Characteristic Response of Electrochemical Nonlinearity to Taste Compounds with a Gold Electrode Modified with 4-Aminobenzenethiol

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(Received October 30, 1992)

The nonlinear electrochemical responses for various taste compounds were measured using a gold electrode modified by 4-aminobenzenethiol. The results were analyzed quantitatively based on a data-processing method proposed by the authors. The nonlinearity of the response was found to be enhanced by the modification, showing a marked dependence on the categories of taste compounds as well as on their concentrations. Our new concept concerning chemical sensing has been found to be promising as a powerful analytical tool when a suitable modification of the electrode surface is performed.

In general, the electrochemical characteristics of a solid/liquid interface are highly nonlinear, i.e. the capacitance and conductance are voltage-dependent.[1] Recently, we proposed a novel sensing method to evaluate electrochemical nonlinearity in a quantitative manner. It has been shown that electrochemical nonlinearity affords abundant information concerning both the test solution and the electrode surface in various electrochemical systems.[2—4]

Although in the past there have been numerous studies concerning the complex impedance in electrochemical systems, most studies on nonlinear characteristics have concerned only second harmonics.[1] In order to clarify the novel aspects of our method it is essential to notice that the concept of 'the higher harmonics' was developed based on a linear approximation.[1] In previous papers[2,3] we stressed the importance of electrochemical nonlinearity, and reported on a new methodology to shed light on the electrochemical nonlinear response from both theoretical and experimental point of view. Since the nonlinear characteristics are quite general in electrochemical systems, we believe that the utilization of information concerning nonlinearity is quite useful for developing various kinds of sensors.

We have also recently demonstrated that various chemical species can be distinguished and quantified based on information yielded by the amplitude, frequency, shape, and modulation of electrical oscillation using artificial excitable membranes.[5—8] Such an interesting oscillatory phenomenon is associated with nonlinear characteristics in artificial membranes. It is also observed on artificial lipids membranes.[9—12]

Under these circumstances, it may be expected that the modification of a working electrode would afford much more useful information concerning test solutions.

In the present work we modified a gold electrode with 4-aminobenzenethiol (4-ATP), and then studied the effect of this modification on the electrochemical nonlinearity of various taste compounds. Since various mercaptans are chemically adsorbed spontaneously onto a gold surface,[13—18] 4-ATP is also a nice candidate for the adsorbant.

Experimental

The experimental apparatus is shown in Fig. 1. A sinusoidal voltage (frequency: 1 Hz, range of voltage: 0 V to 0.5 V) was applied between the working and reference electrodes. A gold wire (length: 20 mm, Diameter: 0.5 mm) was used for the working electrode. The procedure for preparing the modified electrode is as follows. A gold wire is immersed in an ethanoic solution of 4-ATP at room temperature (20°C) for 5 hours. The modified electrode is then gently washed with ethanol and water. Modification of the electrode is confirmed using a cyclic voltammogram of horse-heart cytochrome c in a phosphate buffer solution (pH=7.0).[18] Details concerning the measurements are the same as those used in the previous studies.[2—4] It has been confirmed that the experimental error remains at less than 5% for the modified electrode, at least for three days. Aqueous solutions of various taste compounds, such as sodium chloride (NaCl; salty), hydrochloric acid (HCl; sour), D-glucose (sweet), nicotine (bitter), and L-glutamic acid (delicious), were measured at 20±1°C. These compounds were chosen so as to compare the response of the modified electrode with that of the bare electrode. All of the chemical reagents were purchased from Wako (Tokyo).

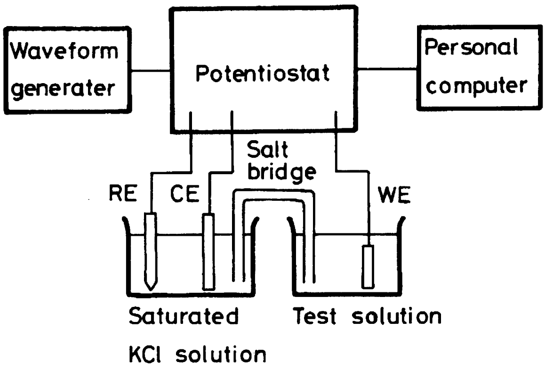

Fig. 1. Experimental apparatus. WE; Working electrode, CE; Counter electrode (Graphite), RE; Reference electrode (Ag/AgCl).

