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Identifying natural and artificial odours through noise analysis with a sampling-and-hold electronic nose

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Abstract

A sampling-and-hold type electronic nose was used to investigate "frozen" sensor dynamics. The sensor was heated to the sensing temperature and exposed to a chemical environment for a short time. Then, while keeping the sensor in the chemical environment, the heating was switched off so that the sensor cooled down to room temperature. Chemicals species become trapped in the sensor film, and therefore, the current transport in the film is changed. The trapped chemicals are usually located at grain boundaries, and they influence the charge transport in the grains and between the grains. This gives random fluctuations to the local conductivity. Resistance noise was employed to extract chemical information from the sensor in the cold state. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electronic nose; Gas sensor; Noise spectroscopy; Fungi

1. Introduction

The resistance of a gas sensor at the sensing temperature is significantly influenced by exposure to various chemical species. Resistance fluctuations are known to occur in most conducting media [1,2], and the effect of various vapours on the power spectrum of the resistance fluctuations has been studied for polypyrrole thin-film resistors [3,4]. Recently, a method based on the measurement and analysis of the conductivity noise spectrum of a commercial gas sensor has shown that even one single sensor may be sufficient for realising a powerful electronic nose [5].

After cooling of the sensor to a temperature below the dissociation temperature of O_2^-, the O^- ions stay frozen for a long time on the semiconductor surface [7]. A pulsing of the sensor temperature between 200 and 400°C has been used in commercially available gas sensors and has been shown to be efficient in reducing, for example, the sensitivity to CH_4 in CO detection [8]. Very recently, a new kind of electronic nose has been proposed [6]. It uses a "frozen" sensor dynamics. The sensor was heated up to the operating temperature, at which the detection dynamics and the sensitivity of the sensor are satisfactory, and exposed to the chemical environment for a short time as done in regular measurements. Then, while keeping the sensor in the chemical environment, the heating was switched off so that the sensor cooled down to room temperature. Subsequently, in the cold state of the sensor, we carried out chemical analysis by extracting information from the resistance fluctuations of the sensor in the usual way [5].

Among the many applications of electronic noses, food analysis has probably been the topic of most interest [9]. Mankind has used fungi for production of food aroma and texture during centuries. Examples of foods that are produced using fungi are beer, bread, cheese, sausage, wine, tempeh, sufu, lao-chao and soy sauce. Fungi can also be used in industry for production of enzymes, organic acids (e.g. ascorbic acid) and antibiotics. However, the same types of fungi that are used for food production or in the industry can also spoil fruit and vegetables. Some fungi can also produce mycotoxins, which can be harmful both for humans and animals.

Some isolates of *Penicillium roqueforti* are used for cheese production (blue cheeses such as those of Roquefort type). The *P. roqueforti* is a common spoilage agent in refrigerated stored foods, meat and meat products, rye-breads and silage. This fungus is usually found on grain that is stored (especially in airtight silos) in a cold climate such as the Scandinavian one. These specific fungi can produce several mycotoxins, such as PR-toxin,

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mycophenolic acid, roquefortine C and isofumigaclavine A and B.

Penicillium verrucosum is also common in Scandinavia; its habitat is cereal with low lipid content (during storage), cheese, nuts, meat and dried fish. *P. verrucosum* produces the mycotoxin ochratoxin A. This mycotoxin is frequent enough that it can be found in the blood of every Swede.

Aspergillus-genera are common in tropical climates, although *Aspergillus flavus* is found also in Sweden. This fungus produces kojic acid, 3-nitropropionic acid, cyclopiazonic acid, aflatoxin B_1 and aspergillic acid. The most important, and also the most toxic, of these mycotoxins is aflatoxin B_1 The habitats for the fungi are groundnuts, spices, oil seeds and dried fruits. This fungus is a problematic mycotoxin producer in peanuts and pistachio.

This paper reports our data on the identification of *P. verrucosum, P. roqueforti*, and *A. flavus* by use of the new sampling-and-hold type electronic nose. These fungal species belong to the storage fungi and infect food and feed, and they are frequently located close to each other.

2. Experiment

Commercial gas sensors (NAP 11AN and NAP 11AS) manufactured by Nemoto & Co. Ltd. were used. The sensors are of Taguchi type. The NAP 11AN sensor has a high sensitivity to nitrogen oxides, and the NAP 11AS sensor has an excellent sensitivity to various smells generated from a normal living environment (indoor odour sensor). The gas sensor was heated with 5 V applied to a resistor and exposed to the chemical environment for 5 min. Then, while keeping the sensor in the chemical environment, the heating was switch off so that the sensor cooled down to room temperature. The cold sensor was then placed into a grounded metallic enclosure, and noise measurements were carried out after the enclosure was shut. A stable dc current was fed through the two terminals of the sensor resistor by a battery; the current transforms the resistance fluctuations into voltage fluctuations. A computer measured the dc voltage on the sensor and the voltage fluctuations (after preamplification) with a data acquisition board. The sampled output signal was transformed from the time domain to the frequency domain by means of a fast Fourier transformation. The power spectral density of the voltage fluctuations, $S_V(f)$, was measured in the range of frequencies between 0.1 Hz and 100 kHz. Measurements were carried out for three different fungi, ethanol and acetone vapours.

