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On the possibility of molecular recognition of taste substances studied by Gábor analysis of oscillations

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Abstract

A liquid membrane oscillator containing nitromethane as membrane material has been investigated. The influence of substances responsible for taste belonging to four classes (sweetness, saltiness, sourness and bitterness) on oscillation patterns of liquid membrane oscillators with cationic surfactant benzyldimethyltetradecylammonium chloride (BDMTAC) was examined. A new approach based on Gábor transformation is proposed for obtaining the power spectra of the observed oscillating signals and for establishing "fingerprints" of the investigated substances. It was shown that two-dimensional form of these power spectra might be used efficiently for this purpose.
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Keywords: Liquid membrane oscillators; Molecular recognition; Gábor transformation; Chaotic oscillation; Taste sensing

1. Introduction

Nonlinear phenomena are often observed in biological systems, such as nerve or taste cells [1,2]. Due to the high complexity of these latter, artificial systems have been designed as models for investigation of processes appearing in biomembranes. One of the most useful approaches is based on liquid membrane oscillators [3–7].

Basically, liquid membrane systems are constituted of water immiscible organic phase in bulk or polymer supported form, which is separating two aqueous phases (Fig. 1). The first of these aqueous phases called donor phase (*d*) contains all the chemical components characterizing a given system. It plays the role of source for any transport processes across the organic phase, the actual liquid membrane phase (*m*). This latter may or may not contain additional substances. When liquid membranes are used for separation purposes, they contain carrier molecules which facilitate the membrane crossing by associating with the transported species. The second of the aqueous phases called acceptor phase (*a*) may be only pure water, or it may

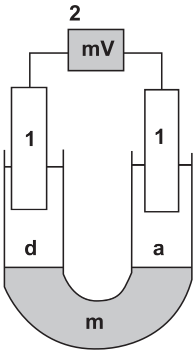

Fig. 1. Experimental setup, (*d*) aqueous donor phase, (*m*) liquid membrane, (*a*) aqueous acceptor phase, 1-Ag/AgCl/Cl-electrodes, 2-mVm controlled by PC.

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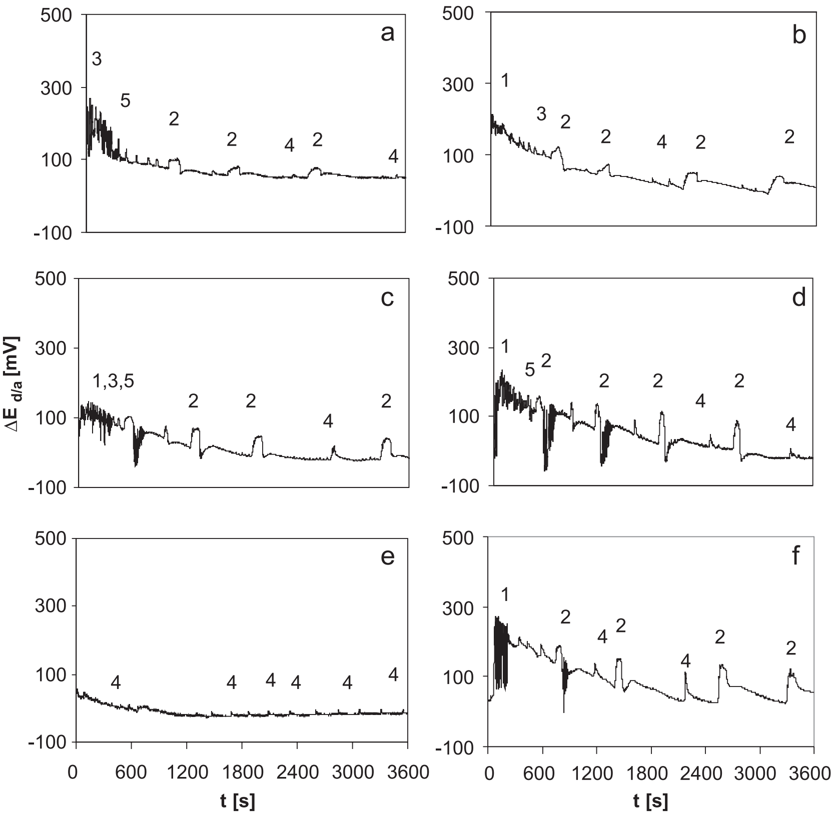

Fig. 2. Oscillation patterns of liquid membrane oscillator containing different substances responsible for taste; (*d*), BDMTAC (5×10^{-3} M) in ethanol (1.5 M)–water mixture; (*m*), HPi (1.5×10^{-3} M) in nitromethane; (*a*), panels (a) sodium chloride (0.1 M), (b) potassium chloride (0.1 M), (c) citric acid (0.1 M), (d) acetic acid (0.1 M), (e) quinine hydrochloride (0.05 M) and (f) caffeine (0.05 M). The numbers above the peaks designate their characteristic type (see text).

contain also additional substances in order to influence the physicochemical behavior of the membrane system in a specific way.