Results and Discussion

In an aqueous solution of ordinary electrolytes, such as potassium chloride or sulfuric acid, a gold electrode shows no oxidation–reduction peak in a cyclic voltammogram over 0 V to 0.5 V vs. SCE.[17,19] In order to factor out the effect on the impedance with the modification, it is desirable to minimize the effect of the electrode reaction. We, thus, performed electrochemical measurements using this voltage range.

Figure 2 shows the current (*I*)–voltage (*E*) loops for various test solutions with bare and modified electrodes. Each loop deforms in a different manner, indicating that the electrochemical nonlinearity changes in a way that is characteristic for different solutions or with different electrodes.

When a sinusoidal voltage is applied to a system of parallel circuits comprising a linear capacitor and a linear resistor, the shape of the *I*–*E* loops should be elliptical. On the other hand, in an actual electrochemical system, the *I*–*E* loop generally deforms from an ellipsoid, as shown in Fig. 2, due to the nonlinear electrochemical characteristics.[2,3]

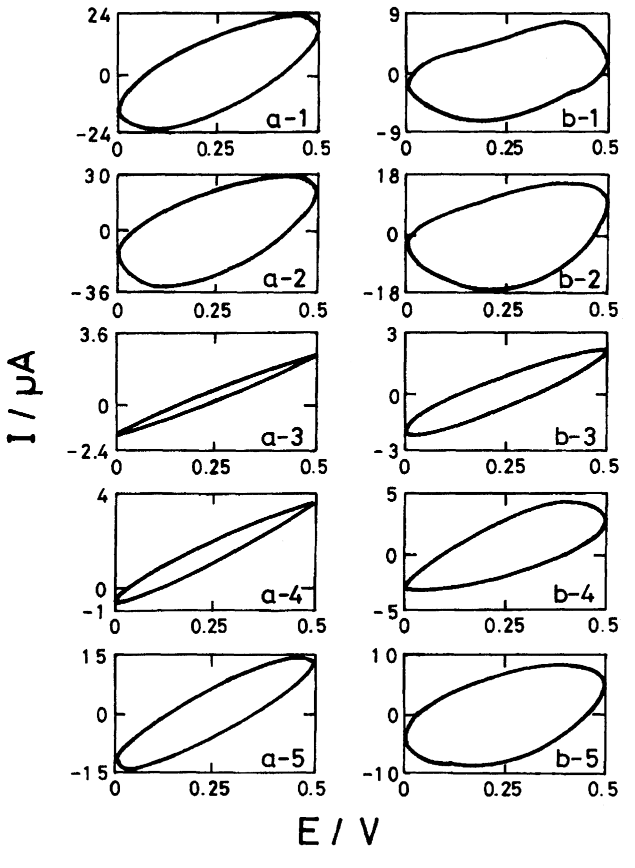

Fig. 2. Current–voltage (*I*–*E*) loops for test aqueous solutions of 10 mmol dm^{-3} taste compounds. The frequency of the sinusoidal voltage is 1 Hz. (a) and (b) are the results with the bare electrode and the modified one with 4-ATP, respectively. (1) to (5) indicate the results for NaCl, HCl, D-glucose, nicotine, and L-glutamic acid in that order.

The loops with a bare electrode do not deviate very much from an ellipsoid, except for those in NaCl and HCl solutions. The slight deformation of these loops implies that the electrochemical nonlinearity for a bare electrode is rather small. On the other hand, the modified electrode with 4-ATP exhibits a marked nonlinear response, as shown in Fig. 2b. Only the loop for D-glucose exhibits a small deformation, indicating the characteristics of a rather pure capacitor. The loops for other solutions, however, deform more significantly than do those with a bare electrode, suggesting pronounced nonlinear characteristics in the modified electrode.

In order to evaluate the nonlinearity in the response in a quantitative manner,[2,3] a fast Fourier transformation (FFT) of the time trace of the output current to the frequency domain was performed. Here, the real and imaginary parts (R_1 and I_1) at the fundamental frequency (1 Hz) correspond to the linear contribution of the conductance and the capacitance, respectively. A frequency of 1 Hz was chosen, so as to observe the nonlinear characteristics in a pronounced manner.[2,3] Here, the intensities of the higher harmonics in FFT are associated with the nonlinearity of the system. Figure 3 shows the intensities of the real and imaginary components of the fundamental and higher harmonics. It has been confirmed that harmonics higher than the forth exhibit only a negligible contribution. The intensity pattern of the harmonics in Fig. 3 clearly indicates the difference in the nonlinear response between each other.

