

SELECTED TOPICS IN APPLIED PHYSICS

Smell identification of spices using nanomechanical membrane-type surface stress sensors

To cite this article: Gaku Imamura *et al* 2016 *Jpn. J. Appl. Phys.* **55** 1102B3

View the [article online](#) for updates and enhancements.

Related content

- [Physics of the Atmosphere: Thermodynamics of moist air](#)
R Caballero
- [Fault tolerant architecture for artificial olfactory system](#)
Nasser Lotfivand, Mohd Nizar Hamidon
and Vida Abdolzadeh
- [Effect of film thickness and viscoelasticity on separability of vapour classes by wavelet and principal component analyses of polymer-coated surface acoustic wave sensor transients](#)
Prashant Singh and R D S Yadava

Recent citations

- [Discrimination of Methanol from Ethanol in Gasoline Using a Membrane-type Surface Stress Sensor Coated with Copper\(I\) Complex](#)
Michihiro Nishikawa *et al*
- [Effects of partial attachment at the interface between receptor and substrate on nanomechanical cantilever sensing](#)
Kosuke Minami and Genki Yoshikawa
- [Development of a Mobile Device for Odor Identification and Optimization of Its Measurement Protocol Based on the Free-Hand Measurement](#)
Gaku Imamura and Genki Yoshikawa



Smell identification of spices using nanomechanical membrane-type surface stress sensors

Gaku Imamura^{1,2}, Kota Shiba¹, and Genki Yoshikawa^{1,3}

¹World Premier International Research Center Initiative (WPI), International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan

²International Center for Young Scientists (ICYS), National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan

³Materials Science and Engineering, Graduate School of Pure and Applied Science, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

*E-mail: IMAMURA.Gaku@nims.go.jp

Received May 15, 2016; revised July 9, 2016; accepted July 10, 2016; published online September 26, 2016

Artificial olfaction, that is, a chemical sensor system that identifies samples by smell, has not been fully achieved because of the complex perceptual mechanism of olfaction. To realize an artificial olfactory system, not only an array of chemical sensors but also a valid feature extraction method is required. In this study, we achieved the identification of spices by smell using nanomechanical membrane-type surface stress sensors (MSS). Features were extracted from the sensing signals obtained from four MSS coated with different types of polymers, focusing on the chemical interactions between polymers and odor molecules. The principal component analysis (PCA) of the dataset consisting of the extracted parameters demonstrated the separation of each spice on the scatter plot. We discuss the strategy for improving odor identification based on the relationship between the results of PCA and the chemical species in the odors. © 2016 The Japan Society of Applied Physics

1. Introduction

Olfaction is the only human sense that has not been fully realized as a practical sensor. As olfaction plays an important role in our daily lives, artificial olfaction is expected to be applied to various fields such as food, medicine, environment, cosmetics, and safety.¹⁾ One of the reasons for the lack of artificial olfaction is the complex mechanism of the olfactory system. In the case of humans, odor molecules inhaled through the nose are detected by olfactory receptors in the nasal epithelium. The resultant neural signals are then transmitted to the olfactory bulb, in which odors are identified according to the induced pattern on the bulb.^{2,3)} To realize an artificial olfactory system, therefore, both an array of chemical sensors and appropriate data analysis methods are required.

Over the past decades, several types of chemical sensors, such as metal-oxide sensors,⁴⁾ conducting polymer sensors,⁵⁾ and optical sensors,⁶⁾ have emerged. Several groups have reported odor identification using such chemical sensors.^{1,7)} Not only single-component gases but also complex mixtures of gases were identified using an array of chemical sensors.^{8,9)}

For more valid identification of odors, however, several issues should be addressed. One such issue is the effect of solvents. Although humans often recognize odor molecules in the air at the concentration of several parts per million (ppm), the vapor of liquid samples (e.g., juice, wine, and whiskey) contains even higher concentrations (~1%-level) of solvent vapors (e.g., water and ethanol), making it difficult to distinguish odor molecules by means of chemical sensors. Thus, it is essential for artificial olfactory systems to distinguish odor molecules from solvent vapors.

