Odor-sensor Technology Based on an Array of Quartz Crystal Resonators Coated with Plasma-deposited Organic Film

Michiko Seyama†*, Masayuki Nakamura, and Akiyuki Tate*

Abstract

Odor information is new network content that has the potential to enable highly realistic telecommunication and novel services. Our goal is to develop odor sensing technology that translates odors into information that can be shared with others. This article reviews our odor sensing system, which is composed of an array of quartz crystal resonators coated with plasma-deposited organic film and uses a data processing algorithm based on chemometrics.

1. Introduction

Odor includes useful information for various situations in our lives and is expected to be a new type of content for network services (**Fig. 1**). For example, odor can add realistic environmental information to sound-and-vision-based telecommunication. Odor information can appeal to a consumer and also helps consumers evaluate merchandise when shopping online. Biogas odor such as breath or body odor includes useful indicators of a person's health [1]. Active utilization of odor in the air that we breathe unconsciously is attracting increasing interest because of a recent scientific report on human psychological and physiological effects of odor in aromatherapy [2]. And offensive- or nuisance-odor assessment has become an important task for administrative organs of the Japanese government [3]. It is difficult for humans to objectively assess nuisance-odor because the recognition of bad smell depends on personal experience, cultural background, and one's personal circumstances. For example, food odors coming from a restaurant may attract guests but irritate neighbors.

We have developed an odor-sensor that is an input device of odor information to network. Odor is one or more volatile molecules having a molecular weight of about 20 to 400 in air. The sensor must catch odorous volatile components that are easily diffused in air and diluted and must also generate information that we can share with others. Therefore, a highly sensitive sensor, a compactly assembled sensor system that is applicable to monitoring in homes, factories, or in the field, and an easy and clear presentation of odor information are all required. Our odor sensor system consists of a compact sensor array of quartz crystal resonators (QCRs) coated with plasma-deposited organic adsorption films (PPFs) and a data processing program that was developed based on chemometrics[*1]. In this article, we introduce the concept of our odor sensor system and then review the technical details of its components.

2. Concept and overview of the odor sensor system

The odor sensor is analogous in concept to the human olfactory system, which is said to be able to discriminate several hundred thousand odorous compounds [4]. Biological research on the human olfactory system indicates that odor molecule discrimination originates from the molecular selectivity of olfactory receptor protein (ORP) that exists deep in the nose and only about 350 kinds of DNA determine

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† NTT Microsystem Integration Laboratories
Atsugi-shi, 243-0198 Japan
E-mail: michiko@aecl.ntt.co.jp

[*1] Chemometrics: The coined term that means the fusion of "chemistry" and "metrics". A chemical discipline that uses mathematical and statistical methods to treat chemical data in order to provide maximum relevant chemical information (e.g., a predicting model) by analyzing chemical data with techniques of optimization, pattern recognition, library search, calibration, and neural networks.

the molecular structure of ORPs [5]. When an odor compound binds selectively with ORP, a G protein stimulates an enzyme and a stimuli-transmitting substance called cyclic adenosine monophosphate (cAMP) opens an ion channel through the lipid membrane so that a neuro-signal is generated, as shown in **Fig. 2**. Similarly, when an odor sensor system catches an odorous compound, it generates a signal representing the odor's molecular information.

Our odor sensor system expresses a detected odor in a way analogous to how human olfactory system does. Odor has no unit like wavelength (for light) or

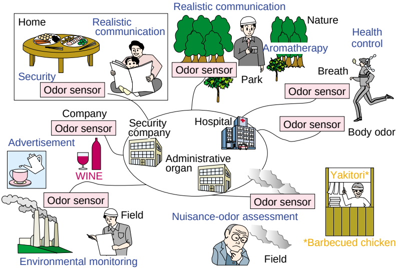

Fig. 1. Expected services with odor sensor technology.