Liquid membranes proved very efficient in separation processes, and the mechanism of their functioning is well understood [8]. Therefore, they are ideal artificial models

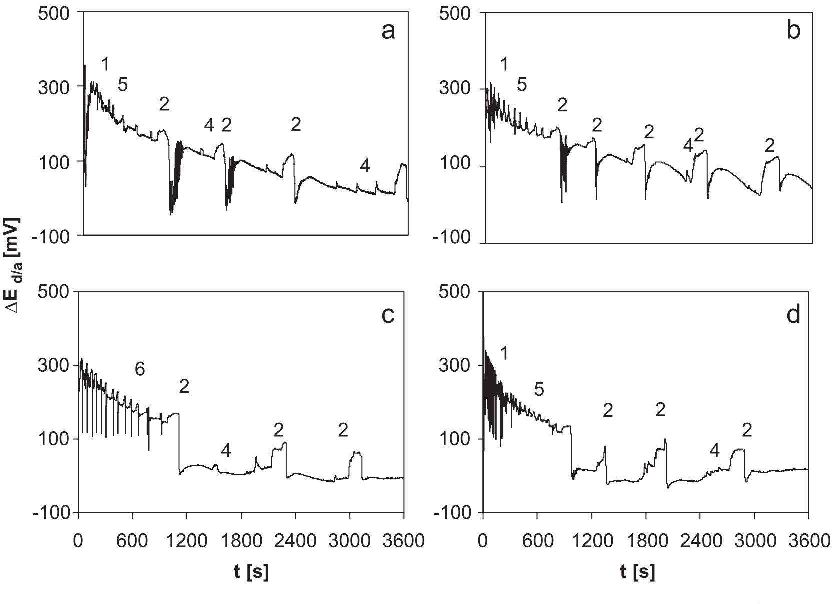

Fig. 3. Oscillation patterns of liquid membrane oscillator containing different sweet substances; (*d*), BDMTAC (5×10^{-3} M) in ethanol (1.5 M)–water mixture; (*m*), HPi (1.5×10^{-3} M) in nitromethane; (*a*), panels (a) sucrose (0.1 M), (b) glucose (0.1 M), (c) lactose (0.1 M) and (d) fructose (0.1 M). The numbers above the peaks designate their characteristic type (see text).

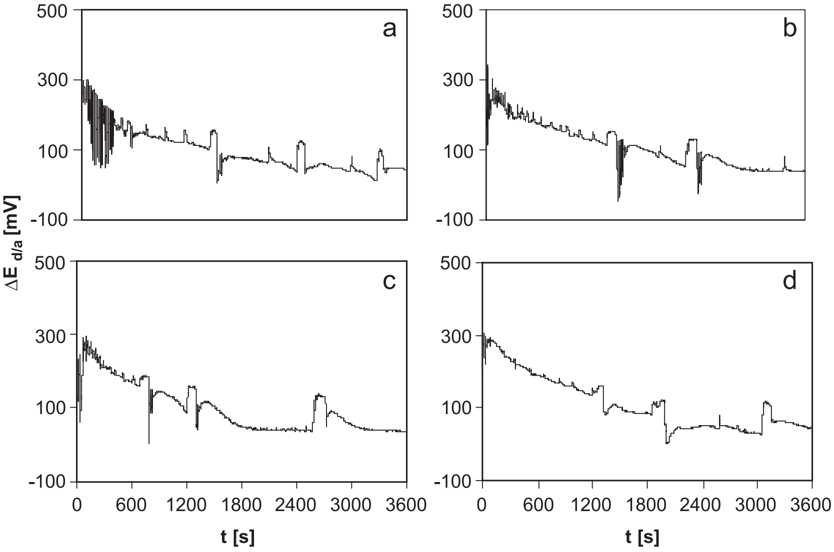

Fig. 4. Oscillation patterns of liquid membrane oscillator containing different sucrose concentrations; (*d*) BDMTAC (5×10^{-3} M) in ethanol (1.5 M)–water mixture; (*m*), HPi (1.5×10^{-3} M) in nitromethane; (*a*) aqueous solution of sucrose at various concentrations: (a) 0, (b) 0.001, (c) 0.01 and (d) 1 M.

