

ODOUR INTENSITY CLOSE TO DETECTION THRESHOLD

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INTENSYWNOŚĆ ZAPACHU W POBLIŻU PROGU WYCZUWALNOŚCI

Zgromadzono 550 indywidualnych ocen intensywności zapachu (S) 62 próbek powietrza zanieczyszczonego 2-propanolem (stężenie: $c = 46\text{--}21000\text{ mg/m}^3$). Dane wykorzystano do obliczeń progu wyczuwalności zapachu 2-propanolu metodą ekstrapolacji do $S = 0$ w układzie współrzędnych $S\text{-log } c$. Otrzymane wartości porównano z wynikami testów trójkątowych oraz danymi publikowanymi w piśmiennictwie. Wskazano przyczynę pozornych dodatnich odchyień od prawa Webera-Fechnera w zakresie małych intensywności zapachu.

Summary

550 individual odour intensity (S) assessments of 62 samples of air polluted with 2-propanol were collected (concentration $c = 46\text{--}21000\text{ mg/m}^3$). The data were used to establish odour detection threshold of 2-propanol by extrapolation to $S = 0$ in the coordinate system of $S\text{-log } c$. The obtained values were compared with triangular tests results and data published in the literature. A reason for apparent positive deviations from Weber-Fechner law within a range of low odour intensities was indicated.

INTRODUCTION

Odour air quality is forecasted on the basis of information about odorant's concentration, its detection threshold and parameters in adequate psychophysical equations. According to the popular Weber-Fechner law odour intensity (S) is directly proportional to logarithm of odour concentration (the amount of European odour units in a cubic meter of gas under standard conditions) c_{od} [ou_E/m^3], which is the quotient of concentration (c) by detection threshold (c_{th}) [3–5]:

$$S = k_{\text{W-F}} \cdot \log c_{\text{od}} = k_{\text{W-F}} \cdot \log c / c_{\text{th}} \quad (1)$$

Odour detection threshold and Weber-Fechner coefficient ($k_{\text{W-F}}$) are empirical constants determined by methods of sensory analysis. Odour detection threshold is defined as odorant

concentration in such a sample whose odour is detected by a half of panel members (a group representative for a population).

Odour detection threshold values of various chemical compounds considerably differ from each other. In many cases they are approximate to or imperceptibly lower than the highest admissible concentration in working environment, adequate liminary concentrations determined for ambient air, or than ignition or blast limit etc. In these situations pollutant odour may play a valuable role as a warning signal. Little reliability of available data limits taking full advantage of that possibility. Differences between c_{th} values published by different authors significantly vary between each other. It is illustrated by the example concerning odour of 2-propanol, shown in Fig. 1 [1, 2]. Reasons for such a considerable results differentiation have not been explained yet.

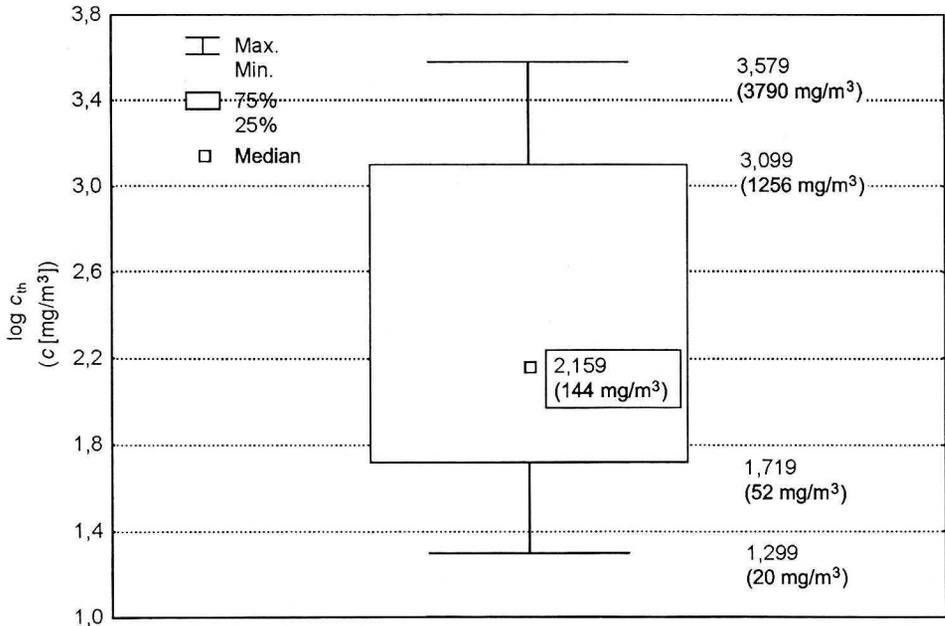


Fig. 1. Illustration of differentiation of 2-propanol odour threshold published values (according to [4, 5])