The fungal isolates used in this work were *P. roqueforti* IBT 3815, *P. verrucosum* IBT 3038 and *A. flavus* IBT 18119 from the IBT collection at the Department of Biotechnology, Technical University of Denmark, Lyngby, Denmark. The isolates were three spots inoculated on malt extract agar (MEA) and incubated for 7 days at 25°C. The agar surface was flushed with 0.5 ml pepton water, and the conidia suspension was counted and diluted to 10^6 conidia ml^{-1}.

Each species was inoculated as three replicates with a 100 μl conidia suspension. We used broad inoculation (meaning that the whole agar surface was inoculated at the same time) with two glass beads (115.790–2, Kebolab, Stockholm, Sweden) that were shaken around in a 250 ml Duran flask (110.403–250, Kebolab, Stockholm, Sweden) containing 25 ml sigma yeast extract (Sigma Y-4000) sucrose agar (SYES). Three non-inoculated 250 ml Duran flasks containing 25 ml SYES were used as negative control. Cotton wool was placed in the openings of the flasks so as to let some air penetrate. Both non-inoculated and inoculated flasks were incubated for 3 days at 25°C before the analysis was performed.

3. Results

The NAP 11AN sensor was exposed to saturated ethanol and acetone vapours. A 5 V signal was applied to the heating resistor for 10 s while the sensor was in the vapour, and the power spectral density was subsequently measured for the sensor in its cold state. In order to enhance the difference between the shapes of the spectra representing ethanol and acetone vapours, the measured spectra were multiplied by the frequency to the power 1.22 (Fig. 1). Ethanol and acetone vapours could readily be identified from the signals due to the frozen-in chemical species. These signals did not change at room temperature under storage for 24 h. Heating for 1 min in a laboratory air environment restored the regular background noise spectrum.

The NAP 11AN and NAP 11AS sensors were heated and exposed to non-inoculated and inoculated flasks for 5 min. Different measuring conditions were used in order to obtain

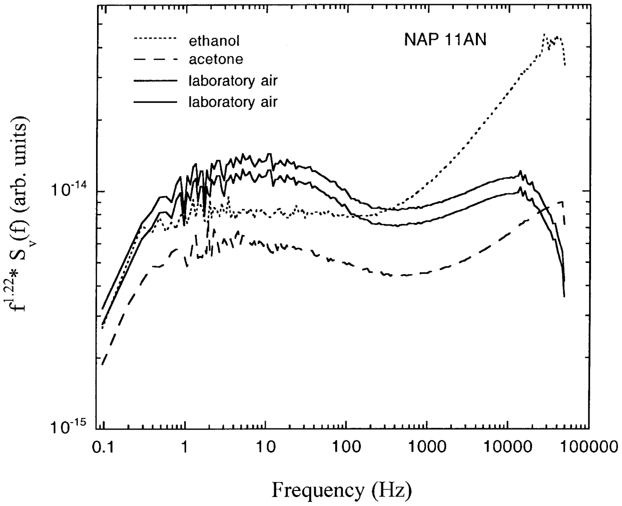

Fig. 1. Spectral density of voltage fluctuations measured for a cold NAP 11AN sensor, multiplied by frequency to the power 1.22. Data were taken after exposure to acetone, ethanol, and laboratory air. The latter measurement was done, heating for 1 min in a laboratory air environment after the sensor was exposed to acetone and ethanol vapours.

