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Quantitative analysis of multiple kinds of volatile organic compounds using hierarchical models with an electronic nose

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ABSTRACT

This paper studies hierarchical discrimination and quantification models in order to simultaneously quantify multiple kinds of odors with an improved electronic nose. Such tasks are first regard as multiple discrimination tasks and then as multiple quantification tasks, and implemented by the hierarchical models with the divide-and-conquer strategy. The discrimination models are the common classifiers, including nearest neighbor classifiers, local Euclidean distance templates, local Mahalanobis distance templates, multi-layer perceptrons (MLPs), support vector machines (SVMs) with Gaussian or polynomial kernels. Similarly, the quantification models are multivariate linear regressions, partial least squares regressions, multivariate quadratic regressions, MLPs, SVMs. We developed several types of hierarchical model and compared their capabilities for quantifying 12 kinds of volatile organic compounds with the improved electronic nose. The experimental results show that the hierarchical model composed of multiple single-output MLPs followed by multiple single-output MLPs with local decomposition, virtual balance and local generalization techniques, has advantages over the others in the aspects of time complexity, structure complexity and generalization performance.

1. Introduction

Odors cannot be seen by eyes and felt by hands. People usually use some vague terms to describe their characteristics, such as strong, weak, stimulative, fragrant, top-quality, second-rate, normal, abnormal, sweet, foul, and abominable [1,2]. We can depict one kind of odor by means of another. For example, an odorous sample may be said to be like orange or banana, but what is the orange or the banana odor? Such questions are very difficult to be answered. Odors ever smelled can remain in our memory and be brought to our mind by imagination, but cannot be quantitatively compared by data or recode. It is not an easy thing to quantify odors only by our olfaction, namely our noses. Accordingly, sensory evaluation of odor qualities is not objective and fair enough, even if given by experts. Under the circumstances, electronic noses (ENs) emerge as the times require [3].

Electronic noses have a wide range of applications. After sensing odors with a gas sensor array and analyzing the resulting data by means of appropriate pattern recognition methods, an EN can determine products' classes, grades and freshness; distinguish genuine from sham; control production processes; readjust prescriptions; monitor environmental pollutions, etc. The application objects include perfumes [4–7], milks and teas [8–10], alcoholic beverages [11–13], fruits [14], fishes and meats [15–17], environmental air [18], water [19,20], medical treatments [21], drugs [22], warfare agents [23,24], and even bloods and bacteria [25,26]. Can we find an absolutely odorless material?

There are many kinds of odors in the natural world, and often tens, hundreds and even thousands of components in one kind. For example, there exist about 50 main aromatic components in a brewing alcoholic drink. If the aroma of the drink changes, an EN is required to judge which components change and how much they change. Currently, ENs are limited in capabilities to carry out the real-time quantitative analysis of odors [1,4–26]. Therefore, there is an urgent need to find suitable pattern recognition methods to both discriminate and quantity multiple kinds of odors, simple or complex [1].

An unfavorable case for odor quantification is that the lower the concentrations of odors, the smaller the differences between them. In other words, different sorts of low-concentration odors may be close to each other in the measure space. The relationships between strengths of multiple kinds of odors and their components may be multiple complex curved surfaces, which may intersect with each other. Therefore, the discrimination and quantification of multiple kinds of odors will bring about great difficulties and challenges to the existing pattern recognition methods, including neural

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networks [1,7,14,18,27] and support vector machines (SVMs) [28,29].

A single prediction model with multiple output units will give multiple predicted values for a specific odorous sample. Can we thus say that the sample belongs both to an odor ω_A with a concentration ρ_A and to another odor ω_B with a concentration ρ_B? It is unallowable. In other words, a single prediction model with multiple output units fails to quantify multiple kinds of odors, regardless simple or complex [1,2,30–34]. In order to recognize many kinds of odors and quantify their concentrations as well, the following approaches are available.

(A) A single multi-output (SMO) discrimination model [1] or a SMO discrimination model followed by multiple multi-output (MMO) discrimination models [30,31] is used. The two solutions actually consider the quantification task as a pure discrimination one, and a concentration point as a class. The disadvantages of these solutions include complicated structures, long learning time and serious imbalance between classes when many kinds of odors and many concentrations exist. Consequently, these two models are only suitable for a small number of classes of odors with limited concentrations [30,31].

(B) An SMO discrimination model followed by multiple single-output (MSO) quantification models, called an SMO–MSO model, or two groups of MSO quantification models in cascade, called an MSO–MSO model [32], is employed. These solutions consider the quantification task first as multiple discriminative tasks and then as multiple quantitative tasks. However, the defects that exist in case (A) will still appear when there are too many kinds of odors and concentration points.

