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ODOUR OF MIXTURES OF CYCLOHEXANE AND CYCLOHEXANONE

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ZAPACH MIESZANIN CYKLOHEKSANU I CYKLOHEKSANONU

Wykonano oznaczenia intensywności zapachu powietrza zanieczyszczonego cykloheksanem (A), cykloheksanonem (B) oraz cykloheksanem z domieszkami cykloheksanonu (mieszaniny M1, M2 i M3; x_B = 0,14; 0,05 i 0,02). Wyznaczono empiryczne parametry równań Webera-Fechnera i Stevensa. Dla mieszanin o stężeniu C = 1500–3500 ppm oszacowano stałą interakcji α_V = 115–130°. Na podstawie wyników weryfikacji znanych modeli interakcji stwierdzono, że możliwości ich zastosowania do przewidywania intensywności zapachu mieszanin cykloheksanu i cykloheksanonu są ograniczone.

Summary

Evaluations of odour intensity of the air polluted with cyclohexane (A), cyclohexanone (B) and cyclohexane with admixtures of cyclohexanone (mixtures M1, M2 and M3; x_B = 0.14; 0.05 and 0.02 respectively) were made. Empirical parameters of psychophysical equations (Weber-Fechner' and Stevens') were determined. Total concentrations of the mixtures were within the range C = 1500–3500 ppm. The interaction constant α_V = 115–132° was estimated for the mixtures. Verification of known models of odour interaction led to the conclusion that possible application of the models for prediction of odour intensity of the air polluted with mixtures of cyclohexane and hexane is limited.

INTRODUCTION

The range of odour nuisance of sources of airborne pollution can be predicted on the basis of sensory measurements of the emission. The measurements of emission concentrations of odorants base on the determination of dilution extent of the gases for which half of representative group of people declares no odour. Sensory determinations are inconvenient and time-consuming. Therefore the possibilities to replace the sensory determinations with classic analyses of pollutant concentrations are being searched.

The solution to the problem seems to be very distant for the case of the industrial off-gases that are complex mixtures of tens and hundreds of compounds. The most advanced is research of:

(i) equations that relate odour intensity to total concentration of mixture (constant proportion of components),
(ii) relationship between odour intensity and relative share of the components in simple binary and ternary mixtures of odorants.

This paper discusses the state of knowledge in the field and present research trends. The results of measurements of odour intensity of the air polluted with binary mixtures of odorants are also presented.

PERCEPTUAL AND PSYCHOPHYSICAL MODELS OF OLFACTORY INTERACTIONS

Equations relating odour intensity to total concentration of odorants are known as psychophysical laws (Weber-Fechner' law and Stevens' law). Knowledge of the equations is essential for forecasting of odour nuisance of industrial emitters of airborne pollutants. The equations enable forecasting of odour intensity in the near-ground layer of the air on the basis of the emitted pollutants dispersion modelling results [2–4].

Relationships between odour intensity and relative shares of the components in simple binary and ternary mixtures are called perceptual and psychophysical models of odour interactions.

Perceptual models of odour interaction relate odour intensity of the mixture (I_{AB}) to the intensities of the mixture' compounds (I_A, I_B). Among them are the following equations [1]:

$$I_{AB} = k\ (I_A + I_B) \quad \text{(Berglund, Berglund and Lindvall 1971)} \quad (1)$$

$$I_{AB} = (I_A^2 + I_B^2)^{0,5} \quad \text{(Patte and Laffort 1979)} \quad (2)$$

$$I_{AB} = (I_A^2 + I_B^2 + 2\, I_A I_B \cos \alpha_V)^{0,5} \quad \text{(vector summation; Zwaardemaker 1908)} \quad (3)$$

$$I_{AB} = I_A + I_B + 2 \cos \alpha_U \cdot (I_A \cdot I_B)^{0,5} \quad \text{(model U; Patte and Laffort 1979)} \quad (4)$$

where k, α_V, α_U are the empirical coefficients characteristic of the given mixture A+B.

It is assumed that interaction coefficient α_V in equation (3) is approximately constant for a given mixture. Typically it falls in a range 109–115°, though lower values (99–102°) were also reported [1]. Vector summation postulates that the mixture intensity is typically lower than the stronger component' intensity ($I_A > I_B$, $I_{AB} < I_A$). The observation seems to be most valuable from the standpoint of the quality assessment of the environment. The intensity of mixtures of equally strong components is narrowly higher than intensities of the components presented alone ($I_A = I_B < I_{AB}$).

Vector summation does not predict the situation when the intensity of mixture (I_{AB}) is higher than arithmetic sum of components' intensities ($I_A + I_B$). Such cases are predicted by the U model of interaction (equation 4).

Psychophysical models of odour interaction are the ones that relate odour intensity of the mixture to the concentrations of odorants. The models are based on psychophysical laws – relationships between intensity of sensation and strength of the stimulus. Odour intensity (I) and odorant concentration (C) are related to each other logarithmically or exponentially. The laws can be given by following equations [6–8]:

$$I = k_F \cdot log\,(C / DT_F) \quad \text{(Weber-Fechner law)} \tag{5}$$

$$I = k_S \cdot C^n \quad \text{(Stevens law)} \tag{6}$$

or $$I = k_S \cdot (C - DT_S)^n \quad \text{(Stevens law)} \tag{7}$$

Symbols k_F, k_S, DT and n denote empirical constants. Among them only DT – odour detection threshold – is clear-cut defined from the psychophysical standpoint. It is concentration of the odorant(s) that cause(s) olfactory sensation in half of representative group of people. Symbol DT_F stands for the odour detection threshold determined using extrapolation toward $I = 0$, in a system I – log (C), after assessments of odour intensities of samples of different odorant concentrations.