Here, we report odor identification using nanomechanical sensors and demonstrate the identification of dried spices by smell without being affected by the solvent issue. Nanomechanical sensors have been attracting great attention owing to their potential for highly sensitive detection and intrinsic versatility.^{10,11)} By utilizing a membrane-type surface stress sensor (MSS),¹²⁾ we successfully distinguish the smells of spices. An appropriate feature extraction protocol as well as the use of dried samples makes it possible to identify the *pure* smells of spices. A mobile artificial olfactory system

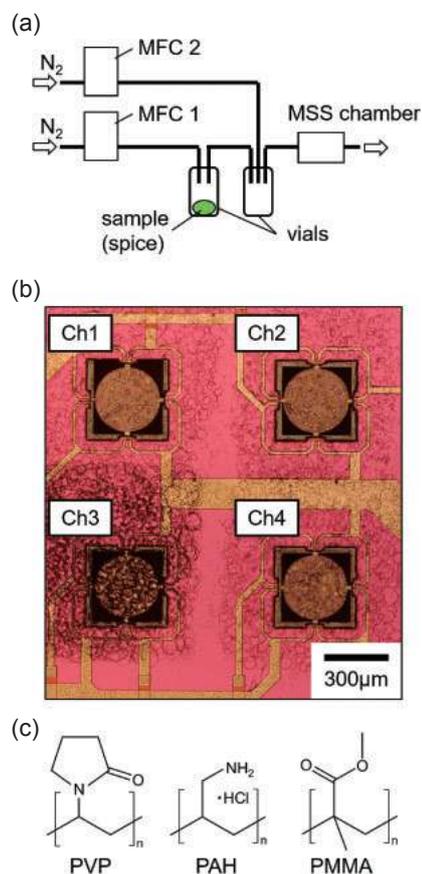


Fig. 1. (Color) (a) Gas flow system for measurement. (b) Optical microscopy image of MSS chip with polymers coated on each channel. (c) Molecular structures of the polymers.

would be feasible in conjunction with a compact measurement module that can be realized by using MSS.

2. Experimental methods

In this study, we employed the gas flow system shown in Fig. 1(a) to measure the odors of spices. Spices were placed in the vial connected to mass flow controller (MFC)-1. The “smell” of a spice saturated in the headspace was injected to

