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Extracting information from noise spectra of chemical sensors: single sensor electronic noses and tongues

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Abstract

Electronic noses and tongues can utilize noise data taken at the output of a chemical sensor. It is shown that even one single sensor may be sufficient for realizing an electronic nose or tongue.

Keywords: Sensor principle; Electronic nose; Electronic tongue; Excess noise spectroscopy

1. Introduction

Intensive research has been going on during the past several years to use chemical and biological sensor [1–5] elements to develop systems known as electronic noses and electronic tongues [6–10]. They consist of several sensor elements and a pattern recognition unit comprising data acquisition and usually a neural network software. The neural network, or a similar pattern recognition tool, is necessary due to the nonlinear character of the sensor system, which 'learns' to interpret data during a calibration process. There are several important practical issues, such as ways to decrease the number of necessary sensors, ascertaining sufficient sensitivity, obtaining reproducibility, diminishing the need for frequent calibration, and establishing the most suitable pattern recognition technique. This paper addresses the need for multiple sensors and demonstrates that measurements of conductivity noise in a sensor can lower the required number of sensors to, in principle, only one.

Conductivity noise in conducting polymer sensors was studied by Bruschi and coworkers [11,12] who pointed out that such data provided information of interest for sensing. The authors demonstrated that the conductance noise spectrum is a sensitive measure of the chemical environment. The exact origin of the microscopic noise component, due to the chemical environment is presently unclear. It can certainly be associated with fluctuations of the carrier mobility and density, due to concentration fluctuation and motion of chemical fragments, originating from the chemical environment (ambient gas or liquid). The resultant resistance fluctuations provide an ac signal with wide frequency bandwidth, which obviously carries more information than the dc resistance, that is normally recorded in a sensor. In addition to being able to detect multiple species, the noise technique enhances the sensitivity and selectivity of the sensor.

2. The new nose/tongue principle

We propose to use the random temporal fluctuations (noise) of the measured physical quantity in artificial noses and tongues, see Fig. 1. We would like to emphasize that the generality of the principle, makes it of secondary importance only to consider the actual sensor device [1–5] (film, transistor, optical surface, etc.) and the corresponding physical quantity (voltage, current, resistance, capacitance, light intensity, angle, etc.) applied for sensing. The mathematical expressions given below hold for any measured quantity which is used for chemical sensing. However, for the sake of simplicity [13], we use here the term resistance to represent the pertinent physical quantity.

Assuming then a resistive sensor exposed to a chemical environment, we propose the use of the *resistance noise* $dR(t)$ of the sensor resistance R instead of using the induced static change dR of its mean value. The exact origin of resistance fluctuations [14–20] in solids is a longstanding unsolved problem [15–17]. Different results have been interpreted in different ways, and even basic issues are

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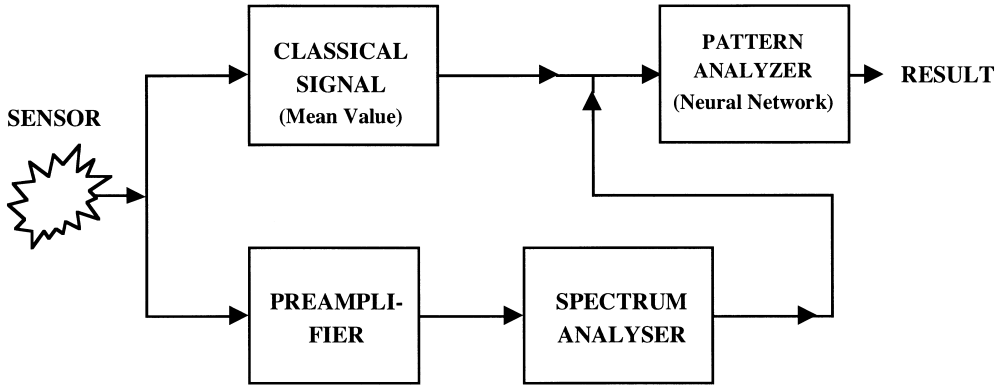

Fig. 1. Possible realization of the electronic nose or tongue principle [13]. The mean resistance and the resistance noise spectrum are measured. The spectrum is analyzed by a pattern recognition technique.

controversial, such as, whether the microscopic origin of the noise is mobility fluctuation or number fluctuation of charge carriers [15–17]. Compared to these basic difficulties, the *phenomenological* origin of noise in chemical sensors is an easier topic [20], as the noise is due to the chemical fragments which originate from an absorbed ambient gas or liquid. After equilibration of the sensor with its environment, the capturing and releasing of molecules becomes a stationary stochastic process. Hence, d*R(t)* is also a stationary stochastic process.

Three important noise sources exist in the systems of present interest [20]: dynamic adsorption–desorption, dynamical percolation [18] of the chemical molecules, and charge carrier trapping noise [14]. These effects provide a noise spectrum characteristic of the chemical species, the applied sensor material, and its microstructure. It is well known that $S(f)$, the power spectrum of the noise, is a much more sensitive indicator of changes in the material structure [18] and in the environment [19] than the change of the mean resistance. In the rest of this section, we compare traditional sensor arrays and corresponding systems employing noise analysis.