Odour detection thresholds are determined by direct sensory methods (yes/no method, differential tests) [3, 6] or by an extrapolation method (odour intensity measurements and extrapolation to $S = 0$ in the coordinate system of S - $\log c$) [6–8]. The extrapolation is based on the assumption of Weber-Fechner law validity within the scope of concentrations close to the threshold. It is often questioned – there are positive deviations from S - $\log c$ straight line observed close to the threshold. It causes leaning towards using other psychophysical equations, i.e. Stevens power law [3, 10]:

$$S = k_s \cdot c^n \quad (2)$$

where: k_s and n – empirical constants.

The location of results of c_{th} determination with triangular differential tests in relation to Weber-Fechner and Stevens functions is illustrated in draft in Fig. 2.

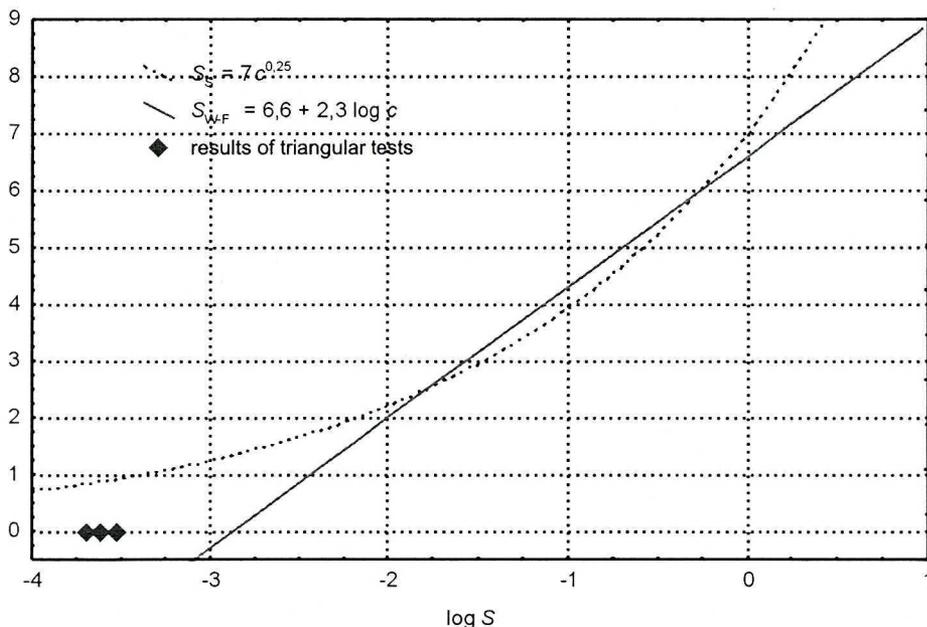


Fig. 2. Location of results of c_{th} determination by triangular differential tests in relation to Weber-Fechner and Stevens functions
 S , S_s , $S_{w,F}$ – odour intensity (s – according to Stevens's law, w,F – according to Weber-Fechner law), c [mg/m^3] – odorant's concentration

Verification of 2-propanol odour detection threshold values was considered as the aim of this paper. Propriety of odour detection thresholds and odorants' concentration determination with extrapolation method was resolved to be checked.

EXPERIMENTAL PROCEDURES

POLLUTED AIR SAMPLES PREPARATION

2-propanol played a role of an air pollutant (POCh, purity to HPLC). Basic samples were prepared in bags from heat-resistant foil. Pollutants were introduced with a chromatographic syringe into 10–20 dm^3 of air. The basic sample dilutions with clean air were carried out by a dynamic method and Stroehlein olfactometer. The diluted flow was directed into a mask – the port of odour intensity assessments – or another foil bags (samples presented during triangular tests). A concentration of 2-propanol in evaluated samples was determined with a chromatograph (SRI 8610C Gas Chromatograph, Rtx-1, 30 m, 30°C).

SENSORY ANALYSIS

Sensory assessments were performed in a odorimetry laboratory, equipped with a highly efficient ventilating installation [3, 9]. Odour was assessed by a group of 12 students after a short training course and a training session of measurements. Four to eight samples were assessed during one session. Each sample was evaluated by five to twelve people (9 people on average).

