Detecting Harmful Gases Using Fluctuation-Enhanced Sensing With Taguchi Sensors

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***Abstract*—Sensing techniques are often required to not only be versatile and portable, but also to be able to enhance sensor information. This paper describes and demonstrates a new approach to chemical signal analysis that we call *fluctuation-enhanced sensing*. It utilizes the entire bandwidth of the sensor signal in contrast to more conventional approaches that rely on the dc response. The new principle holds prospects for significantly reducing the necessary number of sensors in artificial noses and tongues, and it can provide improved sensitivity.**

***Index Terms*—Gas electronic noses, intelligent sensors, noise, spectral analysis.**

I. Introduction

ARTIFICIAL noses and tongues are sophisticated systems used in the identification of complex mixtures of chemicals (see, for example, [1]). They employ a number of different sensors, which work simultaneously to obtain enough information for the identification of the mixtures. It is relatively straightforward to demonstrate by using the theory of *linear equation* sets that, to uniquely identify a mixture of N components, the minimal number of sensors with different responses is N [2]. Note that the mathematical treatment in [2] assumes the most ideal case, where the sensor responses are independent, linear, and additive for multiple gases. Less ideal cases, such as nonlinear response or nonindependent response, need more sensors.

Due to the relatively fast aging and the deterioration of properties, the need for reducing power requirements, and the need for portability and versatility, there is a strong interest in identifying the methods that reduce the number of sensors needed in artificial nose and tongue applications.

This fact makes it obvious that signal-processing tools, which can extract more independent information from a single sensor, can be very useful. The primary aim of this paper is to demonstrate that this goal is possible [2]–[6] by measuring and analyzing the stochastic component of the sensor signal. Experimental and theoretical investigations with Taguchi and surface acoustical wave sensors have shown that even a single sensor may be sufficient to qualify as an electronic nose [2]–[8]. One of the promising applications of fluctuation-enhanced chemical sensing is to develop a portable versatile electronic nose for detecting harmful gases. In this paper, we present the general idea of the method and demonstrate its viability with harmful gases. We also present the various aspects of the evaluation of data for sensing various gases with controlled concentration in high-purity, dry synthetic air.

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II. Fluctuations Induced in Chemical Sensors by the Chemical Environment

Superficial examination identifies chemical sensor fluctuations as conventional "noise," while, in fact, this stochastic component contains an important part of the chemical signal. Only this part of the sensor noise is employed (or examined) and can be identified as a signal that is related to the exposure to the sensed chemical. This exposure-induced dynamic signal generally has two different sources.

A. External Sources

The external source of the spontaneous fluctuations is from the occupation of the sensor by the agent molecules. At the microscopic level, molecular adsorption and desorption is a stochastic process due to random residence and absence times. Recent work [10] shows that treating adsorbed thin, multilayer films as varying about a mean thickness holds prospects of providing an accurate description of thin-film adsorption isotherms that theory based on constant film thickness does not provide

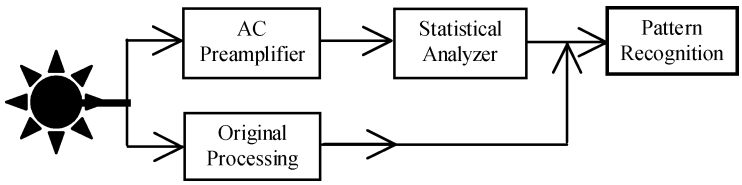

Fig. 1. Proposed arrangement of fluctuation-enhanced sensing. The original processing means measurement of the average value.

(i.e., FHH theory). In addition, if local variability in sensor properties, such as adsorption substrate physical dimensions in granular film sensors, is included (where adsorption energy is dependent on substrate size [11]), then an additional intrinsically variable contribution to film thickness and signal dynamics is added. In sum, the sources of variability in sensor adsorption imply spontaneous density fluctuations of the amount of adsorbed chemicals [2], [12], [13]. This kind of noise is a characteristic feature also in quartz and other kinds of solid-state resonators [12], [13].