Supporters of the Stevens' law often use equation (6) which suggests that they limit the research to concentration range $C >> DT$ (Stevens law assumes that $DT = 0$). In the case of lower concentration range the equation (7) should be used. Most reliable values of DT_S can be obtained during direct sensory measurement (determination of odorants concentrations that causes odour sensation in half of representative group of people) [6].

The results of the research made so far do not allow the opinion that one of the laws has advantage over the other.

Example psychophysical models of odour interaction presented in this paper are based on the exponential Stevens' law [1].

The UPL2 model (Laffort, Etcheto, Patte and Marfaing; 1989) [1] is a modified version of the U model (equation 4). In the UPL2 model the interaction coefficient α_U is replaced with coefficient α_{UPL2}. The latter coefficient is calculated using information about relative shares of mixtures' components and values of constants: k_S and n in Stevens' equations for the components alone. Mathematically the coefficient α_{UPL2} is given as follows:

$$cos\ \alpha_{UPL2} = (I_A\ cos\ \alpha_A + I_B\ cos\ \alpha_B) / (I_A + I_B) \tag{8}$$

where:

$$I_A = k_{S,A} \cdot C_A^{n_A} \tag{9}$$

$$I_B = k_{S,B} \cdot C_B^{n_B} \tag{10}$$

$$\cos\alpha_A = [1 - P^{n_A} - (1-P)^{n_A}] / [2P^{n_A/2} \cdot (1-P)^{n_A/2}] \tag{11}$$

$$\cos\alpha_B = [1 - P^{n_B} - (1-P)^{n_B}] / [2P^{n_B/2} \cdot (1-P)^{n_B/2}] \tag{12}$$

$$P = I_B^{1/n_B} / [I_A^{1/n_A} + I_B^{1/n_B}] \tag{13}$$

The ERM interaction model (Equiratio Mixture Model, Frijters and Oude Ophuis, 1983) [1] applies to binary mixtures of odorants or tastants with constant ratio of the components (p,q). It was affirmed that odour or taste intensity of the AB mixture of the $C_{AB,pq}$ concentration can be calculated using Stevens' equation in a following form:

$$I_{AB.pq} = k_{S,AB} \cdot C_{AB,pq}^{n_{AB}} \tag{14}$$

where $k_{AB,pq}$ and n_{AB} are the constants characterising mixtures with constant ratio of components (p, q):

$$p = S_A/(S_A+S_B) = const \quad \text{and} \quad q = 1-p \tag{15}$$

For calculation of the constants following equations are used:

$$n_{AB} = p\, n_A + q\, n_B \tag{16}$$

$$k_{S,AB} = p \cdot k_{S,A} + q \cdot k_{S,B} \tag{17}$$

or

$$k_{S,AB} = k_{S,A}^{\,p} \cdot k_{S,B}^{\,q} \tag{18}$$

The scope of the research aimed at verification of presented models is not large so far. It seems very appropriate to complete the existing set of available data with information about binary mixtures of different odorants. It was decided that the research should be made in systems of odorants of similar and different physicochemical and olfactory characteristics. Large set of such data should facilitate the explanation of reasons of observed phenomena.

Choosing the object of research it was assumed that the odorants used can not be harmful for the subjects. The odorants should not be detectable in a range of very low concentrations for which the measurements are burden with significant errors.

The conditions mentioned above are met, among other compounds, for hexane, cyclohexane, cyclohexanol and cyclohexanone. It is possible that the results of research of interactions between compounds with the same number of carbons in molecules will enable the explanation of the role of the molecules structure.

First series of the measurements were carried in a system cyclohexane – hexane [5]. The results of the next stage of research are presented below.

PURPOSE AND SCOPE OF THE RESEARCH

The characterisation of type of odour interaction in the mixture of cyclohexane (A) and cyclohexanone (B) was the purpose of presented research.

Evaluations of odour intensity of the air polluted with single odorants enabled determination of the constants k_F and DT_F in Weber-Fechner' equation. DT_F values were used to calculate the constants k_S and n in Stevens' equation:

$$I = k_S \cdot (C - DT_F) \tag{19}$$

Determined values were used during interpretation of evaluations of odour intensity of the air polluted with three mixtures AB (three different relative concentrations of both components). Parameters of psychophysical equations (5) and (19) were determined for each mixture. Values of constants k_F, DT, k_S and n for single odorants and mixtures were used during attempts to verify the selected odour interaction models: vector summation (3), U model (4), UPL2 model (4 and 8-13) and ERM model (14-17).

In calculations using equations (9) and (10) of the UPL2 model, values of the concentrations C_A and C_B were replaced with respective differences ($C_i - DT_i$).

The results of verification of the ERM model based on the Stevens' law were compared with the results obtained assuming that the Weber-Fechner' law can be used similarly:

$$I = k_{F,AB} * log\ (C_{AB}/DT_{AB}) \tag{20}$$

where:

$$DT_{AB} = x_A \cdot DT_A + x_B \cdot DT_B$$

For the purpose of distinction of the "classic" ERM model (equation 14-18) and its version (equation 20) the models were denoted with symbols ERM_S and ERM_F respectively.

RESEARCH METHODOLOGY

The experiments were made in an odour laboratory equipped with a highly efficient air condition installation. The laboratory consisted of the chemical laboratory with sample preparation room ("dirty" part) and waiting room adjacent to the test room ("clean" part with separate entrance). The subjects stay in the "clean" part of the laboratory. The window between the sample preparation room and the test room enables contact between subjects and research manager.

The stimuli were cyclohexane and cyclohexanone (ppa, POCh, Gliwice, Poland). High purity of the chemicals was confirmed using GC-MS technique (HPCHEM).

The samples were prepared using:

- 10 dm^3 foil containers (bags) with teflon tubes;
- Hamilton Syringe (Model S-1500) for measuring clean, odourless air;
- 10 µl Hamilton Syringes (700 Series) for measuring liquid cyclohexane and cyclohexanone.