Within triangular tests the assessors were presented with three samples in identical foil bags. Two of them contained pure air, the third one – air polluted with 2-propanol of a concentration close to the detection threshold. After comparing the samples the assessors were obliged to indicate a sample which was different from the two others. In the next test odorant's concentration in a polluted sample was increased or decreased. A corrected ratio of correct indications of the polluted sample was calculated on the basis of the set of tests results:

$$W = \frac{(X - Y)}{100 - Y} \cdot 100 \quad (3)$$

where: W – corrected ratio of correct indications (%),

X – observed ratio (%),

Y – ratio of correct indications in the situation in which the difference is not detectable (random hits, 33.3%).

An odour detection threshold (concentration for which $W = 50\%$) was determined by the interpolation method in the coordinate system of W -log c .

Odour intensity was quantified using n-butanol scale of standards [2]. The standards were water solutions of n-butanol of concentrations composing a geometric sequence. The solutions were placed in conical flasks of 50 cm³ capacity. They were prepared of a basic solution (symbol NrB = 1) which was made by diluting 8 cm³ of n-butanol with distilled water up to 100 cm³. NrB = 2 standard was obtained by adding 13 cm³ of water to 7 cm³ of the NrB = 1 solution. In a similar way standards NrB = 3 ÷ 10 were prepared. Odour intensity was defined as:

$$S = \text{NrB}_{S=0} - \text{NrB} \quad (4)$$

where: $\text{NrB}_{S=0}$ – number of the standard corresponding to individual odour detection threshold of n-butanol,

NrB – number of the standard recognized by an assessor as an odour equally strong with the sample.

RESULTS

Results of twelve triangular tests conducted by twelve assessors are shown in Fig. 3 in the coordinate system of W -log c (corrected ratio of correct indications of a polluted sample – logarithm of 2-propanol concentration, c [mg/m³]).

Trials to determine a straight line equation and estimate detection threshold (c_{th}) were taken despite a large dispersion of measurement points. On the basis of equation:

$$W = -52.34 + 47 \cdot \log c \quad (5)$$

the result of $c_{th} = 146 \text{ mg/m}^3$ ($\log c = 2.16$) was determined almost precisely equal to the median of literature data (144 mg/m^3 , Fig. 1).

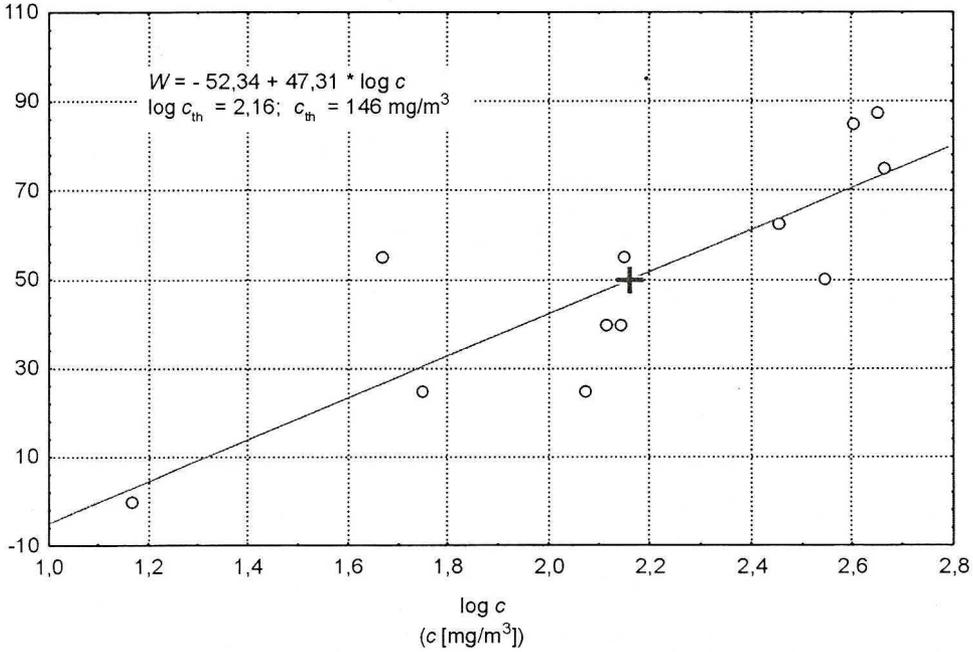


Fig. 3. Results of 2-propanol detection threshold determinations by triangular tests c [mg/m³] – odorant’s concentration