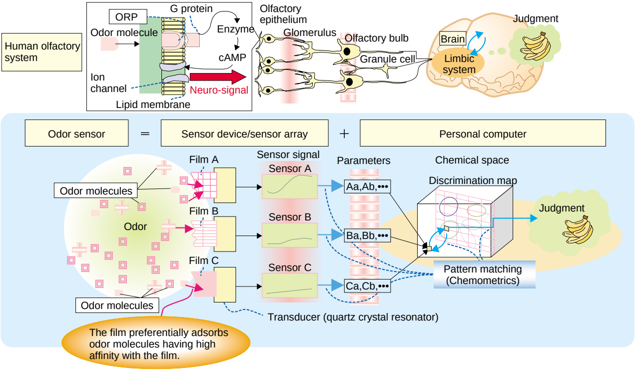

Fig. 2. Concept of odor sensor.

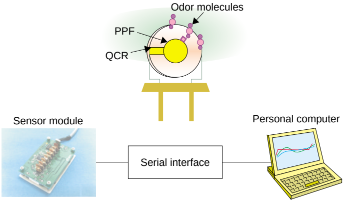

Fig. 3. Odor sensor system.

frequency (for sound). In our daily lives, we describe odors by referring to a typical familiar odor. For example, one might say that something smells like fish. The sensor system identifies odors in a similar way: sensor devices with different molecular selectivities are assembled in an array. When the sensor detects an odorous compound, it generates an electrical signal that carries information about the odor's molecular structure. Next, the characteristics of sensor signals are extracted, combined, and stored as a response pattern for a particular odor. By matching the generated response pattern with one of the many response patterns stored in the database, the system judges that the detected odor is a particular odor. Our sensor device consists of a PPF as an adsorption layer and a mass-sensitive transducer, QCR [6]. The compact sensor module is shown in **Fig. 3**. The circuit board contains an oscillation circuit for each QCR, a frequency measurement circuit, and a data transfer interface. Eight QCRs are set in the module along with one bare QCR used as a standard device for frequency measurement. The resonant frequency difference between the QCR and the standard device is measured using a multiplexer. The resonant frequency change data are fed into a personal computer through a serial interface. Multiple sensor modules can be connected together and used at the same time with one personal computer.

3. Details of odor sensor system based on PPF

3.1 PPF-coated QCR sensor

PPFs are deposited on both sides of the QCR by radio-frequency sputtering. The total PPF thickness is around 1 μm. As a sputtering target, we have used many organic solids: amino acids (e.g., D-phenylalanine), nucleotide (e.g., adenine), biological gels (e.g., agarose), and synthetic olefin polymer (e.g., polyethylene and poly(ethylene-*co*-vinyl acetate)) and synthetic fluoropolymer (e.g., poly(chlorotrifluoroethylene)) [7]. The sputtered organic molecules are excited in the plasma through reactions with electrons, light, and ions. These excited molecules form new chemical bonds, and polymerized film is deposited on the QCR substrate. The molecular structure of the PPF is related to that of the starting material and changes in plasma conditions affect the molecular structure of the deposited film. For example, exciting the sputtered molecules by illuminating them with ultraviolet light produces a PPF with a higher molecular density. Therefore, PPFs with various kinds of molecular structures can be prepared.

The adsorption of odor molecules by the PPFs is explained as a solvation phenomenon in which a small 'solute' of odor molecule is adsorbed/absorbed in the 'solvent' of the PPF film matrix [8]. The concept of numerical quantitative analysis of solute/solvent interaction, which is called the linear solvation energy relationship (LSER), is applied to predict the molecular selectivity of PPFs. The solvation phenomenon is treated as the total interaction of characteristic detailed interactions, represented by polarizability (R or r), dipole-dipole interaction (s or π), hydrogen-bonding ability that is divided into acidity (a or α) and basicity (b or β), and lipophilicity (logL, l), as follows.

$$\text{Solubility} = \mathrm{R} \cdot r + \mathrm{s} \cdot \pi + \mathrm{a} \cdot \beta + \mathrm{b} \cdot \alpha + \log \mathrm{L} \cdot l \quad (1)$$

Each interaction is expressed by multiple 'solute' parameters (italics) and 'solvent' parameters. (The logL is the same value as the Ostwald coefficient determined by molecular solubility in n-hexadecane.) Solubility is related to the partition coefficient of solute in a solvent, so it is directly related to the increase in the mass of the PPF-coated QCR by the adsorption of molecules. The solubility parameters of various volatile molecules have already been determined [9]. Each volatile molecule has different values of solubility parameters. Therefore, the selectivity of PPF for target odorous molecules can be adjusted by designing the molecular structure of the PPF so as to increase or decrease the value of the solubility parameter so that it matches the solubility parameters of target odors.

