Odour Chromatography
GC Detector Treated as Sensors Field

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Abstract

Odour intensity is one of the odour characteristics deciding on quality of the ambient air, viands, household goods etc. Authors of the following paper made a trial of combining a gas chromatograph and neural networks to search for possibility of an objective method of measuring the characteristic. Binary mixtures of acetone and ethanol were diluted staticly with ambient air and presented to a panel assessing odour intensity. There were chromatographic analysis of the samples performed simultanously. Values of GC detector signals were combined with corresponding sensory assessments of odour intensity and fed into an artificial neural network. Dependency of neural networks quality on the number of variables defining odour intensity was investigated. It was found that for binary mixtures the relationship is unexpectedly small.

1. Introduction

Odour intensity of ambient air among its hedonic quality and frequency of odour appearance is one of the features which mostly influence odour nuisance perception. In order to settle many disputes between inhabitants of industrial areas and an industrialist responsible for odour polution, a specific group of at least 4 people of a verified smell sensitivity can play a role of a panel assessing odour occurence in samples presented with a dynamic olfactometer according to EN 13725:2003.

However engaging human panels whose reliability must be constantly verified before, during and after measurements seems to be a tremendous and highly-expensive method of odour nuisance assessments. That is the reason for undertaking many trials of acquiring an instrument which could substitute human beings. There are various electronic noses available on the market. One of the major difficulties related to general application of EN instruments is that each of many sensors should react in a different way so that the sensors field could produce a different description of a complex mixture. Differentation of the sensors available on the market is still not satisfying [1]. The main difficulty is to chose and prepare an appropppriate set of sensors for an analysed gas mixtures.

In authors opinion chromatographic data is a source of many more pieces of information than a sensors array of a typical electronic nose. The set of variables defining the odour characteristic can consist either of compounds concentrations, peaks areas [2, 3] or as a novelty – values of a GC detector signals registered with a required frequency [4, 5].

The aim of the paper was to verify capabilities of utilising a set of following chromatographic detector signals (defining variables) as information about odour intensity (defined variable) and investigate whether neural networks can interpret a set of time-distributed defining chromatographic data in an analogical way as a set of space-distributed signals from a sensor field of an electronic nose.

2. Methodology

There were 70 samples of binary mixtures of acetone and ethanol prepared and diluted with ambient air in the Laboratory for Odour Quality of the Air equipped with a highly-efficient air conditioning instalation. Volumes of pure components were mixed with a proportion of x_{ac} = 0,2-1 (x_{ac} – mass ratio of acetone). Static dilutions were performed in foil bags (Toppits Melita, sleeve width = 31 cm) with Hamilton sampling syringes (500 ml, 1500 ml).

Odour intensity of samples consisted in comparing a sample with n-butanol scale of standards by eight assessors. The scale was composed of 10 aqueous n-butanol solutions in Erlenmayer flasks set in a row of concentrations decreasing in a geometrical sequence. Each panelist determined his own individual odour threshold of n-butanol (number of the flask at which the odour was perceived + 0,5) and then compared odour intensity of the sample with the scale of standards. The panelist determined the number of the standard whose odour was as intensive (or a little more) as the odour of the sample. The odour intensity was determined by a difference:

S = number of the threshold standard – number of the standard acuired for the sample.

Sensory assessments were performed simultanously with chromatographic analyses of the samples. SRI 8610C chromatograph with a Restek pillar (d=0,53mm, MXT-WAX 1,5 μm) was utilised. Analysis were performed in isothermal conditions; pillar: 30˚C, injector and detector: 120˚C, at a constant hydrogene pressure – 21 psi and air pressure – 7 psi.