Precision of the conducted odour intensity determinations is characterised by examples placed in Fig. 4: histograms of individual assessments of odour intensity of 2-propanol samples (concentrations of 20.3 g/m^3 and 9.3 g/m^3) – Figs. 4 a and 4 b and charts of $S = f(\log c)$ straight lines, made on the basis of two assessors’ opinions – characterised by the greatest and the smallest evaluations repeatability – Figs. 4 c and d. Standard deviation (SD) of odour intensity determinations was found to be equal approximately $1.0 \div 1.2$ of scale unit. It means that the results obtained by the nine-people panel are standard error-laden:

$$SE = \frac{SD}{\sqrt{9}} = 0.3 \div 0.4.$$

Odour intensity determinations results of all 62 samples of 2-propanol concentration $c = 46 \div 21000 \text{ mg/m}^3$ are shown in Fig. 5 in the coordinate system of S - $\log c$. The diffused set of 550 individual sensation assessments was found to be approximatable with a logarithmic equation:

$$S_{med} = -6.224 + 3.104 \log c \tag{6}$$

which allows for calculating the detection-threshold:

$$c_{th} = 10^{6.224/3.104} = 101 \text{ mg/m}^3 (\log c_{th} = 2.005).$$

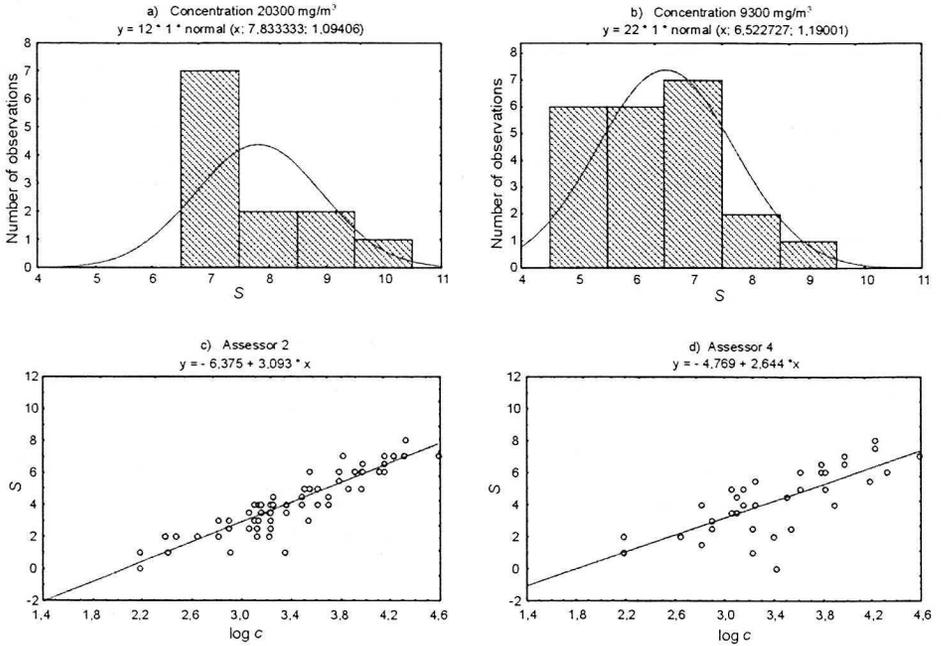


Fig. 4. Histograms of individual assessments of odour intensity of 2-propanol samples and charts of $S = f(\log c)$ straight lines; examples concerning the assessor of the greatest (a, c) and the smallest (b, d) evaluations repeatability