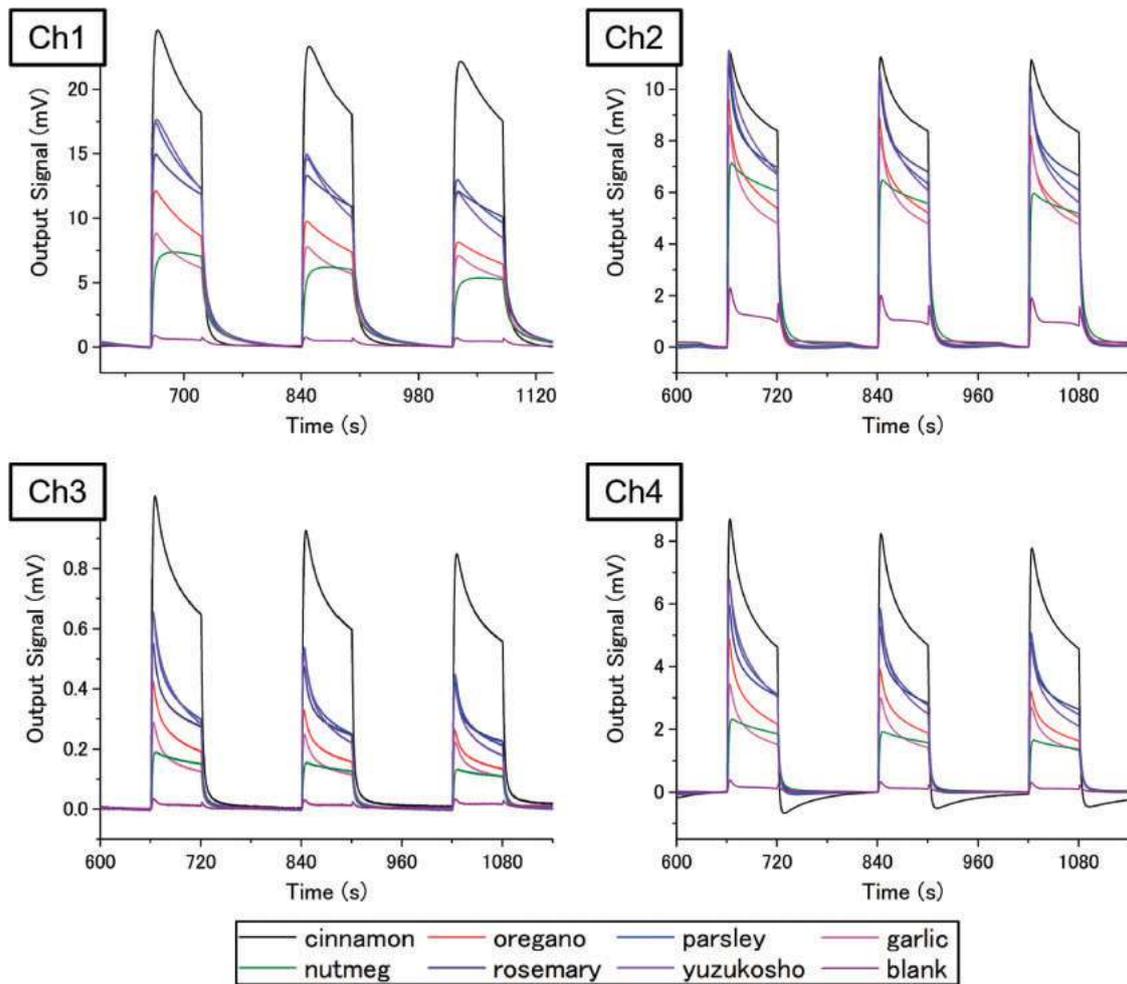


Fig. 2. (Color) Obtained sensing signals for measurement. Baseline correction was applied to all the signals to deal with baseline offset and drift.

the sensor chamber with 100 sccm N_2 . MFC-2 was used for the N_2 purge (100 sccm). In this measurement, the headspace vapor was injected for 2 min, followed by 2 min N_2 purge. The cycle of injection and purge was repeated 5 times, and the last three cycles were used for analysis. We utilized a third-generation MSS (3G-MSS) chip, which has a two-dimensional (2D) array of MSS on a single chip and consists of four channels (2×2). Each channel has the same dimensions as a 2G-MSS with a membrane diameter of $300 \mu\text{m}$.¹³ The following polymers were coated on each channel using a commercial spray coater, as shown in Fig. 1(b): poly(vinyl pyrrolidone) (PVP), poly(allylamine hydrochloride) (PAH), poly(methyl methacrylate) (PMMA), and PVP/PMMA hybrid (PVP : PMMA = 1 : 1 in weight) for channels number 1 (Ch1), 2 (Ch2), 3 (Ch3), and 4 (Ch4), respectively. The chemical structures of these polymers are shown in Fig. 1(c). Signals were measured at a sampling rate of 10 Hz, applying a bias voltage of -0.5 V to the Wheatstone bridge circuit in the MSS. We measured the smells of seven spices: cinnamon, oregano, parsley, garlic, nutmeg, rosemary, and *yuzukosho* (citrus-flavored pepper). Each spice was well dried and used as flakes or powder.

3. Results

Figure 2 shows the output signals obtained at each channel. It is clear that each spice leads to different sensing

responses in accordance with the chemical composition of the vapor.

To identify the spices by smell, appropriate features must be extracted from the sensing signals. We focus on both *static* and *dynamic* information for signal analysis, namely, signal intensity ratio and decay time constant. We defined the signal intensity of channel number i , I_i , as shown in Fig. 3(a). Odors can be identified using I_1 – I_4 through pattern recognition. However, the pattern recognition using I_1 – I_4 strongly depends on their absolute values: the total concentration of odors. To identify the odors by their chemical characteristics without being affected by their concentration, relative intensity ratios were employed for signal analysis instead of I_1 – I_4 . In this study, we used signal intensity ratio of Ch2–Ch4 to Ch1 (I_2/I_1 , I_3/I_1 , and I_4/I_1). In our experimental setup, the concentration of odors during the measurements can be regarded as constant for each spice without a time-dependent fluctuation.