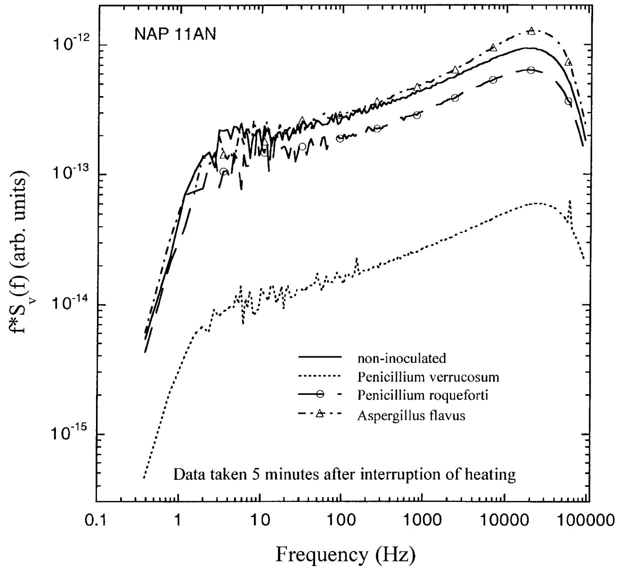

Fig. 2. Spectral density of voltage fluctuations measured for a cold NAP 11AN sensor, multiplied by frequency. Data were taken after exposure to non-inoculated and inoculated flasks with *Penicillium verrucosum, Penicillium roqueforti,* and *Aspergillus flavus* fungi. The measurement was done 5 min after the heating was switched off.

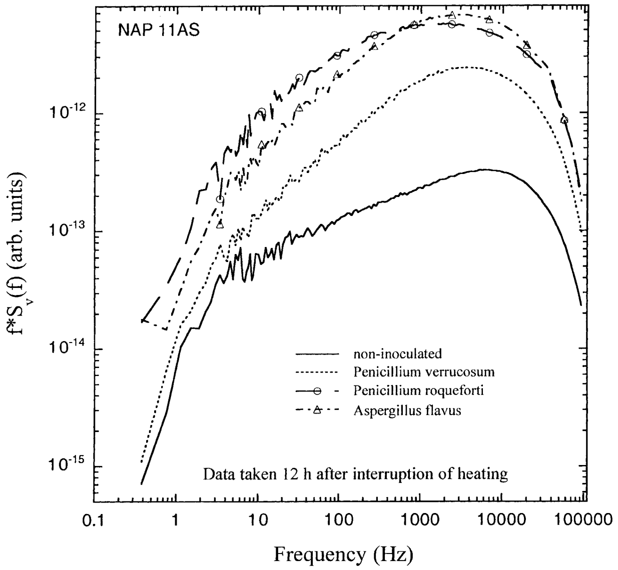

Fig. 4. Spectral density of voltage fluctuations measured for a cold NAP 11AS sensor, multiplied by frequency. Data were taken after exposure to non-inoculated and inoculated flasks with *Penicillium verrucosum, Penicillium roqueforti,* and *Aspergillus flavus* fungi. The measurement was done after 12 h the heating was switched off.

consistent results. Reproducible power spectra of the NAP 11AN sensors were obtained 5 min after the heating was switched off. Fig. 2 shows measured noise spectra for samples being non-inoculated and inoculated with fungi, multiplied by frequency. The spectrum from *P. verrucosum* is clearly different from those of the other fungi and of the non-inoculated sample. The spectra emanating from a non-inoculated sample, *P. roqueforti* and *A. flavus* are very similar, though.

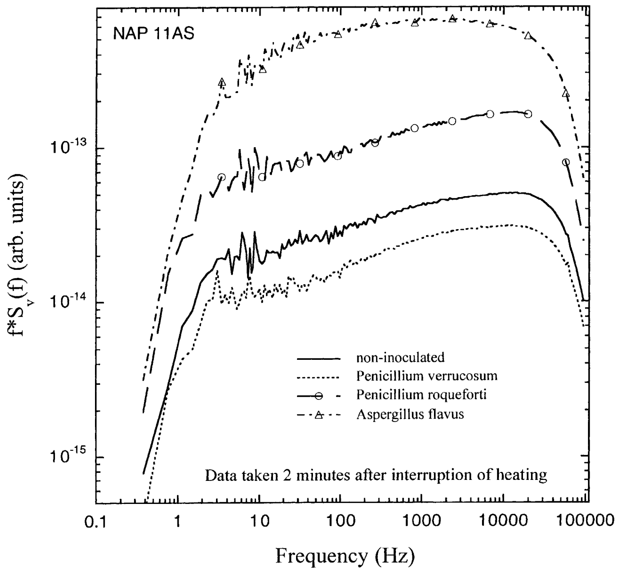

Fig. 3. Spectral density of voltage fluctuations measured for a cold NAP 11AS sensor, multiplied by frequency. Data were taken after exposure to non-inoculated and inoculated flasks with *Penicillium verrucosum, Penicillium roqueforti,* and *Aspergillus flavus* fungi. The measurement was done after 2 min the heating was switched off.