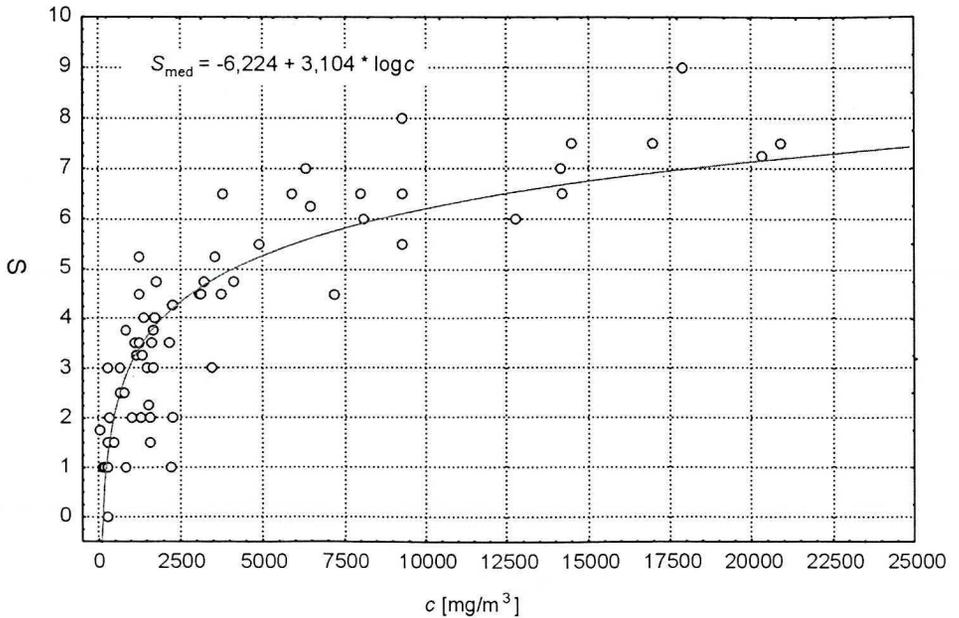


Fig. 5. Dependency of 2-propanol odour intensity on concentration (Weber-Fechner equation)
 S – odour intensity, S_{med} – median of odour intensities, c [mg/m³] – odorant's concentration

DISCUSSION

As a result of triangular tests and the extrapolation in the coordinate system of S -log c odour detection threshold values of 146 and 101 mg/m³ have been obtained. The difference can be considered as small taking account of a specific for sensory measurements uncertainty.

Standard error of odour intensity determinations is $SE = 0.3 \div 0.4$. The assumption that:

$$S \pm SE = S \pm 0.35 = -6.224 + 3.104 \log c$$

leads to threshold values ($S \approx 0$):

$$\log c_{th} = (6.224 \pm 0.4) / 3.104 = 1.88 \div 2.13,$$

which means

$$c_{th} = 76 \div 135 \text{ mg/m}^3$$

A very wide confidence interval is also typical for triangular tests results. Dispersion of measurement points shown in Fig. 3 gives evidence for that. Values of $W \approx 50\%$ were obtained within a range of $\log c = 1.65 \div 2.55$, which corresponds to concentrations $c_{th} = 45 \div 355 \text{ mg/m}^3$.

The main reason for measurement uncertainties is characteristics of human smell – individual sensitivities differentiation and their fluctuations in measurements time caused by many internal and external factors i.e. tiredness, hunger, stress, noise etc. Differentiation of human smell efficiency is illustrated by examples shown in Figs 4c and d. The assessor 2 (Fig. 4c) was characterised by a greater assessments repeatability than the assessor 4 (Fig. 4d). The difference between values of a slope coefficient of $S = f(\log c)$ straight lines is also distinctive. One can assume that an individual feature is not only a height of odour detection threshold but also threshold of difference. It decides on the ability to distinguish samples of a similar concentration or following standards of odour intensity scale.

Increasing repeatability of odour intensity determinations results can be achieved by excluding the assessors of extremely high or low thresholds and of the greatest smell sensitivity fluctuations from the panel. In the case of measurements of odour detection threshold characterising a population such a procedure cannot be considered as a proper one – a selected group ceases to be representative. Increasing measurements precision by enlarging number of panel members and repeating measurements seem to be more advisable.

Comparison of Weber-Fechner straight lines appointed for nine out of twelve participants of the research is presented in Fig. 6a (each assessor conducted not less than 40 assessments). Straight lines equations and values of individual odour detection thresholds ($c_{th} = 64 \div 146 \text{ mg/m}^3$) have been placed next to the charts. The straight lines $S = f(\log c)$ which were determined on the basis of results of odour assessments of the samples of intensity $S = 0 \div 9$ were presented within a range from -1 to +1. Such form of the chart facilitates illustrating changes of "yes" and "no" answers ratios ("I can smell the odour" – "I cannot smell the odour") together with 2-propanol concentration changes. Fig. 6b made for that purpose is an equivalent of the chart illustrating the results of twelve triangular tests (Fig. 3). Picture 6b can be recognised as more reliable than the original one – it was made on