B. Internal Sources

The internal source of the spontaneous fluctuations is induced by the interaction of the molecules of the agent with the sensor surface or with the bulk of the sensor. This kind of fluctuations can have many different modes of manifestation. On one hand, the adsorbed molecules can modify the standard fluctuation generating mechanisms existing in the active zone of the sensor. Alternatively, the diffusive motion of the agent molecules (which is a random walk at the molecular level, in the active zone of the sensor) can lead to various diffusive fluctuations phenomena [9], [11]. These diffusive motions, which can dominate the fluctuations at low frequencies. One example, which has been studied in details [9], is the occupation-fluctuation of the *sweet spot* of surface acoustic wave (SAW) devices due to surface diffusion (random walk) of the agent molecules.

As the spectral analysis provides a frequency spectrum, which is already a pattern, one sensor can replace a number of sensors used in the classical way of evaluating the dc response. The spontaneous fluctuations around the average value of the output, which are the additive stochastic component (noise) of the sensor signal, utilize the entire bandwidth of the sensor signal in contrast to the dc response. Therefore, from a chemical-sensing point of view, it is proper to call this method fluctuation-enhanced sensing (name originating from J. Audia, SPAWAR, U.S. Navy).

III. Sensing Method

The *in situ* sensing method is used under the same conditions as standard chemical sensing [2]. The only difference is that the ac component of the sensor signal is pre-amplified and spectral analysis is conducted on its stochastic component as shown in Fig. 1. The patterns generated by the spectrum and the dc components represent the output information provided by the sensor. It would require an array of sensors to obtain the same output information by the classical procedure.

The *in situ* method utilizes the internal and external sources of spontaneous fluctuations at the same time (see Section II), though one of them may be dominant in the whole frequency range or in a part. Until the specific processes generating the noise in particular materials exposed to particular chemicals are identified, the role of internal noise versus external noise will be unknown.

In [2, Fig. 2], patterns generated by various natural oleoresinous odors in a semiconductor Taguchi sensor (NAP 11 series, RS Component 286–620, used as air quality sensor) are shown. The data indicate that the $f*S_u(f)$ "fingerprint," where f is the frequency and $S_u(f)$ is the power density spectrum of the voltage fluctuations, is sensitive enough to detect these oleoresinous odors and to indicate that they are different [2].

When we have a characteristic spectral pattern, the question arises of how many sensors working in the classical way would be necessary to produce that information. [2] suggests that by using power spectral analysis one can have a single sensor replacing an array of at least six sensors.

IV. Results and Discussions

Using the power spectra to generate characteristic patterns for fluctuation-enhanced sensing of chemicals is an easy solution; however, it is not the only solution. For example, power spectra are not sensitive to the probability density of the noise amplitude, or to higher order fluctuations/correlations hidden in the process. This situation assumes a non-Gaussian noise process. Other statistical tools can be a richer source of information, though their use may be more computationally demanding. For example, [7], the bispectrum function

$$S_{3x}(f_1, f_2) = \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} C_{3x}(k,l) e^{-j2\pi f_1 k} e^{-j2\pi f_2 l} \quad (1)$$

which is the function of two frequencies f_1 and f_2, provides a two-dimensional pattern (however, S_{3x} contains more information than $S(f)$ only for non-Gaussian noise processes). Here, $C_{3x}(k,l) = E[x(n)x(n+k)x(n+l)]$ is the third-order autocorrelation function of the process $x(n)$. [7] shows the two dimensional bispectrum patterns generated by oleoresinous odors and laboratory air. The applied thick-film sensor (NAP 11 series, RS Component 286–636, used as CO sensor) had a large signal volume so the noise was only weakly non-Gaussian, in accordance with the *central limit theorem* for the addition of elementary fluctuations. [8] shows bispectra analysis of the same kinds of sensors with ethanol, and hydrogen in synthetic air. The application of this or similar kinds of methods is for nanometer sized sensors, where the non-Gaussian character can be extremely strong.