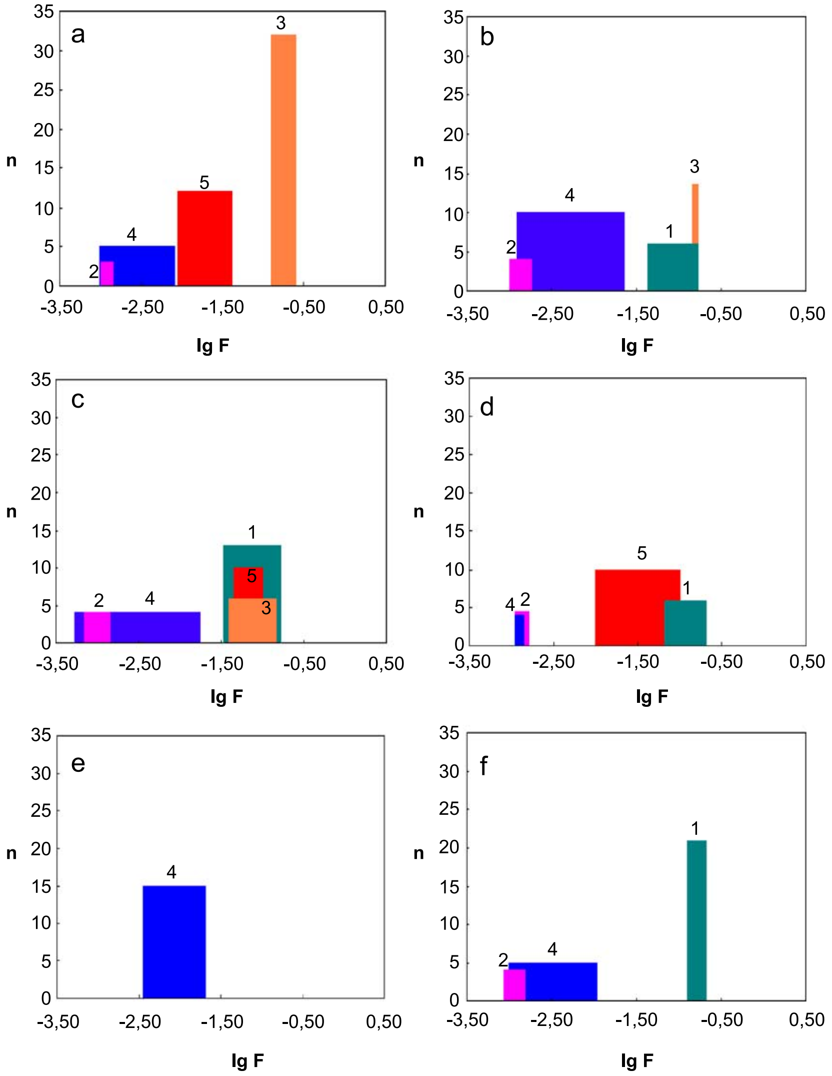

Fig. 5. Histograms for the systems with (a) sodium chloride, (b) potassium chloride, (c) citric acid, (d) acetic acid, (e) quinine hydrochloride and (e) caffeine in the acceptor phase.

for mimicking biomembranes. It was expected that beyond their clear-cut transport processes, liquid membranes could be used also for simulating and studying oscillatory phenomena taking place in biomembranes. It turned out that this is the case indeed. Liquid membrane oscillators show a great variety of oscillating patterns, which are very sensitive to the actual experimental conditions [2].

The molecular events responsible for oscillations are fundamentally nonlinear. Very frequently, the observed oscillations show chaotic behavior. Chaotic systems are reputed to be extremely sensitive to initial conditions, i.e., to their actual composition [9]. This suggests that they might be used successfully for molecular recognition of various chemical substances [4]. Accordingly, it was suggested already that such systems might be applied for quantifying molecules responsible for taste [5,6].

In the present work, we have investigated a system which contains a cationic surfactant (benzyldimethyltetradecylammonium chloride [BDMTAC]) and ethanol in the aqueous donor phase (*d*). The organic phase (*m*) of the oscillator contained picric acid in nitromethane. Various substances responsible for taste were located in the aqueous acceptor phase (*a*) (Fig. 1). The electrochemical potential difference between the two aqueous phases was measured during the transport process from the aqueous donor phase to the aqueous acceptor phase.

The purpose of this paper is to present a new approach based on Gábor transformation to analyse the experimental results obtained for molecular recognition of four classes of taste substances: sweetness, saltiness, sourness and bitterness.