Chromatographic data was registered in ASCII format with frequency of 1 Hz in 180 seconds. A specific 64-second range of data registering was appointed (64 defining variables) which was utilised for preparing a basic set of 430 training cases (Excel spreadsheet). Limiting values in the basic set were the values of the signals registered in the 20th second before occurrence of the maximum of the first peak and in the 20th second after occurrence of the maximum of the other peak. In successive research stages the number of defining variables was reduced by removing every other column of

the set. Training sets consisting of 64, 32, 16, 8, 4, 2 variables were obtained. An example of two sets is illustrated in figure 1.

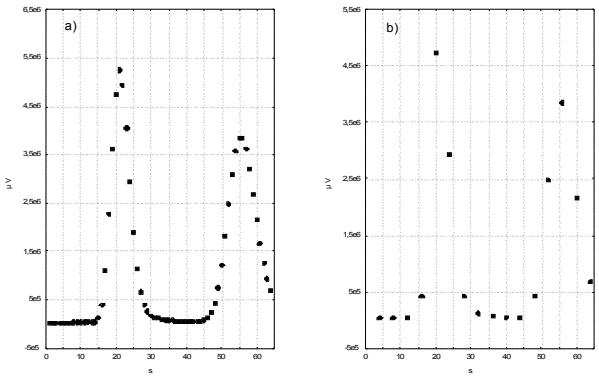

Fig. 1 Illustration of data defining odour intensity of $S = 6$

Sets of detector signals were combined with corresponding individual odour intensity assessments to form training sets for artificial neural networks and divided into three subsets: 156 training cases, 155 verifying cases and 119 testing cases.

3. Results

Individual odour intensity assessments lay within the range of 0 – 7 of n-butanol scale of standards.

30 neural networks were generated using StatSoft Statistica Neural Networks 3.0 (Automatic Network Designer option, number of iterations: 100, number of steps: 1). The prevailing network type was a multilayer perceptron (MLP) with two or three layers of hidden neurons (fig. 2).

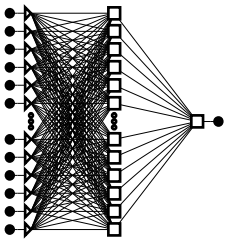

Fig. 2 Exemplary multilayer perceptron with one hidden layer (64 inputs, 1 output)

There was a big differentiation between individual odour assessments of a single sample whereas neural networks gave one evaluation of odour intensity for each sample (value close to a median of individual odour intensity assessments) represented with solid horizontal lines in figure 3.

Medians values of sets of networks answers did not differ more than 1,5 grade of scale from medians of individual sensory assessments sets. In case of utilising the 32-cases set, the difference did not exceed 0,5 grade of scale (figure 4).

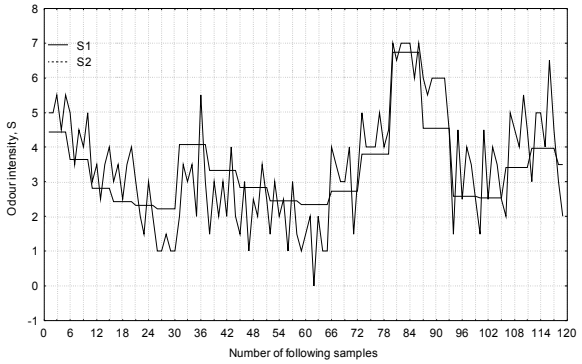

Fig. 3 Individual assessments and results of neural network forecasts of odour intensity of 119 test cases

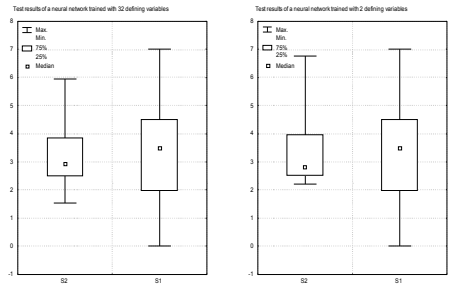

Fig. 4 Comparison of sets of odour intensity assessments and forecasts of neural networks trained with 32 and 2 defining variables

In this case Pearson linear correlation coefficient was equal to $r = 0{,}83$ (fig. 5a). The adequate correlation coefficient, determined for a network trained with two defining variables, was equal to $r = 0{,}77$ (fig. 5b).