3.2 Sensor response characteristics

The raw sensor data is the resonance frequency change (Δf) of the QCR that indicates the increase in mass (Δm) [10]. The relationship between Δf and Δm is expressed as

$$\Delta f = -2\, f_o^2\, \Delta m \,/\, A\, (\rho_q \mu_q)^{1/2}, \qquad (2)$$

where f_o is the fundamental resonance frequency, A is the electrode area, ρ_q is the density of quartz (2.65 g cm^{-3}), and μ_q is the shear modulus of quartz (2.95×10^6 N cm^{-2}). We use an 8-mmϕ QCR whose f_o and A are 9 MHz and 0.13 cm^2, respectively. Therefore, our sensor device is theoretically sensitive to sub-nanogram mass changes by measuring the resonant frequency with an accuracy of 0.1 Hz.

$$\Delta f\ [\mathrm{Hz}] = -1.05\, \Delta m\ [\mathrm{ng}] \qquad (3)$$

Figure 4 shows examples of sensor responses obtained by using a PPF prepared from polyethylene [7]. Odor measurement was performed at around room temperature and Δf data were obtained every 5 s. When odor molecules were adsorbed by the PPF, the resonance frequency of the QCR decreased as indicated in Eq. (3). Samples were petroleum vapors having characteristic odors that are early indicators of oil spills in water sources [11].

The resonant frequency of the PPF-coated QCR in contact with air was stable as shown by the first 30 min in Fig. 4. When the petroleum vapor was applied to the sensor at 30 min (up-arrow in Fig. 4), the resonant frequency shifted. The QCR sensor used in this test was covered with a PPF prepared from polyethylene, which is lipophilic and has a high affinity for hydrocarbons. The rate of increase in Δf was different for different sample gases. Since gasoline and fuel oil are mixtures of various hydrocarbons, their concentrations were estimated from the corresponding concentration of octane, which was confirmed by gas chromatography. The QCR sensor can detect sub-ppm to low-ppb levels of petroleum vapors. After sorption of odor molecules by the QCRs, we applied air to the sensor at 210 min (downward arrow) and the Δf began to decrease immediately, indicating that the adsorbed molecules were desorbing from the PPF. Therefore, a PPF-coated QCR can be used for odor monitoring repeatedly.

Some chiral gas molecules smell differently to humans. Many natural and artificial flavors include volatile chiral molecules. For example, chiral limonenes are often found in citrus flavors. (–)-limonene, which rotates the optical plane counterclockwise, smells like oil, whereas (+)-limonene, which rotates the optical plane clockwise, smells like fresh lemon. Since volatile chiral components are relevant to flavors or aroma quality, a sensor device that can discriminate them would contribute to the

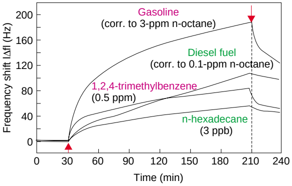

Fig. 4. Odor sensor response to volatile compounds.

advancement of high-precision odor sensing technology. We have developed a PPF prepared from chiral amino acid [12]. The QCR coated with this PPF can discriminate chiral odorous compounds generated at sub-ppm concentrations.

3.3 Response parameters and discrimination

The rate and amount of adsorption are related to the total molecular interaction between 'solute' odorous molecules and the 'solvent' PPF matrix, as mentioned in section 3.1. The time versus Δf curve is expressed using the model Langmuir presented, where the diffusion of small molecules in the solvent PPF matrix is the rate-determining step [13]:

$$\Delta f = a\,[1-\exp(-t/\tau)], \qquad (4)$$

where a, the resonant frequency change at time t, corresponds to the mass of adsorbed molecules and τ is a time constant.