This classification of the investigated substances is maintained to facilitate the connection with the literature existing in this field. It is quite clear that any effect provoked by the taste substances will be due to their molecular structure and physical/chemical properties and by no means to their taste properties. With this idea in mind, it is expected that any chemical substance can have some influence on the oscillating properties of liquid membrane oscillators. It is hoped therefore that "fingerprints" might be established for each molecule investigated that could be used for their actual identification.

2. Experimental

Commercial products of analytical grade purity (>99%) were used in all experiments. Picric acid was recrystallized from ethanol–water mixture (1:2 v/v). The water was double distilled.

Liquid membrane solution (*m*) was introduced at the bottom of thermostated U-shaped glass tube (T=25±0.1 °C; Fig. 1). Subsequently, two aqueous solutions were carefully and simultaneously added into the two arms of the tube. The composition of the three phases was the following:

(a) aqueous donor phase, 4 ml of BDMTAC (5×10^{-3} M) in ethanol (1.5 M)–water mixture;
(b) liquid membrane, 5 ml of picric acid (HPi, 1.5×10^{-3} M) in nitromethane; and
(c) aqueous acceptor phase, 4 ml of taste substances in water [sucrose (0–1 M), NaCl (0.1 M), citric acid (0.1 M), quinine hydrochloride (0.05 M), caffeine (0.05 M), KCl (0.1 M), glucose (0.1 M), acetic acid (0.1 M), lactose (0.1 M) and fructose (0.1 M)].

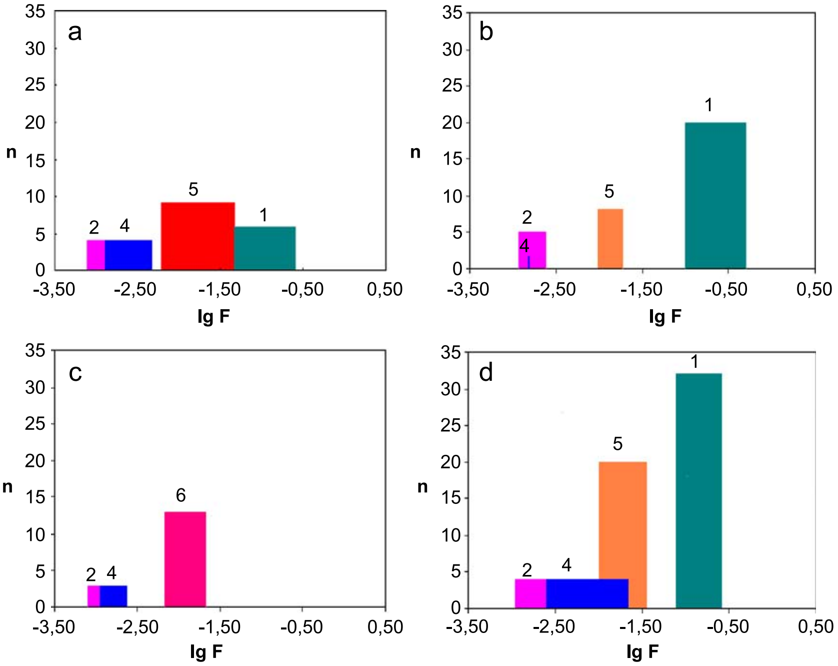

Fig. 6. Histograms for the systems with (a) sucrose, (b) glucose, (c) lactose and (d) fructose in the acceptor phase.

The electrochemical potential difference between the two aqueous phases, $\Delta E_{d/a,}$ was measured by means of two Ag/AgCl/Cl$^-$ reference electrodes using a ~10-MΩ input resistance voltmeter controlled by PC (sampling speed 5 s^{-1}). Each experiment was repeated at least four times. For each case, the oscillation curves were self-similar due to a certain chaotic behaviour of the system.

The time-frequency transformation of the observed signals was realized using Gábor analysis [10]. This was implemented in Igor Pro, a scientific data analysis environment. Gauss function and different time and frequency shift parameters were chosen to cover the whole time-frequency plane [11,12] of the experimental data. In this method, the actual time domain is divided into a series of subdomains of constant time intervals, and Fourier transformation is realized in each subdomain.