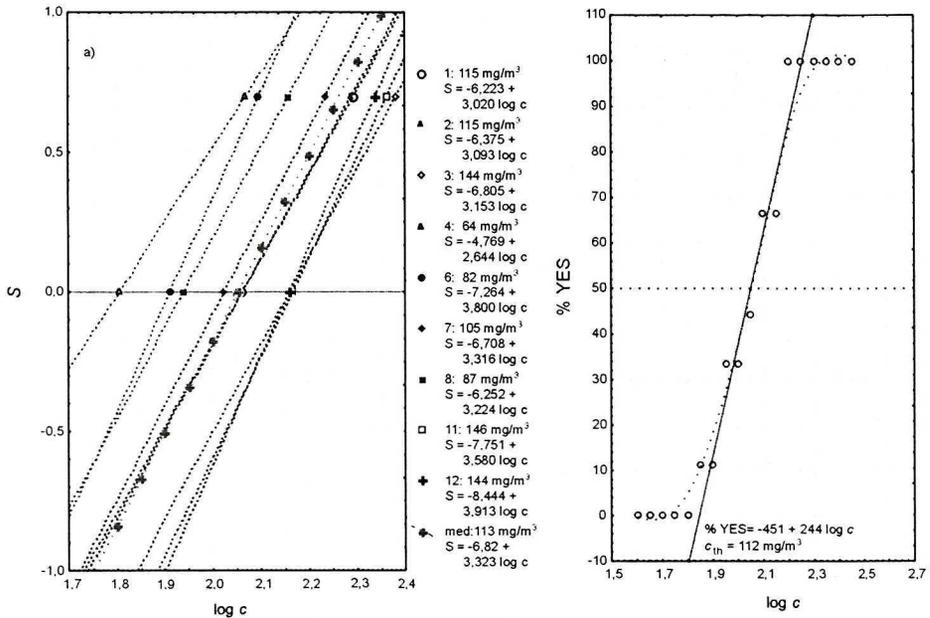


Fig. 6. Modification of procedure of odour threshold determination by yes/no method (example of its application) a) Weber-Fechner straight lines appointed for nine out of twelve participants of the research, b) Dependency of ratio of opinions "yes" (H) on logarithm of concentration determined on the basis of figure a

the basis of over 500 individual odour assessments. It means that $c_{th} = 112 \div 113 \text{ mg/m}^3$ value is more reliable than $c_{th} = 146 \text{ mg/m}^3$.

Straight lines equations $S = f(\log c)$ determined on the basis of individual odour assessments of samples of different concentrations can also be used to determine a course of a function $S_{mean} = f(\log c)$, where S_{mean} – mean of individual assessments. They also allow for forecasting distributions of odour intensity assessments of a sample of any concentration.

An example of ten hypothetical straight lines utilization (Fig. 7a) for making histograms of distribution of odour intensity assessments of samples of a very low odorant's concentration (Fig. 7b) was presented in Fig. 7. Points of intersection of the straight lines with lines determining composition of four samples A, B, C and D of a decrescent concentration were marked. They allow for reading odour intensity classes indicated by all hypothetical assessors (lower limit of a range was included into a class).

An odour of sample A was included by two people into class 0–1, by three people into classes 1–2 and 2–3 and by two people – into class 3–4. A symmetrical distribution of assessments of a median and mean $S_{mean} = S_{med} = 2$ was obtained (a square in Fig. 7a). An odour of sample B was imperceptible for two people (calculations result: $S_{cal} < 0$). In the histogram opinions of those people were included into class 0–1 (lack of a perceptible odour, $S = 0$). It caused occurrence of distribution asymmetry. A mean of all sample B assessments can be calculated as $S_{mean} \approx 2.5 + 3 \cdot 1.5 + 4 \cdot 0.5 + 2 \cdot 0 = 9 / 10 = 0.9$. In the case of sample C, five values $S > 0$ and $S_{cal} < 0$ (lack of a perceptible odour) were obtained as a result of calculations, which is equivalent to reaching a detection threshold ($c = c_{th}$). After including $S_{cal} < 0$ cases into 0–1 class, eight out of ten opinions were found in the class.