By fitting the time versus Δf curve to Eq. (4), we can extract the values of a and τ as characteristic parameters for the sensor response. These response parameters are obtained from the signals from the QCRs in the module and are combined to make the response pattern of the monitored odor.

In this way, the sensor array can generate a lot of data as response patterns. To extract useful information for odor discrimination, we perform a principal component analysis (PCA), which is a powerful tool for reducing the dimensionality of a data set. We applied our sensor array to measure various monogases [14] and also odors composed of various volatile molecules (**Fig. 5**). Samples were six kinds of woody odors and seven kinds of citrus odors generated from essential oils, which are extracted from natural plants and used for fragrances and cosmetics and in aromatherapy. The concentrations of the tested woody and citrus odors that include various kinds of volatile molecules were expressed by odor strength as determined by the human olfactory system. A 'sample point' that corresponded to one particular concentrated odor among tested odors included two parameters that were extracted by fitting the measured time versus Δf curve to Eq. (4). PCA of a data set consisting of 'sample points' found the first and second principal components (PC1, PC2) that represented the axes to make the 'sample points' the most and the second-most dispersive, respectively. By plotting the loadings of each 'sample point' relative to PC1 and PC2, we obtained two-dimensional PCA score plots as shown in Fig. 5.

Odors that people recognize as a similar group often include common molecules [15]. The PCA score in **Fig. 5(a)** was obtained from QCRs coated with three different PPFs. Visually, plots for the same odor make a group segregated from other groups. The plots for two of woody odors, both of which contained a lot of α-pinene, eucalyptus, and pine, are close together. However, the groups of star anise, sandal wood, and cedar wood, which contained their own representative odorous components other than α-pinene (anethol, santol, and cederene, respectively) are relatively separated from each other. These results indicate that useful data for odor discrimination were extracted successfully by PCA. The discrimination accuracy of plots in the PCA score was evaluated mathematically by using the k-nearest neighbor (kNN) method, which classifies a plot to the nearest group based on the Euclid distance between plots. The discrimination in Fig. 5(a) was good, considering that 91% accuracy was obtained.

The PCA scores in **Fig. 5(b)**, which were prepared from data obtained from four different PPF sensors, indicated the odor discrimination ability of our sensor array of citrus odors. These odors include common volatile compounds represented by limonene and

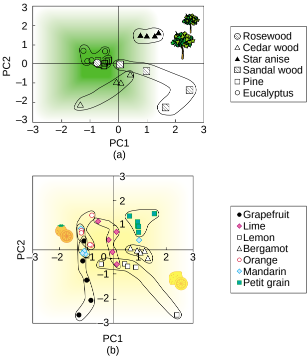

Fig. 5. PCA scores obtained from measurements of various odors with an array of QCRs coated with PPFs. a) woody odors and b) citrus odors.

have different characteristic odorous compounds. The mandarin and orange, which have similar odors to humans, were not discriminated well, but the other odors were discriminated. The discrimination accuracy evaluated by the kNN method was 74%.

3.4 Odor judgment

The odor sensor system can judge a gas sample as belonging to an odor category in the database. The program is based on the learning vector quantization (LVQ) method [16] presented by Kohonen, which is a neural network system. The input signal to the neural network originates from the response pattern obtained from the sensor array, and the output units (cells) are arranged in an array (map) and connected by weights to the inputs. The weights are tuned with the observed data beforehand. The input signal of the odor to be identified (unknown sample) is compared to each output cell's weight vector, and the output vector with the weight nearest to the observed input signal is selected as the 'winner'.