We consider a system with M sensors and N different chemical species. The resistance response of the sensors can be described by a series of equations according to

$$\begin{aligned} \mathrm{d}R_1 &= A_{1,1}\,C_1 + A_{1,2}\,C_2 + \cdots + A_{1,N}\,C_N \\ &\vdots \\ \mathrm{d}R_M &= A_{M,1}\,C_1 + A_{M,2}\,C_2 + \cdots + A_{M,N}\,C_N \end{aligned} \tag{1}$$

where $\mathrm{d}R_i$ is the change of the resistance of the ith sensor, C_j is the concentration of the jth chemical species, and $A_{i,j}$ is a set of calibration functions. The task is to determine the concentrations $C_1, \ldots, C_N$ by the measurement of $\mathrm{d}R_1, \ldots, \mathrm{d}R_N$. Generally, the equations are nonlinear, and the $A_{i,j}$ quantities are functions of all of the concentrations, i.e. $A_{i,j}$=$A_{i,j}(C_1, \ldots, C_N)$. This nonlinearity is the reason, why practical sensor systems need a neural network that 'learns' these functions during a calibration process.

In order to illustrate the technical problem with the help of the simplest mathematical formalism, and for the sake of simplicity, we first assume that the sensors are linear and that their responses are independent for each investigated chemical species. Therefore, the $A_{i,j}$ quantities are only calibration constants. From the basic algebra of linear equation systems, it then follows that one needs N independent equations to solve the equation system (1). Therefore, the number M of different sensors has to be larger than or equal to the number N of chemical species, i.e.

$$M \geq N \tag{2}$$

In a practical case, when the equations are nonlinear, the limit given by relation (2) still holds. However, the situation becomes much more complex, with several possible solutions being allowed, and the application of a neural network is required. The validity of relation (2) makes electronic noses and tongues cumbersome and expensive because all of the sensors have to exhibit different natures of their response.

We now turn to the case of noise spectroscopy and, in particular, consider the important issue of the number of sensors needed to analyze a mixture of different chemical species. It is first assumed that only one sensor is present. If the power density spectrum of the resistance fluctuations in this sensor has K different frequency ranges, in which the dependence of the response on the concentration of the chemical species is different from the response in the other ranges, one can write

$$\begin{aligned} \mathrm{d}S(f_1) &= B_{1,1}\,C_1 + B_{1,2}\,C_2 + \cdots + B_{1,N}\,C_N \\ &\vdots \\ \mathrm{d}S(f_K) &= B_{K,1}\,C_1 + B_{K,2}\,C_2 + \cdots + B_{K,N}\,C_N \end{aligned} \tag{3}$$

where $\mathrm{d}S(f_i)$ is the change of the power density spectrum of resistance fluctuations at the ith characteristic frequency (or frequency range), and the $B_{i,j}$ quantities are calibration constants analogous to the $A_{i,j}$ quantities in the linear response limit. Thus, a single sensor is able to provide a set of independent equations to determine the gas composition around the sensor. Considerations corresponding to those that led to relation (2), then imply that the number K of different applicable frequency ranges has to be

greater than or equal to the number N of chemical species, i.e.

$$K \geq N \tag{4}$$

In principle, even one sensor can be enough to analyze the composition of a number of different gases. If we have P different detectors, and if we can use the same characteristic frequency ranges for all detectors, then we have

$$\begin{aligned} \mathrm{d}S^{(1)}(f_1) &= B^{(1)}_{1,1} C_1 + B^{(1)}_{1,2} C_2 + \cdots + B^{(1)}_{1,N} C_N \\ &\vdots \\ C_2 S\mathrm{d}^{(P)}(f_M) &= B^{(P)}_{M,1} C_1 + B^{(P)}_{M,2} + \cdots + B^{(P)}_{M,N} C_N \end{aligned} \tag{5}$$

where $\mathrm{d}S^{(k)}(f_i)$ is the change of the power density spectrum of resistance fluctuations at the ith characteristic frequency range in the kth sensor. In the best case, the number of independent equations is PK, so the relation

$$PK \geq N \tag{6}$$

holds.

One should note that the mean resistance variation $\mathrm{d}R^{(k)}$ of the different sensors can also be used for detection, and it can provide an additional independent equation. The relevant relation is then

$$P(K+1) \tag{7}$$

3. Illustrative experiment with commercial taguchi sensors

The new sensor principle was demonstrated via noise measurements applied to different types of commercial gas sensors. We used two different semiconducting thick film resistive sensors from the NAP 11 series (RS-components), specifically a NO sensor (#286–642) and an air quality sensor (#286–620). The sensor was placed in a grounded aluminum box with a volume of about 300 cm^3. A dc heating voltage was applied according to the manufacturer's recommendation. The chemicals to be detected in the experiment were placed in a small plastic cup positioned in the measurement box at a distance of about 5 cm from the sensor. Then the box was closed. A stable dc measuring current was fed through the sensor film. The dc voltage on the sensor and the voltage fluctuations (after preamplification) were measured by a computer with an AD converter card, which performed the data analysis. After closing the box, the concentration of chemical vapor (natural odor) inside the box increased, thereby yielding a drift in the recorded dc voltage. When the vapor reached saturation in the box, the dc voltage attained a stable value. This saturation took about 5 min. To increase the visibility of the change in the 'shape' of spectra (the slopes in different frequency ranges), the measured spectra were multiplied by the frequency.