Because the existing pattern recognition models are quite limited in their capabilities for identifying many kinds of odors and quantifying their concentrations as well [30–34], this paper devotes to studying hierarchical models and finding out the appropriate model to accomplish such tasks. The remainder of this paper is organized as follows: Section 2 illustrates an improved electronic nose and introduces its working principle. In Section 3, we propose the structure of a hierarchical model and possible component units. Furthermore, we analyze the time complexities, structure complexities and generalization performances of several hierarchical models. Section 4 presents the experimental results for quantifying 12 kinds of volatile organic compounds (VOCs). Finally, Section 5 comes to our conclusions.

2. Experimental

Fig. 1 shows an improved electronic nose [35], which consists of a test box, a personal computer (PC), six headspace vapor generators and a clean air cylinder. The test box mainly contains a thermostatic chest, an automatic lift device, a sampling needle, a miniature diaphragm vacuum pump, three two-positional two-way electromagnetic valves, a flow meter, two flow valves, a 4-channel direct current (DC) source as well as control and measure circuits. The array, which is installed within the circular chamber in the thermostatic chest, is composed of 16 TGS gas sensors, namely TGS800, 812, 813, 816, 821, 822, 823, 824, 825, 826, 830, 831, 832, 842, 880, 883T, all provided by Figaro Inc., Japan. The load resistor of each gas sensor is fixed at 10 kΩ.

The samples, liquid or solid, and headspace vapors are kept at the constant temperature of $42 \pm 0.1\,^{\circ}$C for 30 min before measured, and the chest always kept at $55 \pm 0.1\,^{\circ}$C. In order to get good repeatability, a sample of 10 ml and its headspace vapor is measured only one time, and a glass flask of 200 ml to hold the sample and thus generate the vapor is also used only once. The responses of gas sensors are limited to the range (0.0, 10.0 V) by hardware.

The gas sensor array is calibrated by clean air before sampling. The clean air from the cylinder passes through the flow valve 2, the electromagnetic valve 3, the outlet, the interior and the inlet of the circular chamber, and the needle in sequence before exhausted into the atmosphere, at the flow rate of 600 ml/min. During the course, the electromagnetic valve 3 is on while the other two are off. Consequently, the gas sensors exactly recover to their preliminary state.

The working principle of the improved electronic nose is described as follows. While sampling, under the roles of the PC and the automatic lift device, the headspace vapor generator rises, and the sampling needle fixed under the inlet of the chamber thus contacts the headspace vapor. With the aid of the miniature diaphragm pump, the vapor in the flask is drawn into the circular chamber where the gas sensor array is mounted in at the flow rate of 600 ml/min, forced to skim across the sensitive films of gas sensors, and finally exhausted into the air at the waste gas outlet. Along with the flow of vapors, the gas sensors produce analogous sensitive responses, which are then converted into digital by the data acquisition card and stored in the PC as a data file. For a sample measured, a 16-dimensional response vector is thus gotten, called a pattern $\boldsymbol{x} \in R^{16}$ hereafter, because the maximum steady-state response of a gas sensor is regarded as a variable.

The purpose of the experiment is to discriminate twelve kinds of VOCs, ethanol, butanol, hexanol, ethyl acetate, ethyl propionate, ethyl butyrate, ethyl valerate, ethyl caproate, ethyl heptanoate, ethyl octanoate, ethyl lactate, and isoamyl acetate, and quantify their concentrations as well by measuring their headspace vapors with the improved electronic nose. These VOCs are the main fragrant components in brewing alcoholic drinks. They are diluted with distilled water into required concentrations.

3. Hierarchical models and their component units

3.1. Structure of hierarchical models

The divide-and-conquer strategy is an effective approach for the discriminative and quantitative analysis of multiple kinds of odors [30–34]. Fig. 2 illustrates a hierarchical model for implementing such tasks. Seen from the horizontal direction, a pair of hierarchical modules represents a specific kind of odor. The former module is responsible for discrimination, whose role is to separate the represented odor from the others, and the followed one is in charge of quantification, whose role is to predict the strengths and concentrations of the represented odor. If there are n kinds of odors, there are n pairs of modules, one for one. Seen from the vertical direction, there exist two parallel columns of modules. The modules in the first column are for discrimination, and those in the second column are for quantification.

3.2. Discrimination models

Because of the nonlinear distributions of odors in the measure space, the classical linear discriminant analysis (LDA) is not adopted [11,36]. The radial basis function (RBF) networks [9,11] and fuzzy inference models [1,37] are not included because they are not often employed for odor discrimination in the electronic noses. *k*-Nearest-Neighbor (*k-NN*) classifiers, Euclidean or Mahalanobis distance templates, multi-layer perceptrons (MLPs) and SVMs are able to form nonlinear decision boundaries and commonly used in the electronic noses [1,11,29–34]. They are thus chosen as the component units of discrimination modules of the hierarchical model shown in Fig. 2. In the following subsections, we will introduce the