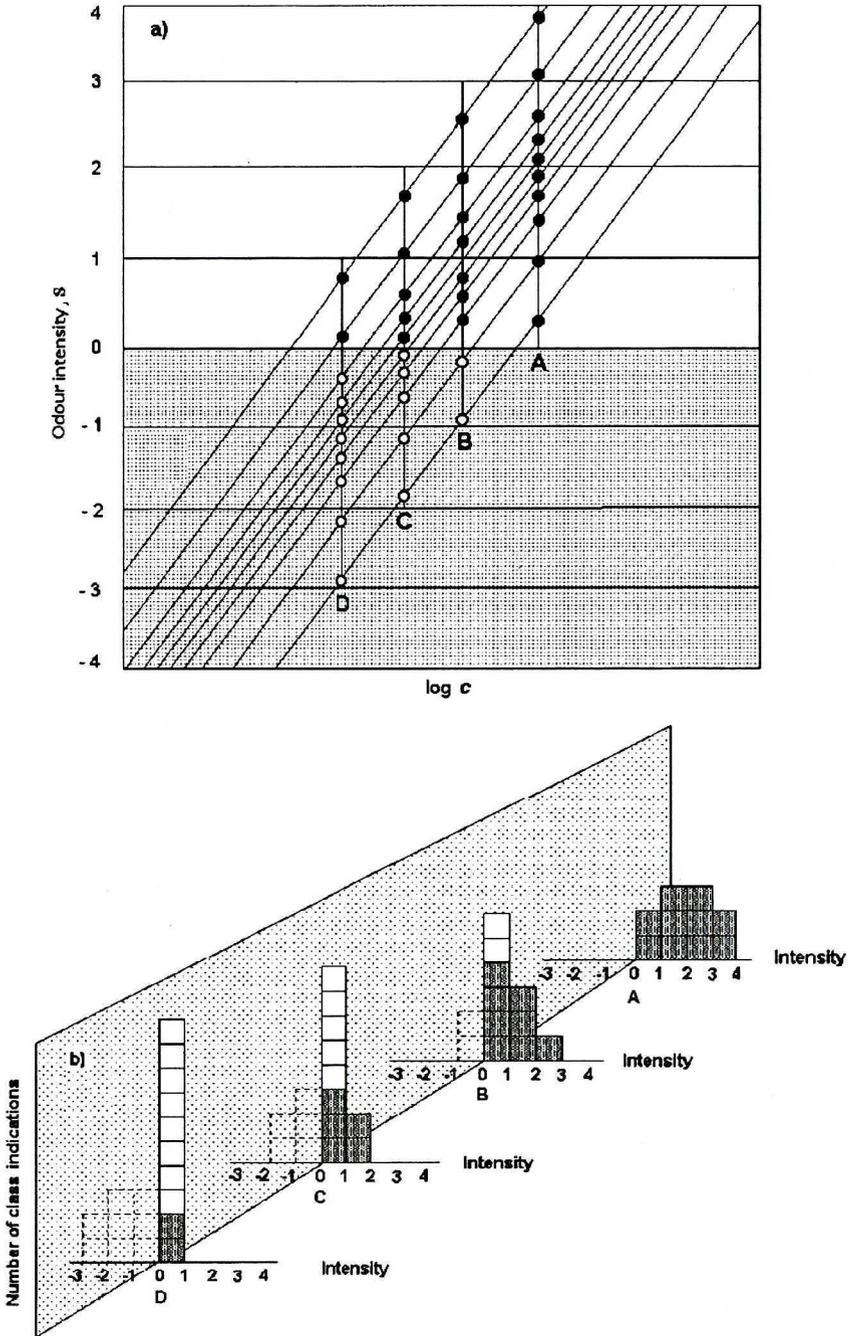


Fig. 7. Modification of procedure of odour threshold determination by yes/no method a) Example of ten hypothetic straight lines utilization, b) Histograms of distribution of odour intensity assessments of samples of a very low odorant's concentration

A mean of sample's C odour assessments set was equal $S_{\text{mean}} \approx 2 \cdot 1.5 + 3 \cdot 0.5 + 5 \cdot 0 = 4.5 / 10 = 0.45$. An odour of sample D remained perceptible for two people who indicated $S = 0-1$ class including in this case all opinions and the mean: $S_{\text{mean}} = 2 \cdot 0.5 + 8 \cdot 0 = 0.10$. Value $S_{\text{mean}} = 0$ is not obtained unless the odour ceases to be perceptible by the person of the most sensitive smell.