The NAP 11AS sensors were heated up and exposed for 5 min to effluents from the flasks with non-inoculated and inoculated samples. Noise spectra were measured at different times after the heating was switched off. The voltage fluctuations became stronger the longer the sensor remained in the cold state. Fig. 3 shows measured noise spectra for the different fungi and for a non-inoculated sample 2 min after the heating was switched off, multiplied by frequency. The spectra from *P. roqueforti* and *A. flavus* are different from those of the non-inoculated sample and the *P. verrucosum*. When the noise spectra were measured 12 h after the heating was switched off, the shapes of the spectra are completely different (Fig. 4); after that the spectra showed no apparent change. The spectrum from *P. verrucosum* is clearly different, while the spectra from *P. roqueforti* and *A. flavus* are similar. We conclude that it is possible to discriminate between odours by using different types of gas sensors and suitable conditions for the noise measurement.

4. Summary

We have presented a new principle for electronic noses based on "frozen" sensor dynamics. The new method relies on resistance fluctuation spectroscopy of the cold sensor after the hot sensor was exposed to the chemical environment. It is shown that the exposure to different vapours causes modifications in the power density spectrum of the resistance fluctuations. It was possible to distinguish between different fungi and alcohol vapours.

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Biographies

Jose Solis received the BSc, MSc and PhD degrees at the Universidad Nacional de Ingenieria, Lima, Peru, in 1987, 1995 and 1997, respectively. Since 1989, after a working period of 2 years in the industry, he has been with the Thin Film Laboratory of the Universidad Nacional de Ingenieria working in the field of chemically and optically sensitive semiconductor films together with their applications. He has been a visiting researcher at the Universidad Federal de Rio Grande do Sul, Porto Alegre, Brazil in 1991–1992 and at the University of Oulu, Oulu, Finland in 1993–1994 and 1995–1996 in the frame of the International Program in the Physical Sciences (IPPS) at the Uppsala University, Sweden. During 1997–1998, he was a postdoctoral researcher at the University of Oulu and now continues his research at the Uppsala University.

Laszlo B. Kish (until 1999, L.B. Kiss) is the leader of Noise and Nanomaterial Research Group at the Solid State Physics Division of Ångström Laboratory, Uppsala University, Sweden. He is an interdisciplinary scientist, and his interest is ranging from new materials, devices and systems to nonlinear science and neural signal research. He received the Doctoral degree in 1984 (JATE, Hungary) and the Habilitation degree in 1994 (Uppsala University, Sweden). He was a guest scientist in several countries, including the USA, Japan, United Kingdom, Germany, Netherlands, and Sweden. He has two patents, co-edited three books, published over 120 papers, and held over 20 invited talks at international conferences. He founded a new international conference series, ‘‘Unsolved Problems of Noise’’ (UPoN’96 Hungary; UPoN’99 Australia; UPoN’02 Washington, DC). Very recently, he started a new journal, Fluctuation and Noise Letters, which will be published by World Scientific from year 2001: http://www.wspc.com/journals/fnl/fnl.html.

Róbert Vajtai is a lecturer at the Department of Experimental Physics, University of Szeged, Hungary. He received his PhD degree in solid state physics in 1991. At present, he is an NSF-NATO awarded visitor scientist at Rensselaer Polytechnic Institute, Troy, NY. Previously, he has been a postdoc in various countries including Sweden, Switzerland and Germany. His interests include laser light-matter interactions, sensors and nanomaterials.

Claes-Göran Granqvist is the head of the Solid State Physics Division at The Ångström Laboratory, Uppsala University, Sweden. His interests include optical materials and coatings, nanoparticles, electrochromic materials and devices. He has written, edited and coedited over 20 books, published over 400 papers and held over 100 invited talks at international conferences. He is a member of several Academies and Learned Societies and has received several awards and prizes.

Johan Olsson finished his PhD in October 2000. The title of the thesis was Modern Methods in Cereal Grain Mycology. He has been working with detection of moulds in cereal grain for 5 years. The main part of the PhD thesis is about the use of mould produced volatile compounds for detection and prediction of moulds and mycotoxin in cereal grain using electronic nose and gas chromatography.

Johan Schnürer is the Head of Department of Microbiology at the Swedish University of Agricultural Sciences, Uppsala. He is the leader of a research group studying moulds, yeast and lactic acid bacteria in relation to food spoilage and biotechnology. He has published 15 articles on methods for mould detection in complex environments using detection of DNA, ergosterol and volatile fungal metabolites in combination with classical cultivation techniques.

Vilho Lantto is the leader of the Materials Physics Research Group in the Microelectronics and Materials Physics Laboratories of the University of Oulu, Finland and also the Dean of the Faculty of Technology of the University of Oulu. His interests presently include surface effects, ferroelectric materials, solid-state sensors, device simulation and modelling, and different techniques for processing of different thin- and thick-film materials and devices. He has published about 150 papers, been a writer in three books and held about 20 invited talks at international conferences.