3. Results and discussion

Oscillation patterns obtained in presence of various taste substances in the acceptor phase of the investigated liquid membrane oscillator are presented in Fig. 2. This figure represents the time series obtained for saltiness (sodium

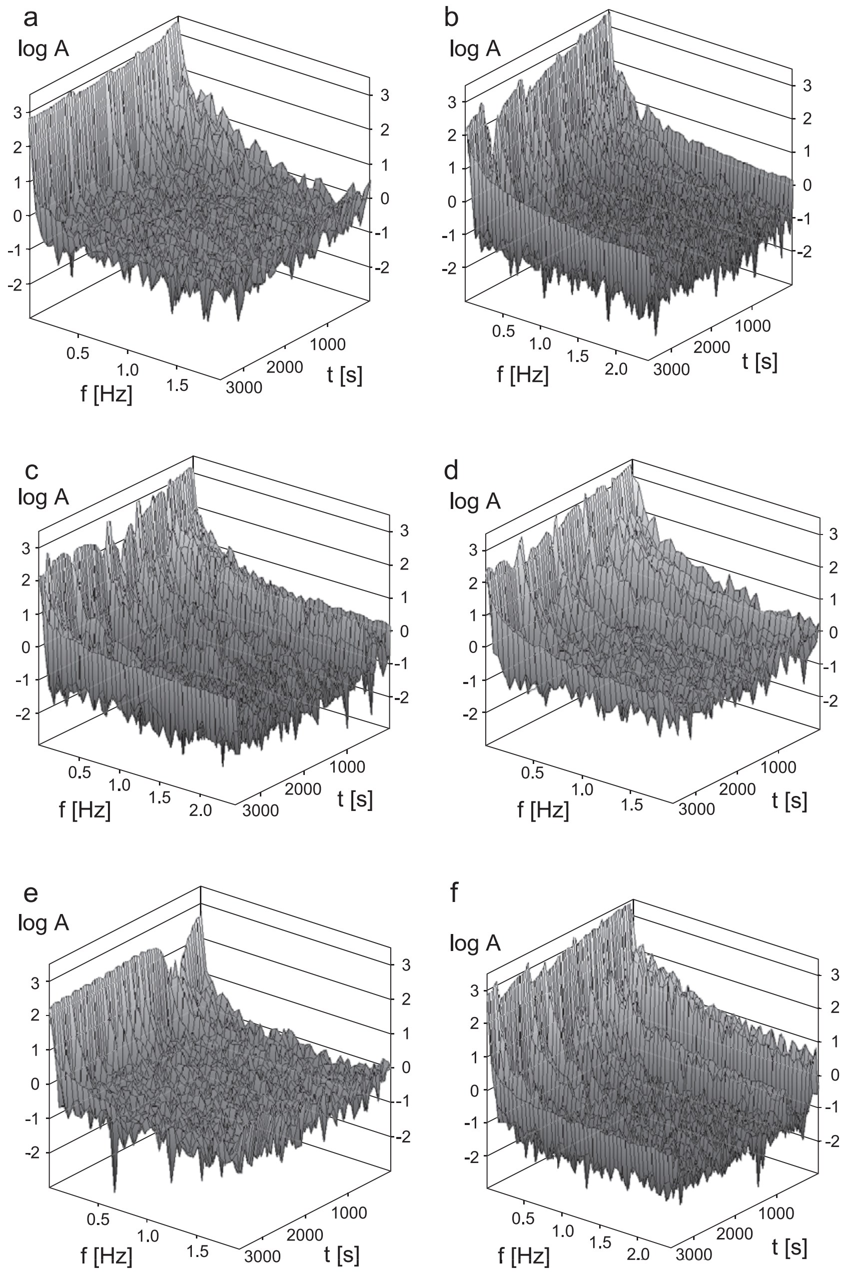

Fig. 7. Power spectra obtained by using Gábor transformation for the system with nitromethane as membrane material and different taste substances in the acceptor phase: (a) sodium chloride, (b) potassium chloride, (c) citric acid, (d) acetic acid, (e) quinine hydrochloride and (f) caffeine.

chloride, potassium chloride), sourness (citric acid, acetic acid) and bitterness (quinine hydrochloride, caffeine).

On the other hand, the influence of sweet substances on oscillation characteristics (sucrose, glucose, lactose, fructose) is shown in Fig. 3. It can be seen that the oscillation patterns are different for each substance responsible for taste. The oscillations start from the beginning of the experiment, and practically no induction periods are observed. The experimental time series (Figs. 2 and 3) show that approximately six types of peaks can be distinguished. At first, narrow peaks of small amplitude are observed. In case of each particular substance, except for quinine hydrochloride, wide peaks appear after a certain period of time.

We can also observe bursting type oscillations when sucrose, glucose, citric acid, acetic acid or caffeine are present in the acceptor phase of the oscillator (Figs. 2c, d, f and 3a,b). It can be seen that the effect of quinine hydrochloride (Fig. 2e) is very different from the other cases. The oscillation pattern is changed, and only small amplitude oscillations are observed.