With the bare electrode the intensity of the fundamental frequency is strong, particularly for sodium chloride, hydrochloric acid and L-glutamic acid. The intensity of the second harmonic is also strong for NaCl and HCl. The other harmonics are rather small. As for the response with the bare electrode, the intensities of the higher harmonics are not significant, due to a intensive contribution of the fundamental component, i.e., the conductance of the system is rater high. On the other hand, the intensity of the fundamental frequency with the modified electrode becomes weaker than that with the bare one. Most of the higher harmonics become more intensive than those with the bare one. As a result, the intensities of the higher harmonics become more effective, and the loops thus show a remarkable nonlinear characteristic response.

The intensities of the higher harmonics are correlated with the nonlinear characteristics of the capacitance or conductance[2,3] as follows.

The nonlinear characteristics of the capacitance ($C(V)$) and conductance ($G(V)$) is generally expressed as polynominals with respect to the voltage (V):

$$C(V) = C_0 + C_1V + C_2V^2 + C_3V^3 + \mathrm{O}(V^4) \qquad (1)$$

and

$$G(V) = G_0 + G_1V + G_2V^2 + G_3V^3 + \mathrm{O}(V^4) \qquad (2)$$

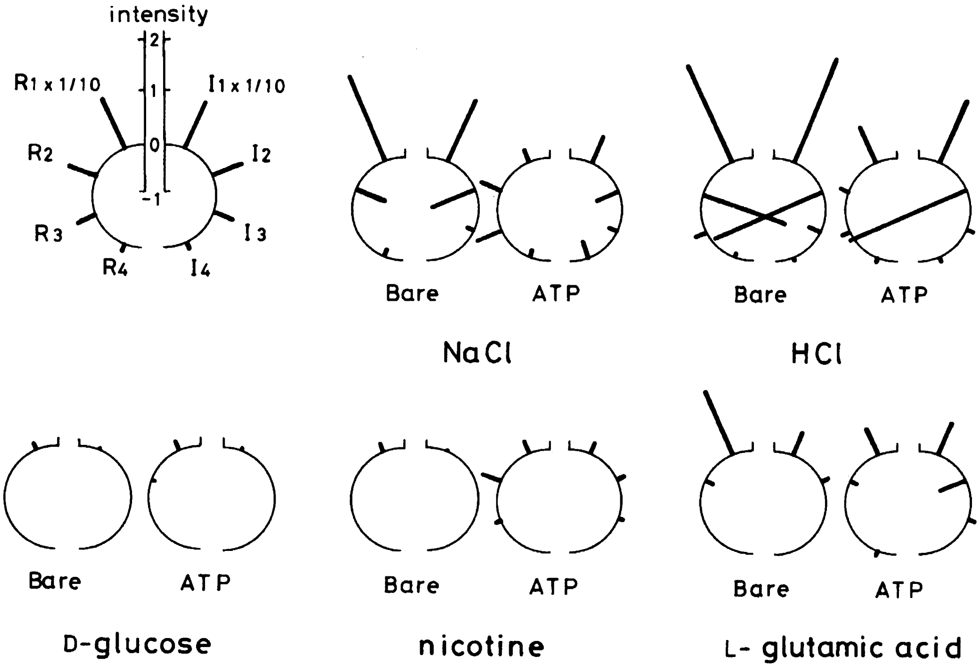

Fig. 3. Intensities of the harmonics of FFT of the output current for 10 mmol dm^{-3} aqueous solutions of taste compounds. R is the real component and I is the imaginary one. Each subscript (1 to 4) indicates the components with the fundamental frequency, second, third and forth harmonics. 'Bare' and 'ATP' are the results with the bare electrode and the modified one, respectively.