Up until now, the concentration of the sensed gas has not been quantified. In addition, the signal separation of multiple gas responses has not been achieved. Instead, only the ability to

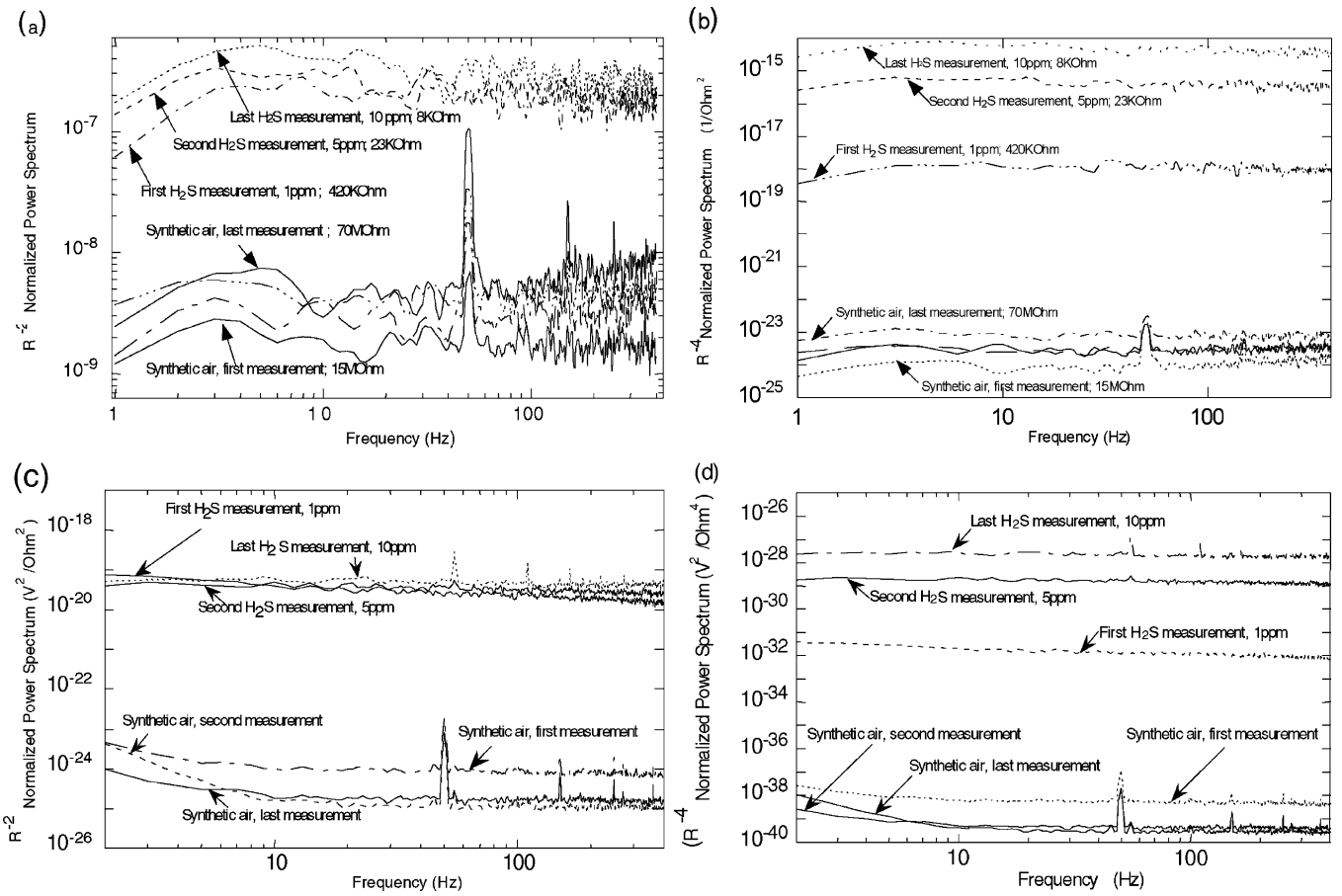

Fig. 2. Normalized spectra measured on homemade (Oulu, Finland) thick-film sensors (SnO_2), at 150 °C temperature, with H_2S gas and synthetic air. (a) $1/R^2$ normalized power spectrum $fS_r(f)/R^2$, (b) $1/R^4$ normalized power spectrum $fS_r(f)/R^4$, (c) $1/R^2$ normalized power spectrum $fS_u(f)/R^2$, and (d) $1/R^4$ normalized power spectrum $fS_u(f)/R^4$.

selectively sense different gases has been demonstrated by experimental data. The rest of this section presents experimental data regarding the sensing of various gases of controlled concentrations in high-purity, dry synthetic air. Various aspects of the evaluation of the data will be discussed.

The experimental setup consisted of a gas mixer, a stainless-steel sensor chamber, a Stanford Instruments preamplifier, and a Stanford Instruments spectrum analyzer. The passive current generator driving the sensor film (two-contact arrangement) and the preamplifier were battery powered. During the experiments, to avoid temperature fluctuations caused by the gas flow, we stopped the gas flow for the duration of the experiment, or, if we kept the flow, we ran preliminary tests to check that the flow was not interfering with the fluctuations in the measured frequency range.

In Fig. 2(a), results obtained on homemade thick-film sensors (SnO_2), at 150 °C temperature, with H_2S gas and synthetic air are shown. The log-log plot for the $f*S_u(f)$ function of the measured voltage, where f is the frequency and $S_u(f)$ is the voltage spectrum, is used for analysis. The reason for using $f*S_u(f)$ is purely perceptual: Most of the measured spectra are scaling roughly as $1/f$ ($1/f$ spectrum) and the human eye can discriminate small deviations from a $1/f$ spectrum in this way. The instantaneous resistance noise amplitude $S_r(f)$ and the measured voltage noise amplitude are related via Ohm's law which for the spectra relevant to $S_r(f)$ and $S_u(f)$ implies a relation scaling with the square of the driving dc current. 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 main objective of this study was not the shape but the intensity of the normalized resistance noise spectrum. In these experiments, the concentration of the measured gas is known, so it is proper to evaluate the normalized resistance power spectrum $S_r(f)/R^2$ [14], where R is the main resistance of the sensor, because in a linear system, with the number of fluctuators proportional to the concentration, this quantity would also, therefore, be proportional to the concentration. For the validity of this statement, one has to assume that the dynamic behavior of the fluctuators does not depend on the concentration. Therefore, to investigate the origin of the noise, from the measured voltage noise and the resistance, the $S_r(f)/R^2$ quantity was determined. Surprisingly, the normalized power spectra is almost independent of the gas concentration, it has at most a square-root like dependence, which indicates that one or several of the assumptions described above is invalid here.

To explore the possibility of using other kinds of normalization for sensing, using data from the same sensor, we have tested the $S_r(f)/R^4$ normalization, which provides distinct levels of response for the different concentrations, see Fig. 2(b). Moreover, the gap between the levels of response for the lowest con-