This first qualitative inspection of Figs. 2 and 3 shows clearly that the observed effects cannot be related to molecular structure in a simple fashion, not to mention taste properties. For instance, ordinary salts have rather similar oscillation patterns (Fig. 2a and b), but sugars present significantly different time series (Fig. 3a–d) as do the two bitter substances (Fig. 2e and f). Eventual influence of concentration of added substances was also tested.

Fig. 4, together with Fig. 3a, represents the time series obtained for different concentrations of sucrose in acceptor phase. We also observed oscillatory behaviour without adding any substance responsible for taste to the acceptor phase (Fig. 4a). The presence of sucrose at different concentrations in the system (0.001, 0.01, 0.1, 1 M) influences the obtained time series (amplitude, phase and width of the peaks) particularly in first part of the oscillations process (0–600 s). It can be seen that after this period of time, oscillation patterns do not differ significantly.

The actual behaviour of the observed time series may be displayed more quantitatively by establishing their histograms [4,13]. These latter are obtained as follows. The observed peaks are classified according to their characteristics: width, amplitude and phase.

The representation of the number of peaks of a given type in function of their frequency domain gives the required histograms. At the beginning of the time series, we can

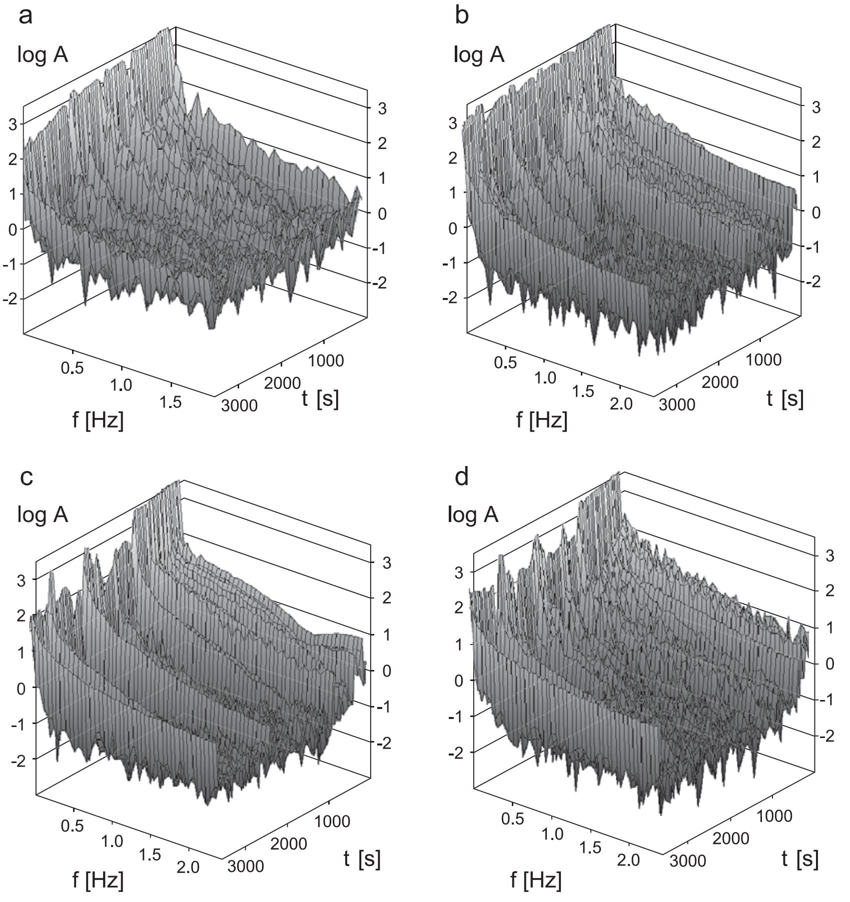

Fig. 8. Power spectra obtained by using Gábor transformation for the system with nitromethane as membrane material and different sweet substances in the acceptor phase: (a) sucrose, (b) glucose, (c) lactose and (d) fructose.

observe the presence of high-frequency narrow peaks of varying amplitude (type 1). Unusually large peaks are also present throughout the oscillation patterns (type 2). Small amplitude regular peaks can be detected in some cases at the early stage of oscillations (type 3). At a later stage, small amplitude peaks are present in between the large peaks (type 4). Regular peaks of upward pointing amplitudes are present in certain cases (type 5). Finally, regular and very narrow peaks of downward pointing amplitude may be present at the early stage of oscillations (type 6).

Accordingly to this classification, the numbers given in Figs. 2 and 3 above the various peaks designate their characteristic type. The appropriate frequency domain for each type of peaks was determined by taking the inverse of the time intervals separating the peaks of a given type. The number of peaks of a given type present in the appropriate frequency domain allowed to establish the corresponding histograms (Figs. 5 and 6).