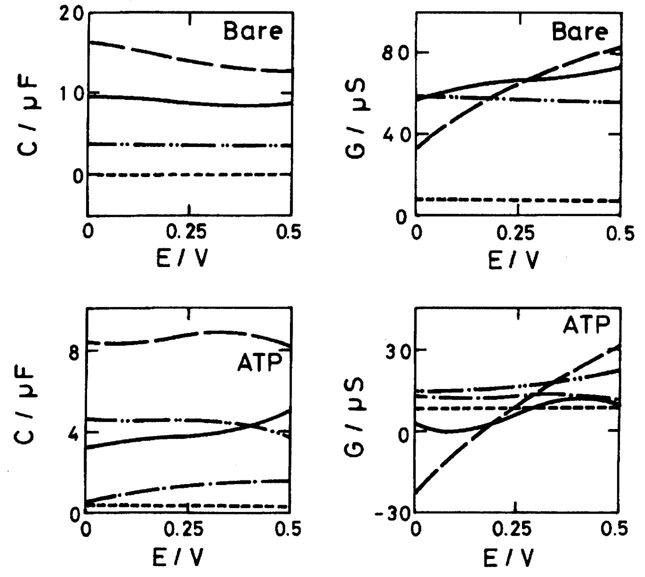

Fig. 4. Capacitance–voltage (C–E) and conductance–voltage (G–E) curves calculated using the Eqs. 1 and 2. 'Bare' and 'ATP' are the results with the bare electrode and the modified one, respectively. —— : NaCl, – – – : HCl, - - - : D-glucose, – • – : nicotine, – •• – : L-glutamic acid. The line for nicotine almost overlaps the line for the D-glucose with the bare electrode.

where C_0 and G_0 are the linear or fundamental components of the capacitance and conductance. When a sinusoidal voltage $V=E_0+E_1 \sin \omega_0 t)$ is applied to a system of parallel circuits with a nonlinear capacitor and a nonlinear resistor, the output current ($I(t)$) is given as the summation of the capacitive component ($I_C(t)$) and the conductive one ($I_G(t)$). In our experiment, the terms higher than the third order in Eqs. 1 and 2 can be disregarded, because the intensities of the harmonics higher than the forth are negligible. The relationship between ($I(t)$) and intensities of the harmonics on FFT is thus expressed as in the following equation:

$$\begin{aligned} I(t) &= I_G(t) + I_C(t) = G(V)V + C(V)(\mathrm{d}V/\mathrm{d}t) \\ &= R_0 + R_1 \sin \omega_0 t + I_2 \cos 2\omega_0 t + R_3 \sin 3\omega_0 t + \\ &\quad I_4 \cos 4\omega_0 t + I_1 \cos \omega_0 t + R_2 \sin 2\omega_0 t + \\ &\quad I_3 \cos 3\omega_0 t + R_4 \sin 4\omega_0 t. \end{aligned} \tag{3}$$

Here,

$$\begin{aligned} R_0 &= G_0E_0 + G_1E_0{}^2 + G_2E_0{}^3 + G_3E_0{}^4 \\ &\quad +E_1{}^2(G_1 + 3G_2E_0 + 6G_3E_0{}^2)/2 + 3G_3E_1{}^4/4, \\ R_1 &= E_1(G_0 + 2G_1E_0 + 3G_2E_0{}^2 + 4G_3E_0{}^3) \\ &\quad +3E_1{}^3(G_2 + 4G_3E_0)/4, \\ R_2 &= E_1{}^2\omega_0(C_1 + 2C_2E_0 + 3C_3E_0{}^2 + E_1{}^2C_3/2)/2, \\ R_3 &= -E_1{}^3(G_2 + 4G_3E_0)/4, \\ R_4 &= -E_1{}^4\omega_0C_3/8, \\ I_1 &= E_1\omega_0\{C_0 + C_1E_0 + C_2E_0{}^2 + C_3E_0{}^3 \\ &\quad +E_1{}^2(C_2 + 3C_3E_0)/4\}, \\ I_2 &= -E_1{}^2(G_1 + 3G_2E_0 + 6G_3E_0{}^2 + G_3E_1{}^2)/2, \\ I_3 &= -E_1{}^3\omega_0(C_2 + 3C_3E_0)/4 \quad \text{and} \\ I_4 &= E_1{}^4G_3/8. \end{aligned}$$

Based on these relationships we can evaluate the voltage-dependence property of both the capacitance and the conductance. Figure 4 gives the calculated nonlin-