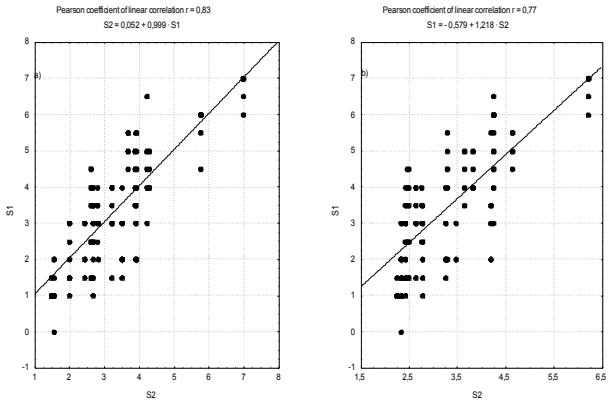

Fig. 5 Illustration of correlation between a set of individual odour intensity assessments and a set of neural network answers

A dependence of median of absolute differences $|S2\text{-}S1|$ on number of defining cases was described with an equation:

$$|S2\text{-}S1|_{med} = 0{,}788 - 0{,}003\ n,$$

where $S1$ – individual odour intensity assessment, $S2$ – neural network answer, n – number of defining variables in a neural network training set. The mentioned equation indicates an unexpectedly small dependence of an

absolute error on a number of introduced data defining odour intensity of a two-component mixture of odorants.

4. Discussion of results

Preparing an integrated instrument for odour assessments composed of a gas chromatograph and a neural network trained on the base of set of sensory assessments will solve a problem of labour-consuming odour measurements. It is the next step on the way of objectivation of odour intensity measurements.

However limitting information to two values of a signal recorded in two constant points of a specific range of an analysed mixture detection inconsiderably aggravates quatlity of neural networks answers.

In case of multicomponent mixtures, where more complex dependencies decide on odour intensity or odour character, such small number of information will be insufficient for describing the odour with a required precision. Amount of information defining odour may be increased in many ways. Utilising different chromatographic split and register conditions will enable to achieve richer data bases for neural network trainings. Figure 6 shows two chromatograms of one sample of unleaded fuel registered in different separation conditions.

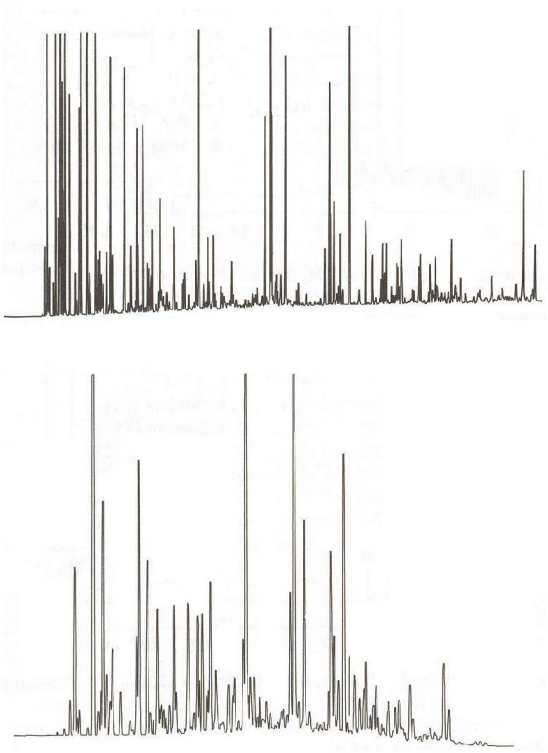

Fig. 6 Chromatograms of unleaded fuel registered in different separation conditions as a dual source of chromatographic data

Chromatographic data sets can be combined in one neural network training set to form a richer definition of any odour characteristics.

References

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