Due to the fact that oscillations are rather irregular, the range of frequencies is represented by a rectangle. As it can be seen, the histograms are different for each system. Furthermore, the characteristic frequency of each peak changes with time, which is shown by the relatively large width of the columns. It can be concluded that histograms might be used as a first approach to the quantitative description of our systems.

Quantitative description of the observed oscillations may be obtained also by spectral analysis of the experimental time series [14]. In general, Fourier transformation method is used to pass from time domain to the frequency domain of the signals. The obtained power spectrum allows to establish the frequency composition of the oscillating signals. This procedure gives excellent results when the various frequencies present in the analyzed signal are not time-dependent, i.e., when the signal is stationary.

However, it can be seen on the oscillation patterns (Figs. 2 and 3) and also on the histograms (Figs. 5 and 6) that the frequencies observed in the present work are changing with time in a chaotic way. In addition, the amplitudes and even phases are time-dependent. In other words, the observed signals are not stationary, and Fourier transformation cannot give correct results in this case.

Therefore, a different method is required for analysing chaotic oscillators. This can be realized using Gábor transformation [10], which was designed to obtain power spectra of nonstationary signals. As a matter of fact, it was shown recently that simple Fourier transformation leads only to averaged spectral characteristics for nonstationary

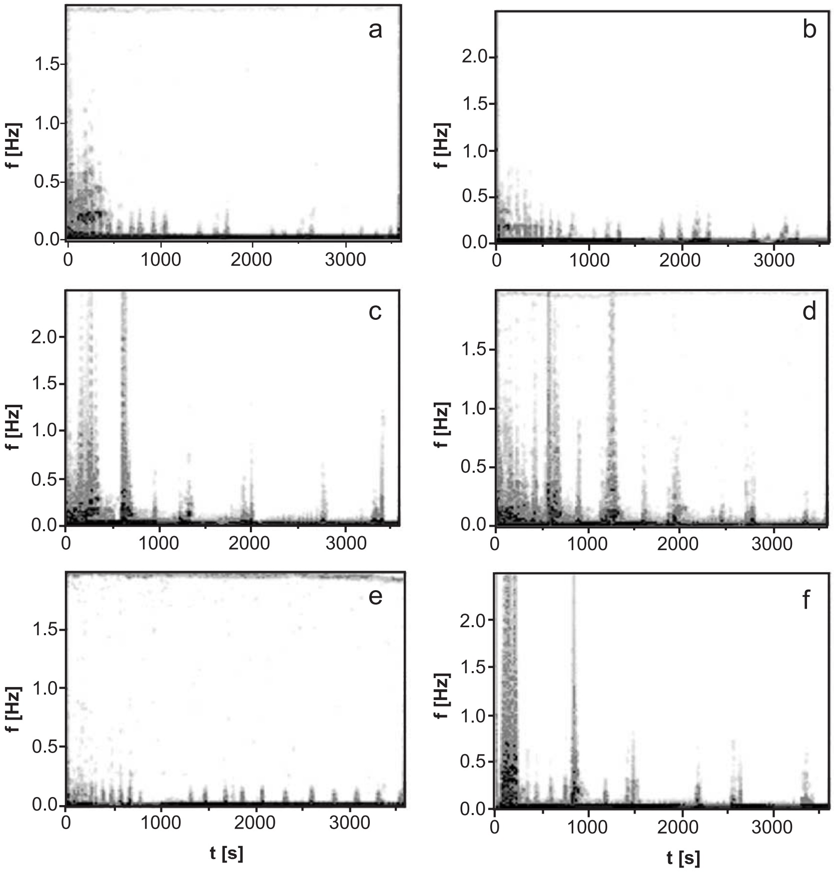

Fig. 9. Cross-sections of power spectra of the system with nitromethane and various substances responsible for taste: (a) sodium chloride, (b) potassium chloride, (c) citric acid, (d) acetic acid, (e) quinine hydrochloride and (f) caffeine.

signals, but it is quite appropriate for stationary signals [15]. The dynamics of nonstationary signals can be disclosed only by Gábor transformation.

The fundamentally new aspect of Gábor transformation is that it divides the whole time domain into definite time intervals. Each time interval is viewed through a Gaussian type window, and it is submitted to Fourier transformation. The results are presented in a three-dimensional diagram where the signal amplitudes are plotted in function of frequency and time.

Gábor transformation was carried out for the time series of all the 10 different substances responsible for taste (Figs. 7 and 8). The obtained results are presented in three-dimensional diagrams: logarithm of signal amplitude in function of frequency and time. We can observe that there are no dominating frequencies in the systems. The presence of a great number of frequencies of more or less constant amplitudes suggests that the observed oscillations have definitely chaotic character.