The reference scale of odour intensity standards was used. It consisted of ten aqueous solutions of n-butanol (ppa) in 50 cm^3 erlenmeyers with glass plugs.

The standards of odour intensity were prepared directly before each session of sensory assessments. The preparation consisted in gradually diluting the aqueous standard solution (8 cm^3 of n-butanol/100 cm^3). The dilution steps differed by factor 2.86 (7 cm^3 of diluted solution + 13 cm^3 of distilled water). Change of odour intensity corresponding to one step of n-butanol dilution was considered the odour intensity scale step (I).

The samples of the stimuli in the air were prepared by injecting 6 dm^3 of the clean air into the foil bags and then injecting the liquid chemicals. After 30–40 minute conditioning period the bags were emptied and the procedure of preparation repeated. The odorant concentration range in all of the assessed samples was $0 \div 3460$ ppm for hexane (index A) and $0 \div 722$ ppm for cyclohexanone (index B).

During the main experiment the assessors completed the following tasks:

- indicating number of the standard solution in which they smell "strange" odour;
- smelling the sample stream directly from the bag;
- indicating the number of the standard solution whose odour intensity was equal or a little bigger than the intensity of the sample.

The main experiment consisted of five series of the odour intensity assessments of the air polluted with cyclohexane (A), cyclohexanone (B) and three mixtures of the compounds. The relative cyclohexanone concentrations in the mixtures (C_B [ppm] / (C_A + C_B) [ppm]) were 0.14 (symbol M1); 0.05 (symbol M2) and 0.02 (symbol M3).

To avoid the "expectation error" the samples were presented randomly. During one day up to three sessions of measurements were carried out. There was always the pause of about 10 minutes between the trials of one session and the pause of 30 minutes between the sessions.

RESULTS

The results of the evaluation of odour intensity of the air polluted with cyclohexane and cyclohexanone are presented in the graph I = f (log C) (Fig. 1.) and in the graph log I = f (log C) (Fig. 2.). The calculated values of Weber-Fechner' coefficient (k_F), odour detection threshold (DT) as well as exponent (n) and multiplicative constant (k_S) in Stevens' equation are given in table 1.

DISCUSSION

The results of the measurements presented in table 1 and in figures 1 and 2 enable calculation of the odour intensity of single components A and B as well as of mixtures M1, M2, M3. The calculations are based on the relationships:

$$I_A = 1.824 \cdot \log(C_A \text{ [ppm]} / 19.4)$$
$$I_B = 3.628 \cdot \log (C_B \text{ [ppm]} / 11.4)$$
$$I_{M1} = 3.878 \cdot \log (C_{M1} \text{ [ppm]} / 156.7)$$
$$I_{M2} = 3.219 \cdot \log (C_{M2} \text{ [ppm]} / 231.9)$$
$$I_{M3} = 4.368 \cdot \log(C_{M3} \text{ [ppm]} / 495.8)$$

Values I_{M1}, I_{M2}, I_{M3} calculated using the relationships were considered the results of the measurements. The values were compared with results of vector summation of the I_A and I_B values (equation 3) as well as with predictions of the U, ERM_S, ERM_F and UPL2 models.

The values of interaction coefficients α_V and α_U for which there was highest consistency between results of calculations and measurements were determined in a process of trial and error. Results of the determination are presented on figures 3 and 4. In both cases diminishing of the admixture relative concentration (B) causes rapid fall of reliability of odour intensity estimations.

In the case of x_B = 0.14 (mixture 1, figures 3a and 4a) the estimated value of interaction constant α_V equals 120°. The largest differences between the calculated and measured values occur when total concentration of the mixture is small. In this range of concentrations real magnitude of olfactory sensation is lower than predicted.

When total concentration of mixture AB is the same as above and relative concentration of the admixture is diminished to the value of x_B = 0.05 (mixture 2, figures 3b