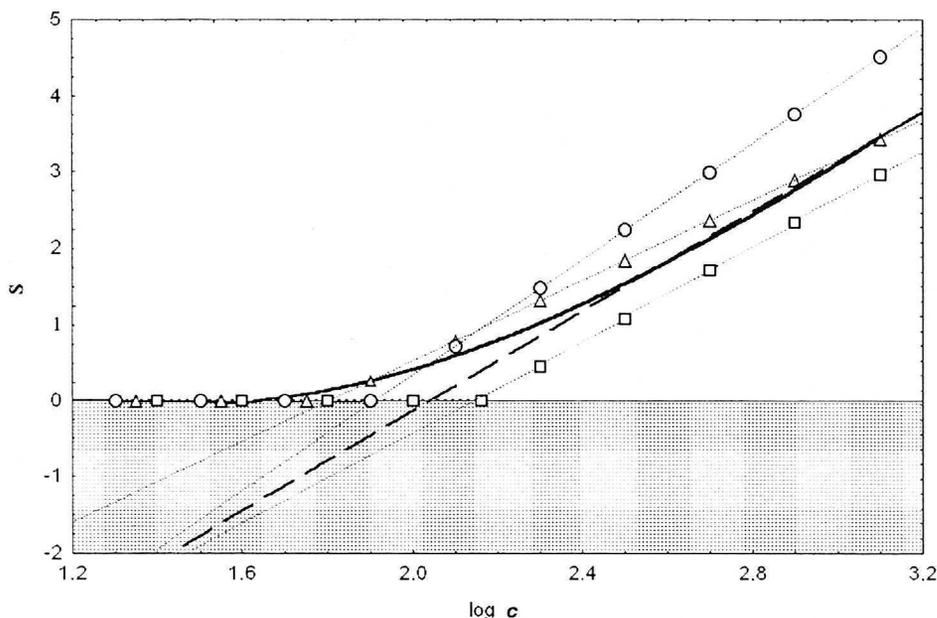


Fig. 8. Illustration of apparent deviations from Weber-Fechner law caused by asymmetry of distributions of odour intensity assessments within low concentrations range (explanations in the text)

Analogical effects can be illustrated with an example concerning the odour of samples polluted with 2-propanol. A chart of $S_{\text{med}} = f(\log c)$ dependency determined on the basis of nine equations of straight lines presented in Fig. 6a (smell characteristics of particular participants of measurements) is placed in Fig. 8. To increase clarity of the figure only three out of nine straight lines were placed in it – dotted lines of a different slope, which intersect $S = 0$ line at different $\log c$ values (individual detection threshold). The dotted straight line and the solid line illustrate $S_{\text{med}} = f(\log c)$ dependency, where S_{med} is a median of nine S_{cal} values calculated for each 2-propanol concentrations in hypothetical samples. The dotted line illustrates results of median calculations conducted in compliance with negative values of odour intensity (assumption of $S = f(\log c)$ equations validity within a subthreshold concentration range). The solid line was determined by changing $S_{\text{cal}} < 0$ values into $S = 0$. The demandable value of odour threshold is indicated by the point of intersection of the dotted line by the line $S = 0$: $\log c = 2.05$; $c = 113 \text{ mg/m}^3$. $S_{\text{med}} \approx 0.4$ value can be read over the point from the solid line (a median calculated from a distribution function; middle value of a set: $S = 0$).

The presented examples indicate the reason for deviations from straight lines S_{mean} or $S_{\text{med}} = f(\log c)$ which were found during odour detection threshold determination by an

extrapolation method. They suggest that straight lines equations should be determined using samples of odour perceptible by all or almost all panel members assessing odour intensity ($S \geq 2 \cdot SD \approx 2$).

More advisable is the above-described procedure utilising psychophysical equations determined separately for each assessor. This way of data collecting and elaborating allows for adjusting measurements range to sensory efficiency of each person (odorant concentrations range, number of samples, number of repetitions). Calculation of a specific for a population odour detection threshold involves collecting a large set of equations complying with established criteria of precision.

CONCLUSIONS

1. Odour detection threshold of 2-propanol determined by a method of extrapolation to $S=0$ in the coordinate system of S -log c equals approximately 100 mg/m^3 (mean $\pm SE = 76 \div 136 \text{ mg/m}^3$). It is insignificantly lower than one determined by triangular tests (approximately 146 mg/m^3). The values determined by both methods are close to the median of values distribution published earlier by different authors (they are situated in the middle part of the quartile interval).
2. Increasing precision of odour detection threshold determination requires conducting measurements with participation of a larger number of people assessing the odour.
3. Calculations conducted by using measurements results of odour intensity (S) of air samples of different concentration (c), conducted independently from each other by more than ten assessors, are the most advisable method of odour detection threshold determination. The number of odour intensity assessments that should be conducted by each assessor during determining function equation $S = f(\log c)$ depends on a person's sensory efficiency.

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