In fact, one of the most characteristic properties of chaotic systems is the absence of dominating specific frequencies [16]. On its way to chaos, the oscillating system has lost its clear-cut oscillatory characteristics by frequency doubling or intermittency. It can be seen also that taste substances cannot be easily recognized from their three-dimensional diagrams. However, these latter can be transformed into two-dimensional diagrams by taking cross-sections at constant signal amplitude (Figs. 9 and 10).

On these diagrams, the colour intensity of a given point defined by its frequency–time coordinates designates the actual signal amplitude. The more intense the colour, the higher is the amplitude. It can be seen that colour intensity varies with frequency.

The obtained diagrams are different for each system and can be easily recognized. Each taste substance has its own sets of frequencies on the two-dimensional power spectrum which represent a “fingerprint” of the substance present in the system.

Actually, the presence of chaos in the system turns into a definitive advantage for characterizing taste substances. Chaotic systems are extremely sensitive to experimental conditions. The presence of different taste substances provokes immediately a different oscillatory response in each case. Subsequent applications of spectral analysis based on Gábor transformation allowed to identify molecules of taste substances present in the acceptor phase of the liquid membrane system. Therefore, this new method is recommended for a more efficient characterization of taste substances.

Its general validity is reinforced by the fact that the obtained fingerprints are fairly concentration-independent and can be used in various concentration ranges.

The actual physical/chemical mechanism of oscillations and that of the influence of added substances is not established as yet. Preliminary results obtained in this connection show that the present oscillators obey a similar mechanism which seems to be general for liquid membrane oscillators [3]; the main factor responsible for the appearing of oscillations is the sudden adsorption and desorption of surfactant molecules at the water phase/membrane inter-

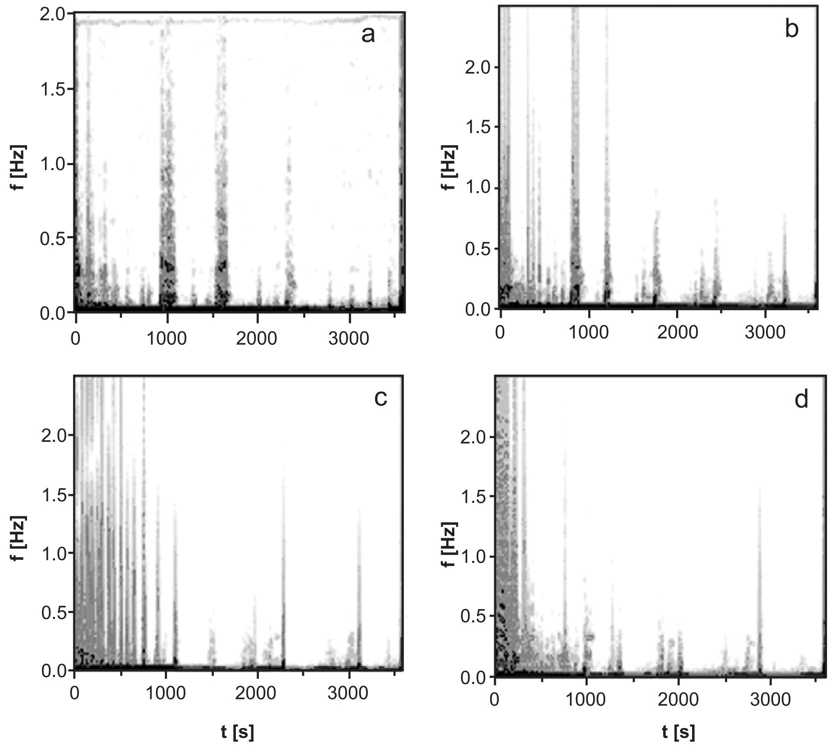

Fig. 10. Cross-sections of power spectra of the system with nitromethane and different sweet substances: (a) sucrose, (b) glucose, (c) lactose, (e) fructose.

faces. However, in the present case, the molecular processes taking place at the acceptor phase/membrane interface are responsible for oscillations, while the donor phase/membrane interface has no active role in the observed oscillations. Further work is in progress for establishing the mechanism of oscillations at the molecular level.

4. Conclusions

The present work reveals that the oscillation patterns obtained in presence of various taste substances for nitromethane based liquid membrane oscillators are different. The Gábor transformation method can be used successfully for obtaining the power spectra of oscillating signals even if these latter have chaotic character. It was shown that power spectra in their two-dimensional form can be used efficiently for identifying various substances responsible for taste. This new approach is more realistic, more efficient and easier to apply than other approaches published in the literature.

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