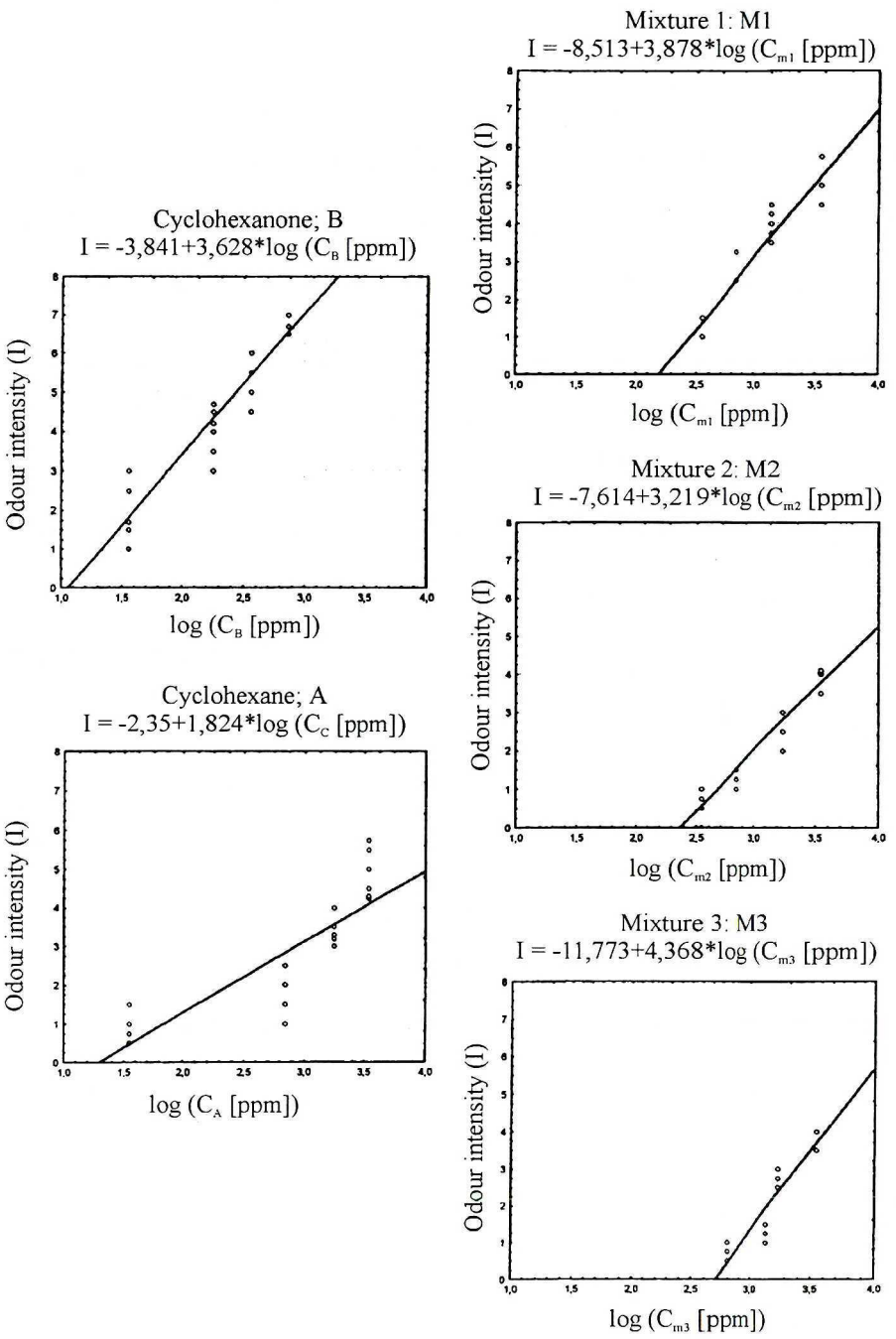

Fig. 1. Results of measurements. Dependence of odour intensity of the air polluted with cyclohexane (A) and cyclohexanone (B) on logarithm of total concentration of mixture AB.

Mixture M1 – molar share of B: $x_B = 0,14$

Mixture M2 – molar share of B: $x_B = 0,05$

Mixture M3 – molar share of B: $x_B = 0,02$

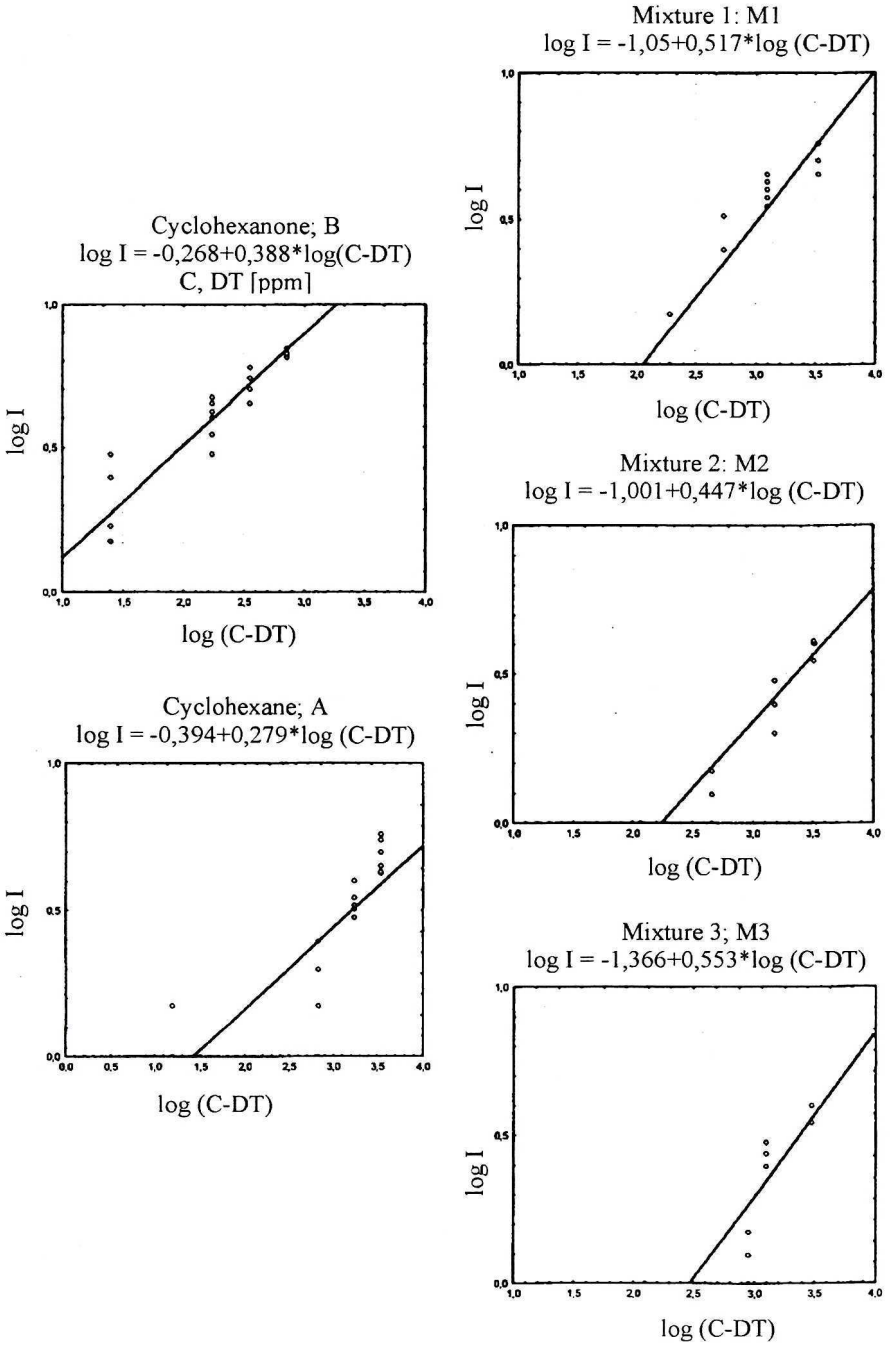

Fig. 2. Results of measurements. Dependence of logarithm of odour intensity of the air polluted with cyclohexane (A) and cyclohexanone (B) on logarithm of total concentration of mixture AB.
Mixture M1 – molar share of B: $x_B = 0,14$
Mixture M2 – molar share of B: $x_B = 0,05$
Mixture M3 – molar share of B: $x_B = 0,02$