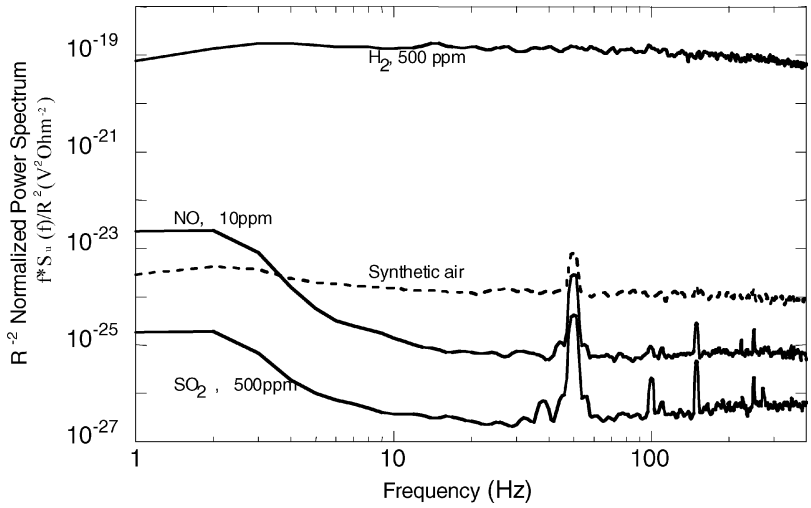

Fig. 3. Normalized spectra measured on homemade (Oulu) thick-film sensors (SnO_2), at 150 °C temperature, with H_2 gas, NO gas, SO_2 gas, and synthetic air.

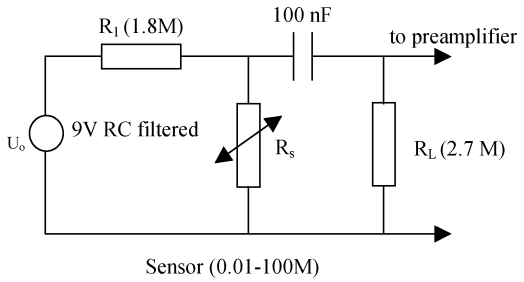

Fig. 4. Measurement circuit relevant to Figs. 2 and 3. The capacitor is chosen so that the low-frequency range should not be limited by the RC cutoff.

centration and the "background" level of synthetic air is opening up by subsequent measurements due to memory effects in the sensor. Another, even more practical, normalization can be applied by using the measured voltage power spectrum $S_u(f)$ instead of using the resistance power spectrum $S_r(f)$. It is the $S_u(f)$ that we measured first and the $S_r(f)$ that is evaluated by taking into account the measurement circuit and the value of elements in it. Using directly the $S_u(f)$ values for calculating the normalized spectra $S_u(f)/R^2$ or $S_u(f)/R^4$ should not be physically different, as far as the obtained normalized noise level is concerned; however, it may have important implications for practical sensing as shown in Fig. 2(c) and (d) and Fig. 3. Using $S_u(f)/R^2$, the level of response against H_2S becomes totally independent of the concentration, as shown in Fig. 2(c). Interestingly, the same level of response is shown against 500 ppm H_2 gas (unfortunately, we have not had the opportunity to test other concentrations). Both the H_2S and H_2 gases show a relatively flat response with this sensor. On the other hand NO and SO_2 gases produce a quite different shape, with an abrupt rise toward low frequencies. Fig. 2(d) shows the advantage of the normalization $S_u(f)/R^4$. The level of the H_2S curve at 1 ppm concentration is six orders of magnitude higher than the highest level for synthetic air. This fact indicates that the $S_u(f)/R^4$ normalization provides a high sensitivity well below the ppm level. In the observed range, the response looks logarithmic like. Using the fact that the 1 to 10 ppm range occupies about three orders of magnitude interval, we can extrapolate that the ultimate sensitivity of the method is below 0.1 ppm. Finally, Fig. 4 is the measurement circuit relevant to Figs. 2 and 3.

V. Conclusion

These investigations demonstrate that the use of statistical analysis of agent-induced fluctuations can strongly enhance sensor information when using single gases. It is particularly important that sensors designed for specific purposes can also be used to detect and identify other agents. It appears that a single sensor has the potential to detect and identify various harmful agents. However, the signal separation and gas recognition with multiple gas components and the various statistical analysis methods are still problems that will require additional investigation.

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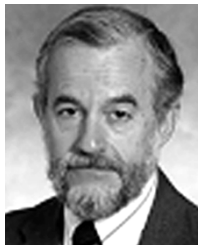

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