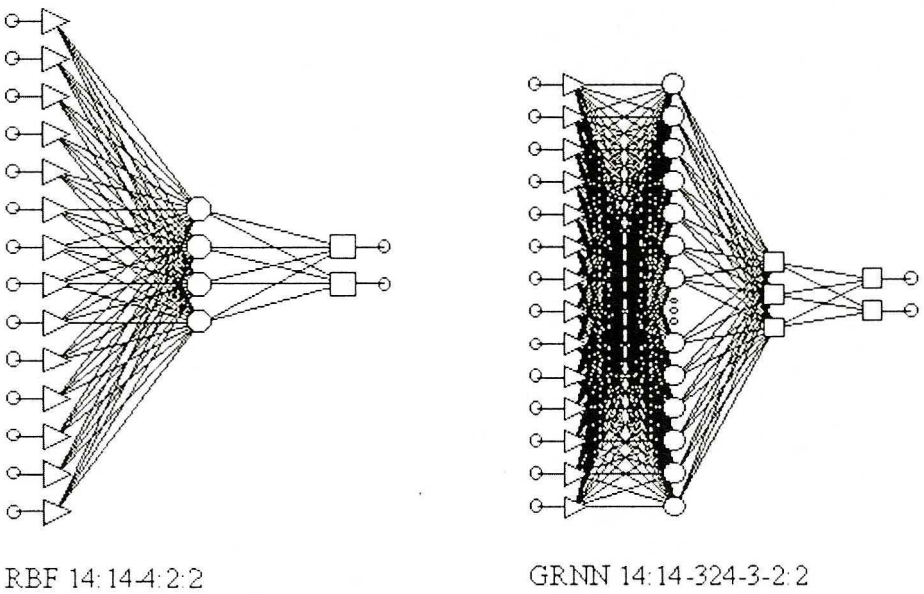

Fig. 4. Exemplary schemes of generated neural networks

In Figure 5 distributions of 12 individual odour intensity evaluations of A and B samples are compared with distributions of 12 generated networks answers. In the case of sample A the values of the 25% and 75% quartile equalled $I1A_{25\%} = 3.75$ and $I1A_{75\%} = 5.0$, and median value equalled $I1A_{med} = 4.25$. In the set of network answers the quartile distribution included $I2A_{25\%} = 4.44$ and $I2A_{75\%} = 4.65$, and median value $I2A_{med} = 4.48$. Values of both medians $I1A_{med}$ and $I2A_{med}$ are similar and the network answers variability range in relation to individual evaluations is considerably lower. Similar remarks refer to sample B's odour intensity measurements and calculations.

In Figure 6 the results of individual evaluations of samples A and B hedonic quality of odour with 12 networks answers are confronted. In the case of sample A the values of the 25% and 75% quartile equalled $H1A_{25\%} = 0.51$ and $H1A_{75\%} = 0.77$, and median value equalled $H1A_{med} = 0.65$. In the set of network answers the quartile distribution included $H2A_{25\%} = 0.682$ and $I2A_{75\%} = 0.686$, and median value $H2A_{med} = 0.684$. Analogical *H1* and *H2*