Table 1. Parameters of Weber-Fechner' and Stevens' equations determining odour intensity of cyclohexane (A), cyclohexanone (B) and mixtures of the two compounds

	Psychophysical law			
	$I = k_F \cdot \log(C/DT_F)$		$I = k_S \cdot (C-DT_F)^n$	
Odorants	k_F	DT_F [ppm]	k_S	n
Cyclohexane (A)	3,628	12	0,540	0,388
Mixture M1; x_B=0,14	3,878	157	0,087	0,517
Mixture M2; x_B=0,05	3,219	232	0,081	0,475
Mixture M3; x_B=0,02	4,368	496	0,030	0,602
Cyclohexanone (B)	1,824	19	0,321	0,310

and 4b) modelling of odour intensity gives better results for values $\alpha_V \approx 126°$ and $\alpha_U \approx 124°$.

The results of calculations made for mixture AB of the relative admixture concentration $x_B = 0.02$ (mixture 3, figures 3c and 4c) and with values α_V and α_U from the range 126–128° are significantly different than values from measurement. The difference is larger than one step of the odour intensity scale. That allows the conclusion that possibilities of applying both vector and U models should be rejected.

The ranges of good and limited reliability of methods of odour intensity calculation are illustrated in figure 5.

Figure 6 presents comparison of results of measurement and results of calculations using UPL2, ERM_S and ERM_F models. It shows low reliability of modelling results.

In the light of observed effects it is evident that the research should be aimed at formation of new models of psychophysical odour interaction. The new models should be based on the knowledge concerning the mechanisms of perception of olfactory sensations. Simplifications in existing models, such as assumption of additivity of the detection thresholds and values of constants k_S, k_F and n, cause occurrence of large errors. The magnitude of deviations from additivity observed for mixtures of cyclohexane (A) and cyclohexanone (B) is shown in the figure 7. The character of presented functions should be established during further research.

CONCLUSIONS

1. Odour intensity of the air polluted with cyclohexane, cyclohexanone or mixture of the two compounds can be predicted on the base of psychophysical laws provided that values of respective constants in equations $I = f(C)$ were previously determined.
2. Possible application of known models of odour interaction for prediction of odour intensity of the air polluted with mixtures of cyclohexane and cyclohexanone is limited. When total pollutant concentration of the mixtures is not lower than 1500 ppm the results of calculations using the vector model are consistent with the results of measurements for values of interaction constant $\alpha_V = 115°–132°$. The lower shares of cyclohexanone in mixture the larger correction of the α_V value. For lower concentrations of pollutants value of odour intensity calculated using such corrections is significantly higher than the measured one. The effect occurs especially in the case of very low relative concentrations of admixture ($x_B < 0.05$).