The input signal is a standardized pattern vector (X) whose original data are sets of normalized a and τ obtained from i kinds of PPF-coated QCR sensors. The dimension of X is $2i$. The sensor response parameter of a is normalized because the value of a (i.e., the mass adsorbed by the PPF) is affected by odor concentrations and normalization among data from i kinds of PPF-coated QCRs can eliminate the concentration effect. First, we create the feature map (e.g., **Fig. 6**) and the starting weight, which is generated from one observed input signal based on

$$W_j(T+1) = W_j(T) + .\varepsilon(T)[X-W_j(T)], \qquad (5)$$

where W_j is the jth weight vector and $\varepsilon(T) = 0.01 (1-T/1000)$. T starts at 1 and increases to 1000. Next, we tune the weight vector using the observed data. If the nearest weight vector belongs to a cell representing the 'correct' odor, then the weight vector is increased and shifted to the input signal. On the other hand, if the nearest weight vector belongs to a cell representing an 'incorrect' odor, the weight vector is decreased and shifted from the input signal according to the rule:

$$Wc(T+1) = Wc(T) \pm \varepsilon(T)[X-Wc(T)], \qquad (6)$$

where Wc is the nearest weight vector of an output cell.

An example of odor judging based on LVQ is shown in Fig. 6 [16]. Each cell in the map represents one of six odors. The numbers shown in the cells in the field indicate the sum of 'winning' times and clearly tell us which odor the sensor system has judged it to be. By making an odor map that covers the range of target odors (including one or more molecules) and training the neural network through tests using real samples, it will be possible to make an odor system optimized for a given application [17].

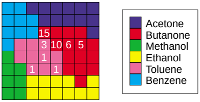

Fig. 6. Odor discrimination based on LVQ.

4. Conclusion

We have developed an odor-sensor system based on plasma-processed organic adsorption film (PPF)-coated quartz crystal resonators (QCRs) that has high sensitivity to various odors consisting of one or more odorous molecules. Our sensor array can discriminate between various odors found in nature and fragrances and also between chiral odorous compounds. A visualized odor discrimination system based on the learning vector quantization method has been developed that is suitable for a particular application by optimizing the PPF-coated QCRs in the sensor array and the learning process with the sensor response database. The sensor array was assembled in a compact module, so it can be used in the factory, office, home, and field. We believe that further miniaturization of the whole odor sensor system will make odor monitoring possible on a more personal level and extend the utilization of odor information.

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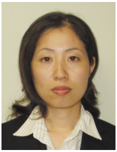

Michiko Seyama

Engineer, Ubiquitous Interface Research Department, NTT Microsystem Integration Laboratories.

She received the B.S. and M.S. in applied chemistry from Waseda University, Tokyo in 1995 and 1997. In 1997, she joined the Integrated Information and Energy Systems Laboratories, Tokyo, Japan. She joined the Lifestyle and Environmental Laboratories in 1999 and the Microsystem Integration Laboratories in 2002. She has researched optical chemical sensing and odor sensing systems. She is a member of the Electrochemical Society of Japan, the Japan Society for Environmental Chemistry (JEC), and the Society of Polymer Science, Japan. She received a research promotion award and a paper award in 1999 and 2001, respectively, from JEC.

Masayuki Nakamura

Senior Research Engineer, Environmental Information Systems Project, NTT Energy and Environment Systems Laboratories.

He received the B.E., M.E., and Ph.D. degrees in mathematical engineering and information physics from the University of Tokyo, Tokyo in 1988, 1990, and 1998. He joined NTT Applied Electronics Laboratories in 1990, NTT Interdisciplinary Research Laboratories in 1991, NTT Integrated Information and Energy Systems Laboratories in 1996, NTT Lifestyle and Environmental Technology in 1999, and NTT Energy and Environment Systems Laboratories in 2002. He has studied information processing in sensing systems. He is a member of the Society of Instrument and Control Engineers and the Institute of Electrical Engineers of Japan (IEEJ). He received a presentation award from IEEJ in 1998 and a research promotion award from JEC.

Akiyuki Tate

Senior Research Engineer, Supervisor, NTT Microsystem Integration Laboratories.

He received the B.S. and M.S. degrees in applied physics from Hokkaido University, Hokkaido in 1976 and 1979, respectively. In 1979, he joined NTT Laboratories, where he has been in charge of the development of various types of optical functional materials, devices, and equipment in areas ranging from organics, semiconductors, silica glass, and opto-magnetic materials to ferroelectric materials for future photonic communications and information processing. He is a member of the Japan Society of Applied Physics, the Physical Society of Japan, Optical Society of Japan, and the Institute of Electronics, Information and Communication Engineers of Japan.