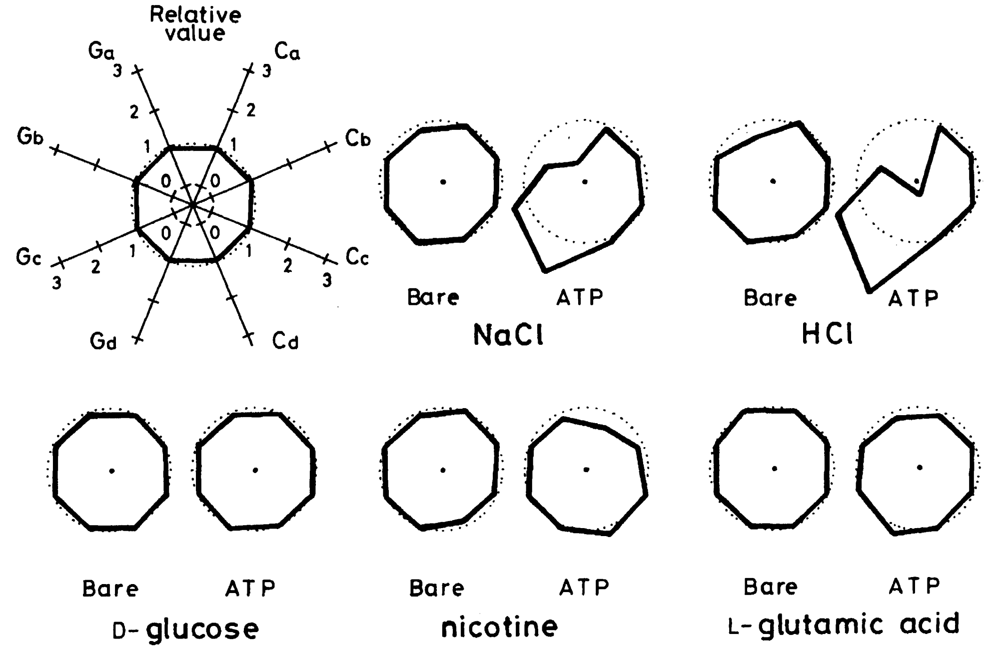

Fig. 5. Patterns of relative values of the capacitances and conductances (C_x and G_x) for each aqueous solution. 'Bare' and 'ATP' are the results with the bare electrode and the modified one, respectively. $G_a = G_{0.1\,V}/G_{0.25\,V}$, $G_b = G_{0.2\,V}/G_{0.25\,V}$, $G_c = G_{0.3\,V}/G_{0.25\,V}$, $G_d = G_{0.4\,V}/G_{0.25\,V}$, $C_a = C_{0.1\,V}/C_{0.25\,V}$, $C_b = C_{0.2\,V}/C_{0.25\,V}$, $C_c = C_{0.3\,V}/C_{0.25\,V}$, $C_d = C_{0.4\,V}/C_{0.25\,V}$

ear characteristics, i.e., voltage-dependency of the capacitance and conductance, for each aqueous solution.

For D-glucose, $C(V)$ and $G(V)$ were rather small, and showed only a slight dependence on the voltage change with both bare and modified electrodes, as shown in Fig. 4. With the bare electrode, a similar voltage-dependence of $C(V)$ and $G(V)$ was observed for nicotine and L-glutamic acid, which are also a nonelectrolyte or a weak electrolyte. For NaCl and HCl, however, which are strong electrolytes, $C(V)$ and $G(V)$ showed marked voltage dependencies with the bare electrode. The variation for HCl is much more remarkable. It can thus be inferred that the bare electrode responds preferably for the ionic species.

With the modification of the electrode, $C(V)$ and $G(V)$ for each taste compound, except for D-glucose, showed a marked change in the nonlinear response. For NaCl and HCl, the voltage-dependencies of $C(V)$ and $G(V)$ showed the characteristic changes, in contrast to those with the bare electrode. For nicotine and L-glutamic acid, the characteristic response was also pronounced due to the modification. These responses indicate that each taste compound characteristically interacts with the modified electrode surface, and the modification with a suitable compound affords a useful analytical tool for discriminating various taste compounds.

In order to obtain a clearer picture concerning the change in the nonlinear response, a new index is introduced, i.e., the relative capacitance and conductance, which were obtained as the relation of the capacitance or conductance at each suitable voltage to that at 0.25 V. Figure 5 shows the relative capacitance and conductance in octagonal patterns which are made from them at 0.1, 0.2, 0.3 and 0.4 V. Although in a linear system the octagon becomes regular, it is clear that each octagon in Fig. 5 deforms characteristically with different solutions and electrodes. Particularly, the deformation is more remarkable for NaCl and HCl with the modified electrode.