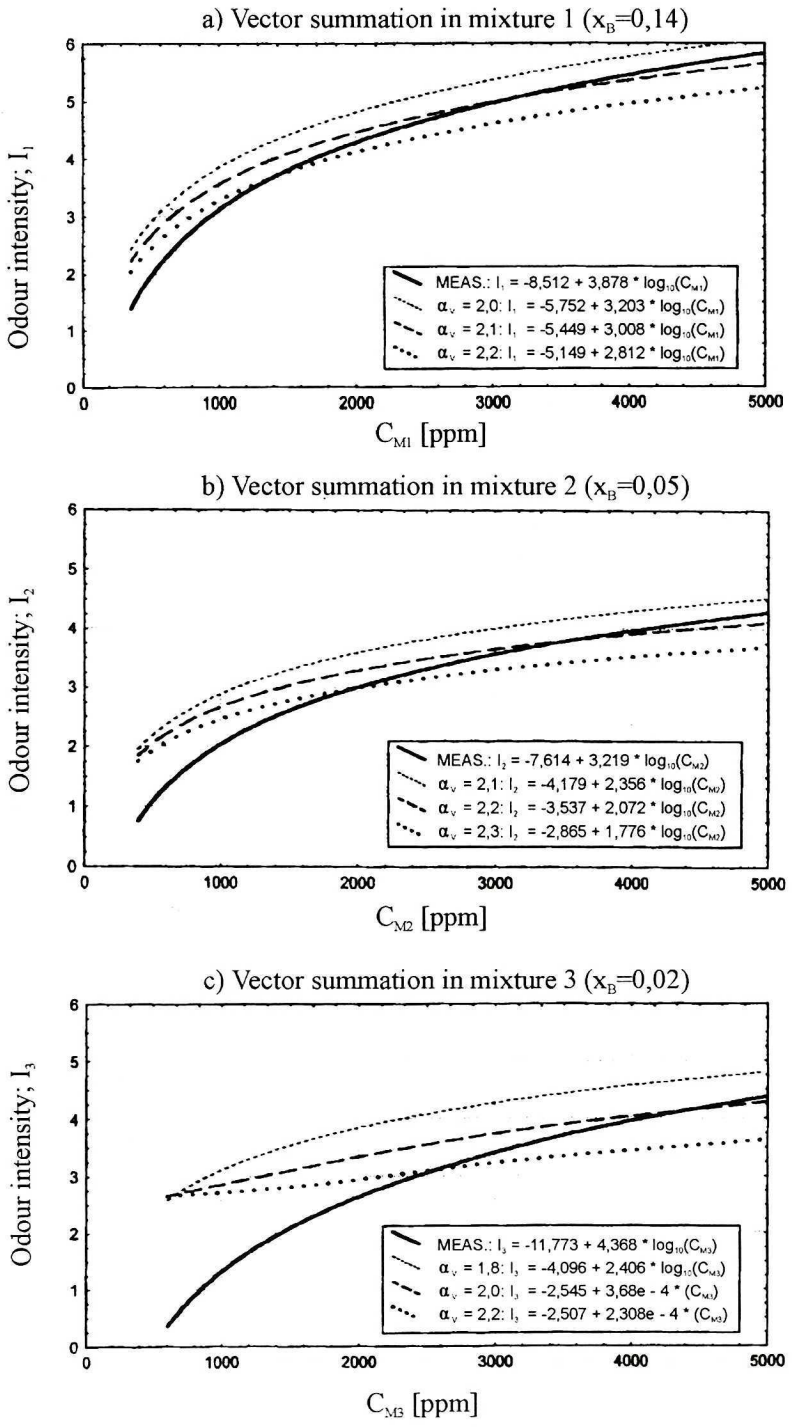

Fig. 3. Evaluation of constant of odour interaction between cyclohexane and cyclohexanone in mixtures of different component proportions (mixtures 1, 2, 3); α_V – constant applied for vector summation of odour intensities of mixture components

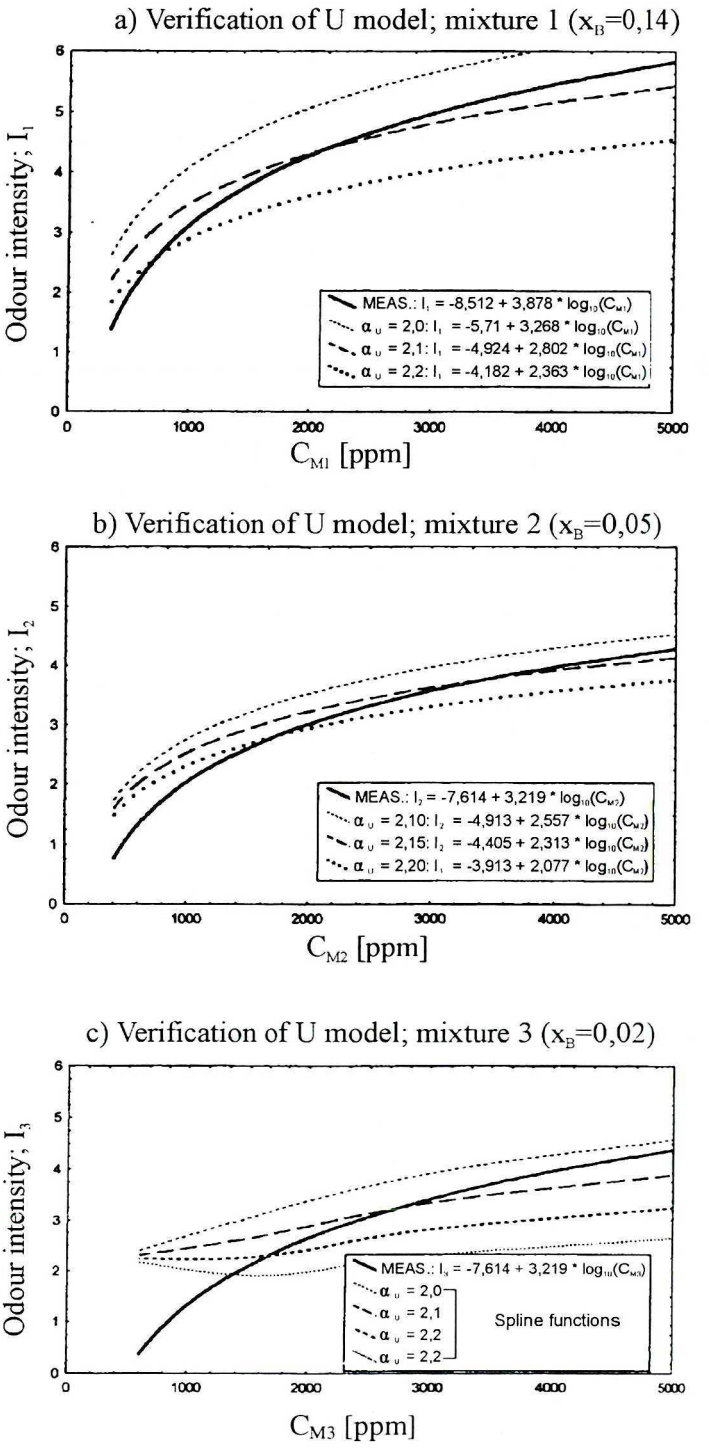

Fig. 4. Evaluation of constant of odour interaction between cyclohexane and cyclohexanone in mixtures of different component proportions (mixtures 1, 2, 3); α_U – interaction constant of U model