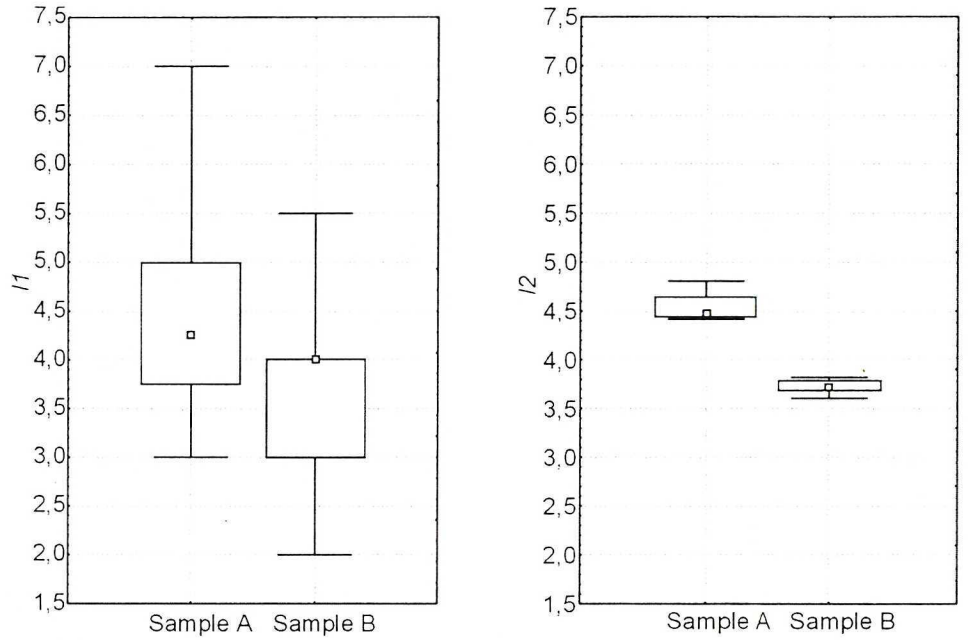

Fig. 5. Comparison of distributions of 12 individual odour intensity evaluations of A and B samples with distributions of 12 generated network answers. Median, quartiles, extreme values of *I1* (measurement) and *I2* (network answers)

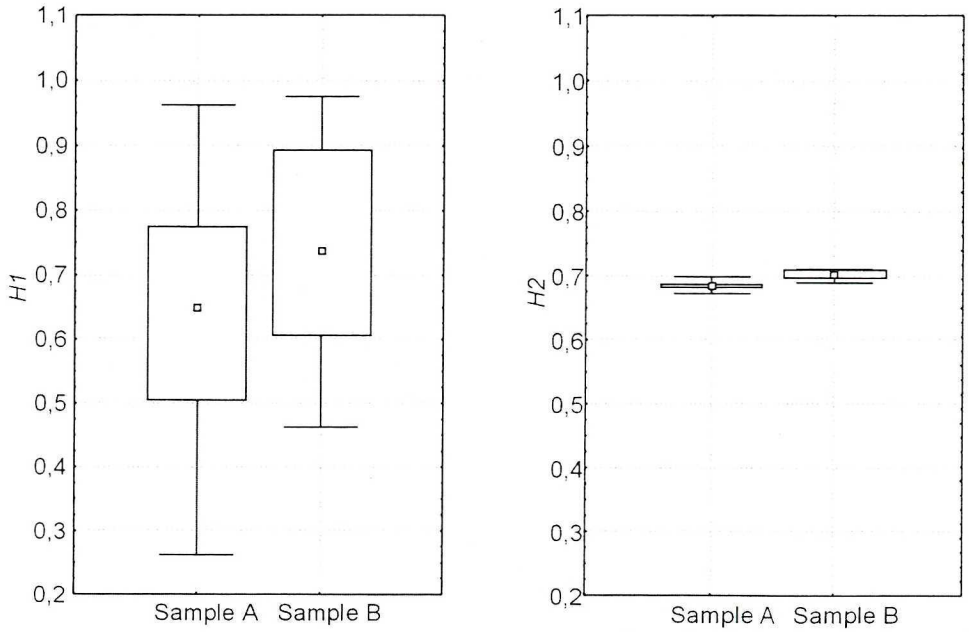

Fig. 6. Comparison of distributions of 12 individual odour hedonic quality evaluations of A and B samples with distributions of 12 generated network answers. Median, quartiles, extreme values of *H1* (measurement) and *H2* (network answers)

values for sample B equalled: $H1B_{25\%} = 0.61$, $H1B_{75\%} = 0.89$, $H1B_{med} = 0.74$, $H2B_{25\%} = 0.696$, $H2B_{75\%} = 0.709$, $I2B_{med} = 0.703$.

When analysing the quoted data one can state that the difference (*H2A – H2B)* is significantly smaller than (*H1A – H1B*). In spite of this fact a level of its significance, determined on the basis of complete sets of network answers, is higher than the value determined on the basis of complete sets of individual sensory evaluations. (*H1A – H1B*) difference significance level equals 0.86. In sets of networks' answers a smaller difference between *H2A* and *H2B* is confirmed with a higher probability equalled almost one.

CONCLUSIONS

1. The analysed samples were aromatised with citrus oil and contained four additional odorants of 56–141°C boiling point temperatures. Even though their odour quality varied to a small extent (similar intensity and hedonic quality) they could be distinguished on the basis of the shape of a chromatogram excerpt obtained with use of non-polar stationary phase. The excerpt does not need to embrace the peaks of the compounds whose boiling point temperatures are higher than 160°C (e.g. limonene, 178°C) and lower than 50°C (e.g. volatile ethers). Its description can be limited to describing fourteen characteristic points on chromatograms.
2. There is a possibility of preparing GC-NN system for monitoring odour intensity and hedonic quality of industrial gases. It will probably require gathering a greater number of sensory-chromatographic data (greater training sets).

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