The characteristic response with the modified electrode changes with the concentration of each aqueous solution, as shown in Fig. 6. In this figure, the relative intensities of each component to the first one of the real part in the FFT were used in order to minimize the experimental error, which always becomes less than 5 percent. Each linear component (I_1/R_1) shown in Fig. 6(6) increased, accompanied by an increase in the concentration of each taste compound in a characteristic manner. This implies that the system becomes more capacitic with an increase in the concentration. In contrast to the linear component, the relative intensities of the higher harmonics were nearly zero at 10^{-4} $\mathrm{mol\,dm^{-3}}$, and each characteristic feature became more apparent, accompanied by an increase in the concentration. For NaCl, most of the components changed remarkably with the concentration. For HCl, nicotine and L-glutamic acid, a few component, such as R_2/R_1 and I_2/R_1, were remarkably affected by the concentration. For D-glucose, there was only a slight change in each component with the concentration.

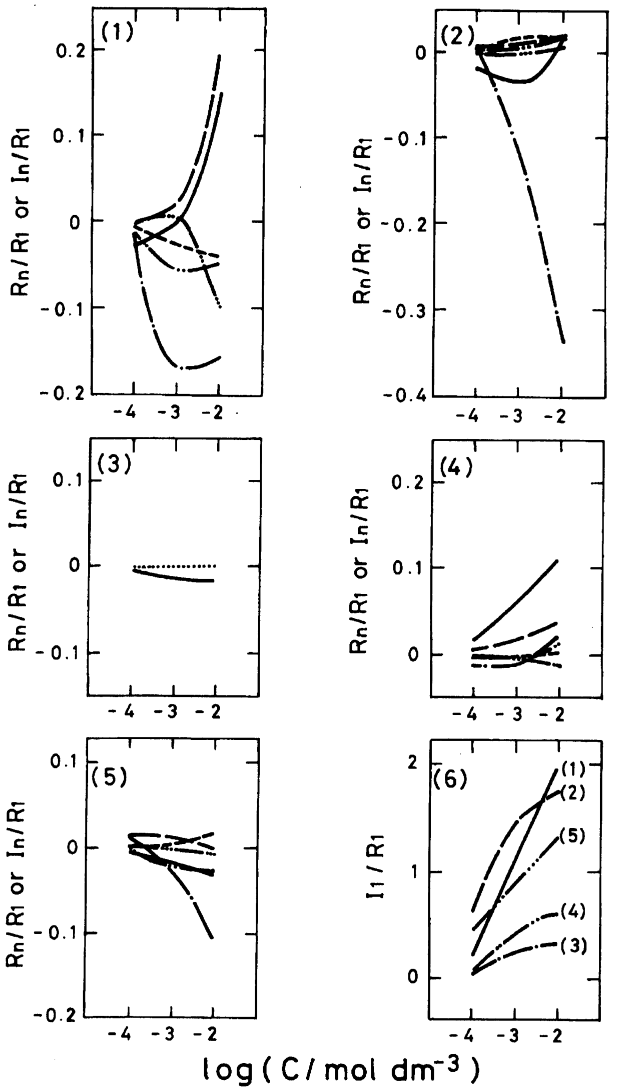

Fig. 6. Variation in the relative intensity (R_n/R_1 or I_n/R_1) in FFT with the concentration of each aqueous solution. (1) to (5) indicate the same meaning in Fig. 2. (6) indicates the intensities of the I_1/R_1 for each solution. In the figures of (1) to (5), each line indicates the variation of the relative intensities. —: R_2/R_1, - - -: R_3/R_1, - - -: R_4/R_1, -·-: I_2/R_1, -··-: I_3/R_1, -···-: I_4/R_1, ····: Overlaps of R_3/R_1, R_4/R_1, I_2/R_1, I_3/R_1, and I_4/R_1.

Summarizing the above results and discussion, it has become clear that a modification with 4-ATP enhances the nonlinear characteristics of the electrode, and that the modification is a useful step for developing a sensor which can detect various taste compounds.

In the present study we only investigated the effect of a limited number of taste compounds. We are now carrying out experiments concerning the nonlinearity for various taste compounds in a systematic manner. As a preliminary result, we have already confirmed that the nonlinear characteristics exhibit a clear change which depends on the taste-category of the examined sample. A study on the effect of a mixture is also under way. Together with the support of information processing based on back-propergation, or a Hopfield algorithm for the neural computer,[20] the proposed mêthod may become quite useful for both detecting and quantifying various chemical species.

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