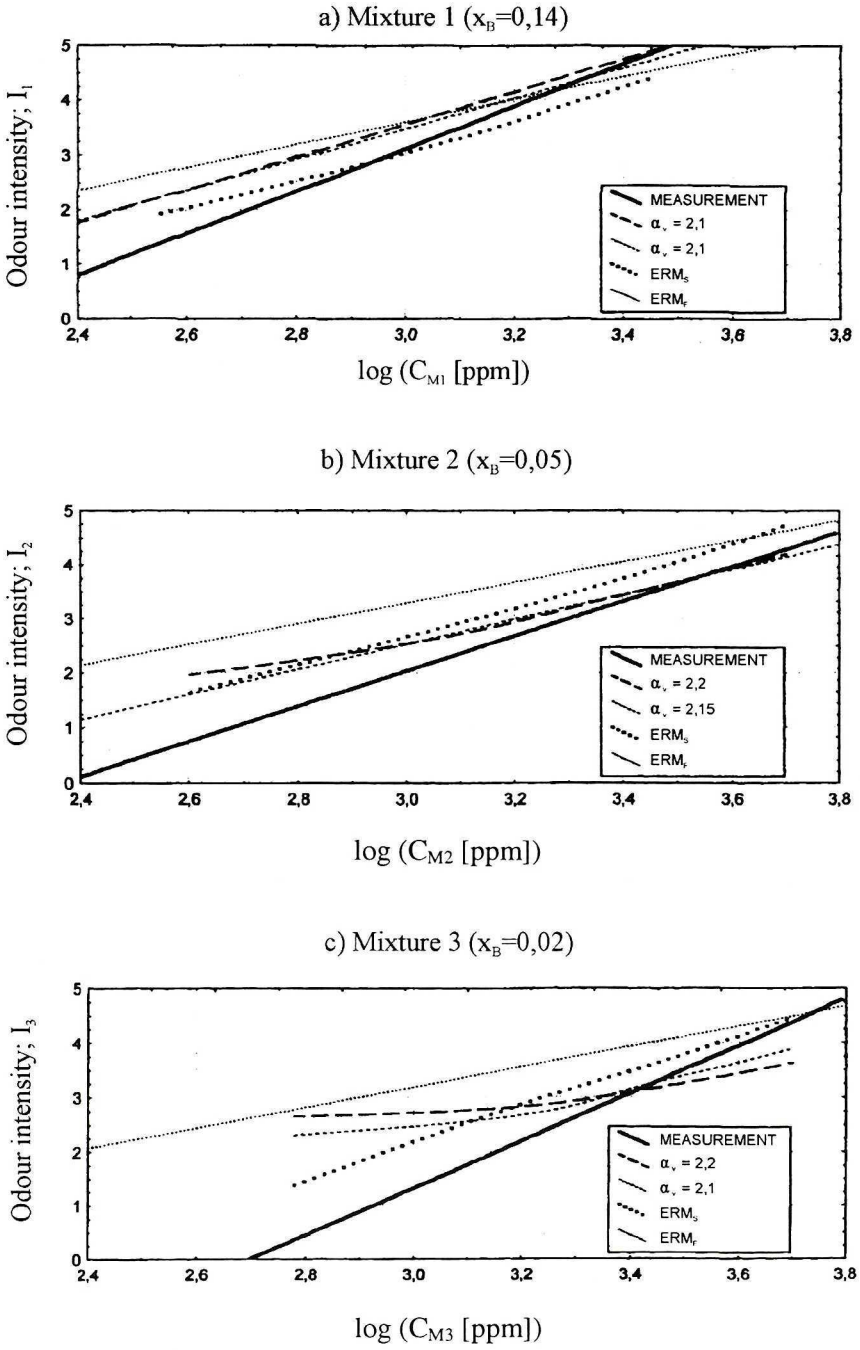

Fig. 5. Verification of models of odour interaction. Odour intensity of the air polluted with mixtures of cyclohexane and cyclohexanone (M1, M2, M3) – values measured and calculated using vector sumation (symbol V) and models: U, ERM_S, ERM_F