The effectiveness of the new chemical sensing principle is demonstrated in Fig. 2 by the analysis of natural oleoresinous odors, such as, senna tea leaves, potato chips and white pepper by the air quality sensor. The log–log plot for the $f^*S(f)$ function of the measured voltage noise is used for analysis. The resistance noise and the voltage noise amplitudes are related via the Ohm's law, which for the spectra implies, a relation scaling with the square of the driving dc current. Note that the main information is contained in the shape of the pattern and not by the actual value of the spectrum at a given frequency. The data show that the $f^*S(f)$ 'fingerprint' is sensitive enough to detect these oleoresinous odors and to indicate that they are different.

Fig. 3, pertaining to vinegar vapor and the NO sensor, shows an example of a possible way of pattern generation from the noise spectrum. We used the mean value of the slope of the log–log plot for the $f^*S(f)$ function in the different frequency decades to generate the pattern. We have

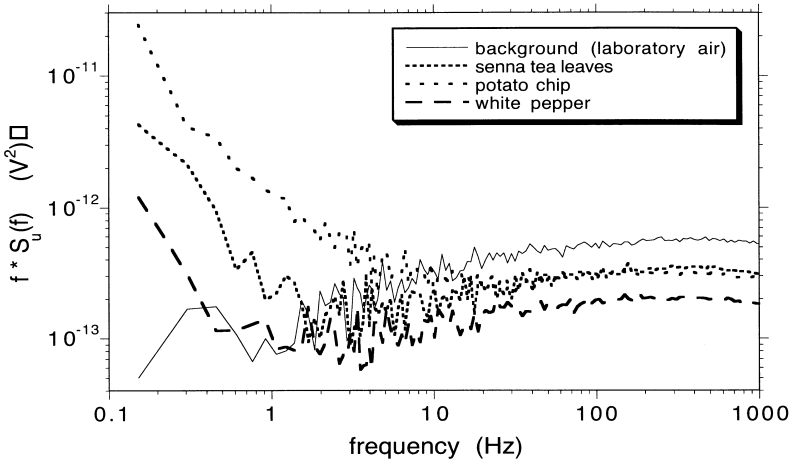

Fig. 2. Demonstration of the usefulness of the new sensor principle. The voltage noise spectrum $S_u(f)$ of the sensor (proportional to the resistance noise spectrum) was measured at a current of 125 μA during exposition of the sensor to different types of natural odors. The differences between the shape of the spectra should be noticed.

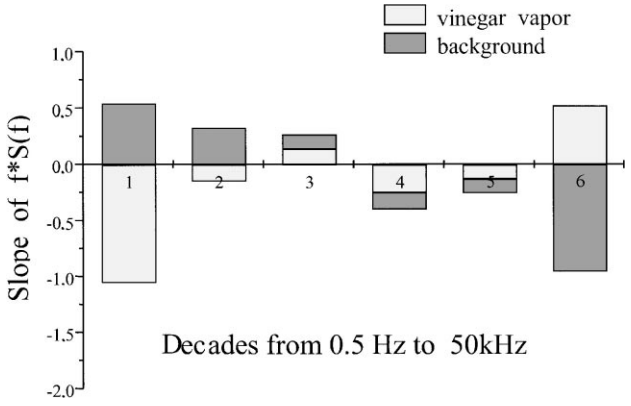

Fig. 3. Example of a way of pattern generation from the noise spectrum. The pattern was generated by the mean value of the slope in the log–log plot of the $f^*S(f)$ function in the different frequency decades. The background data were obtained in the laboratory air.

found that these slopes provide reproducible output quantities for different chemicals. Independent patterns are generated by vinegar vapor and laboratory air (background), and it is obvious that by using noise analysis, one can have a single sensor replacing an array of at least six sensors.

4. Summary

This paper has presented a new principle for electronic noses and other chemical sensor systems, based on resistance noise spectroscopy. It has been demonstrated that even a single sensor can be sufficient to distinguish between a number of different chemical species. Potential advantages of the new technique include a strong reduction of the number of necessary sensors, improved selectivity, and sensitivity.

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Biographies

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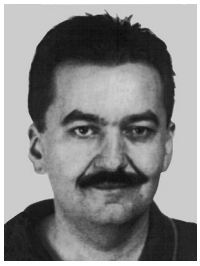

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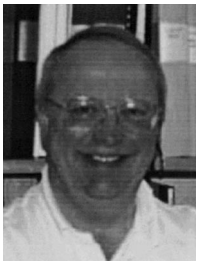

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