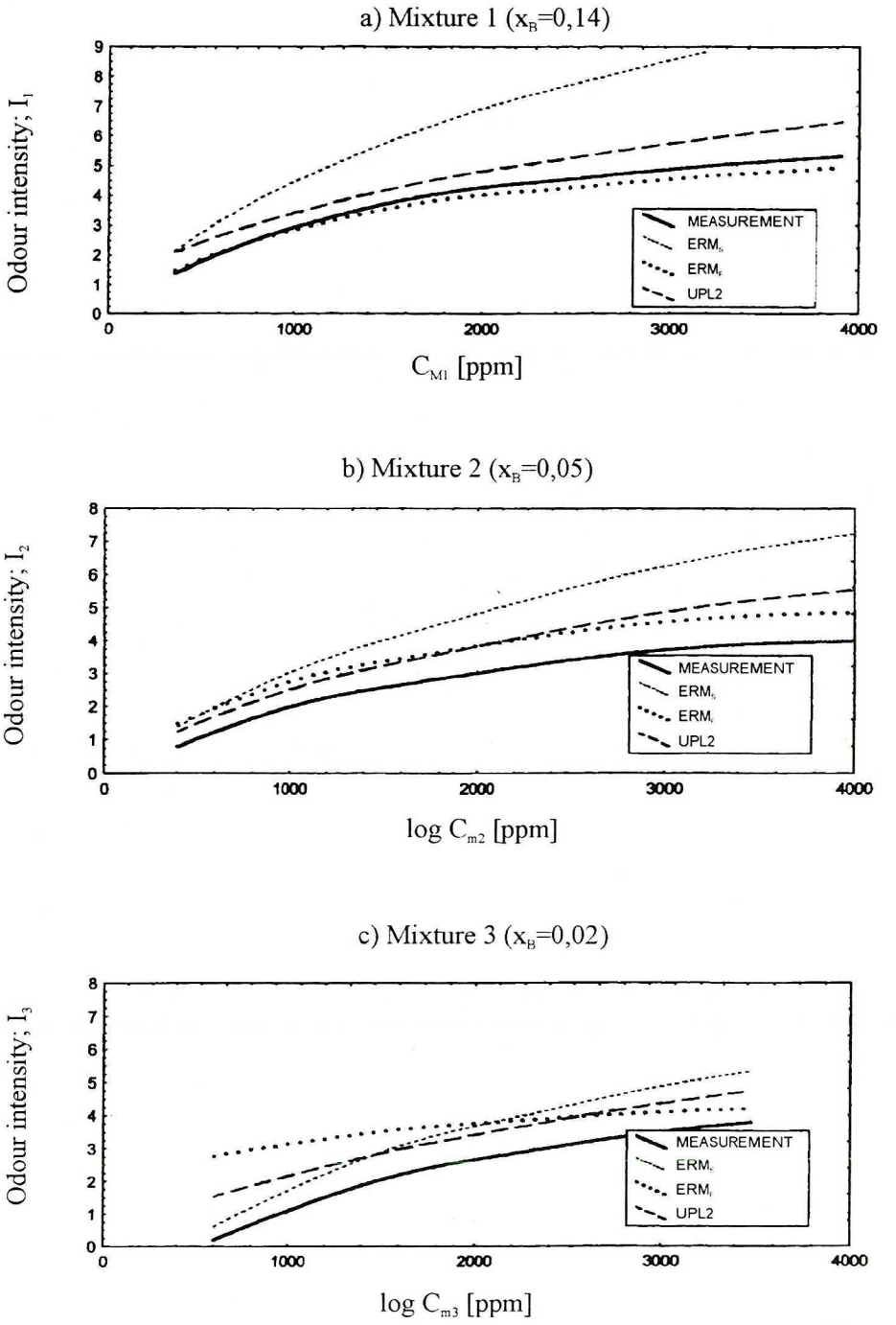

Fig. 6. Verification of ERM and UPL2 models of odour interaction on example of mixture of cyclohexane (A) and cyclohexanone (B)

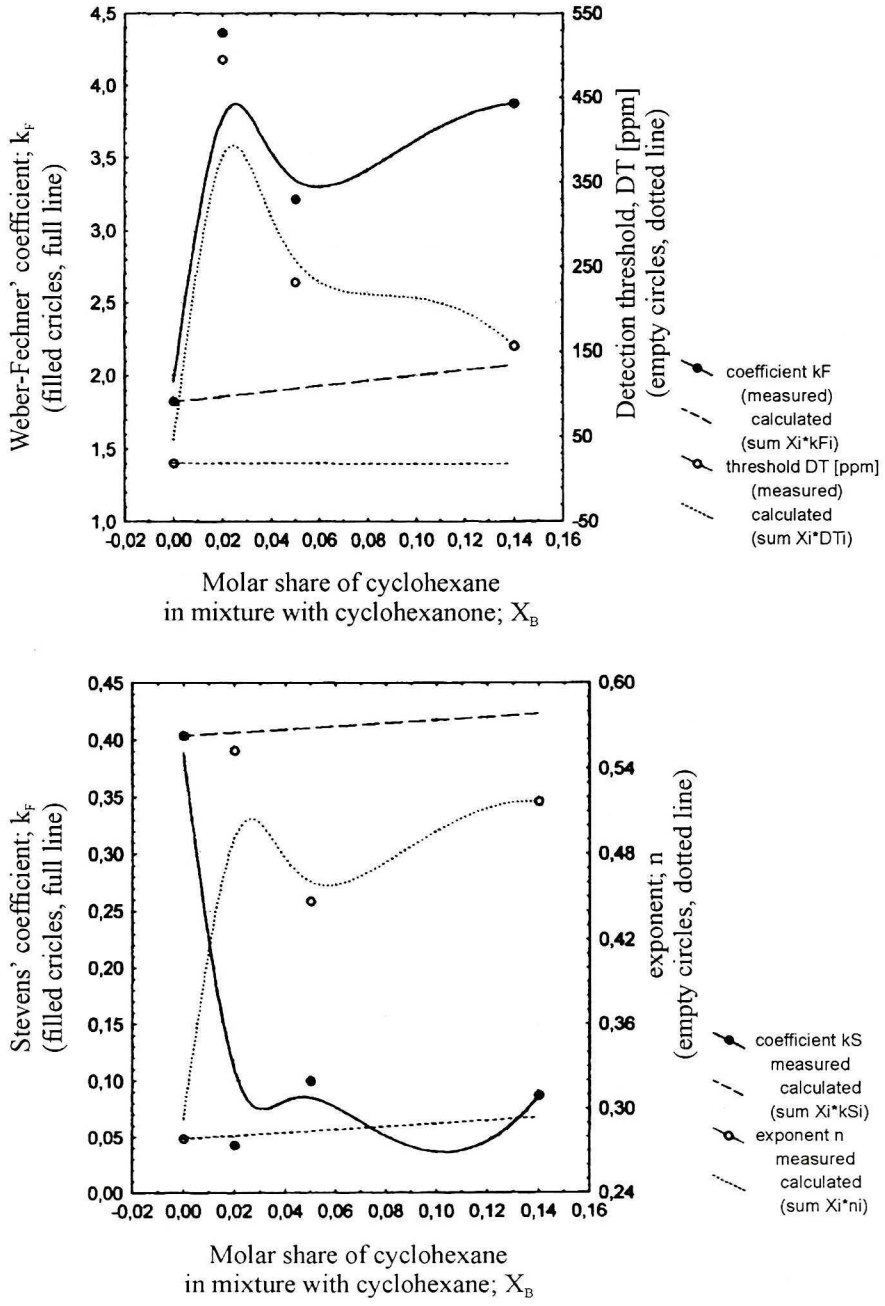

Fig. 7. Parameters of Weber-Fechner' equation (k_F, DT_F) and Stevens' equation (k_S, n) as a function of molar share of cyclohexane (x_B) in mixtures of cyclohexane and cyclohexanone

3. The additivity principle can not be used for calculation of detection threshold of the mixtures. Threshold value of the mixture with very low share of cyclohexanone calculated on the basis of that principle is significantly lower than value obtained from measurement.
4. It is appropriate to collect larger number of information about influence of relative share of mixture' components on the value of detection threshold for mixtures investigated so far as well as for the other binary mixtures. The information should facilitate formulation of new psychophysical models of odour interaction, which in larger extent will take advantage of the knowledge regarding mechanisms of perception of olfactory sensations.

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