Another important feature of the signal is the transient response, which reflects the dynamic information of gas absorption/desorption. Here, we focus on the purge portion of the measurement: the decay curve. Assuming an exponential decay for the purge portion of the sensing signals, the output signal at time t , $V_{\text{out}}(t)$, can be expressed by

$$V_{\text{out}}(t) = V_0 \exp\left(-\frac{t-t_0}{\tau}\right), \quad (1)$$

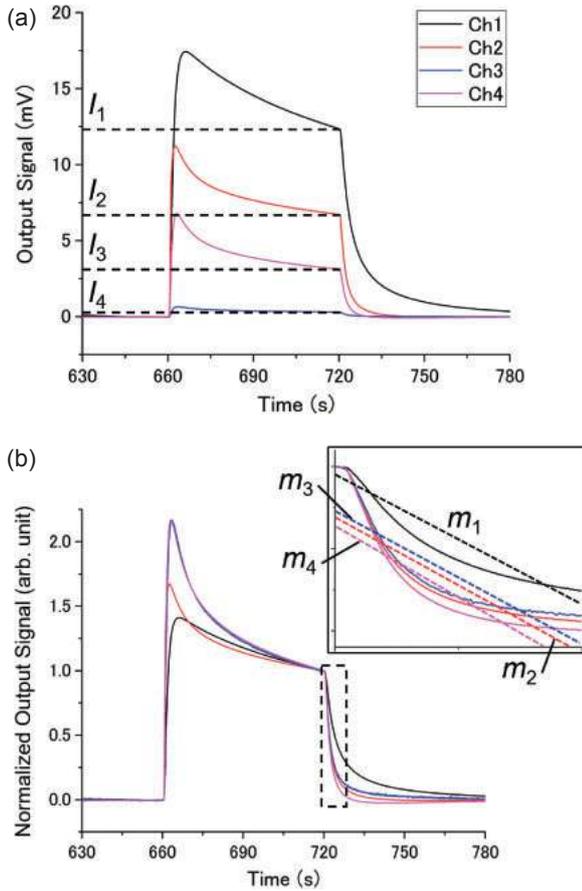


Fig. 3. (Color) Definitions of (a) I_1 – I_4 and (b) m_1 – m_4 .

where τ is the decay time constant, t_0 is the time at which the decay starts, and $V_0 = V_{out}(t_0)$. By fitting all the sensing signals with Eq. (1), τ can be extracted from the four channels (τ_1 – τ_4) for some samples. However, fitting all the sensing signals with Eq. (1) is not applicable because some sensing signals do not show a simple exponential decay (Fig. 2). For example, sensing signals of Ch4 for cinnamon show large undershoots, which cannot be reproduced with Eq. (1). Although it is possible to reproduce such undershoots with the sum of two or more exponential decay functions, it requires a complex fitting algorithm. To extract dynamic information from the decay curve, a linear least-squares fit was applied to the normalized decay curves [Fig. 3(b)]. The linear fit cannot represent the entire feature of the decay curve; nevertheless the slope m reflects the dynamic behavior of the sensing signals to some extent. The linear least-squares fit was applied to every decay portion of the sensing signal, and m values from the four channels (m_1 – m_4) were extracted for every measurement.

On the basis of the discussion above, we extracted the relative intensity ratios ($I_2/I_1, I_3/I_1, I_4/I_1$) and the slopes of the linear fit (m_1, m_2, m_3, m_4) from each cycle of injection and purge, as summarized in Table I. To identify the odors of the spices, principal component analysis (PCA) was performed on the dataset. Figures 4(a) and 4(b) show the 2D and 3D scatter plots of the component scores. Data points obtained for the same spice appear to form a cluster in the scatter plot, and each spice cluster is well separated from others. The scree plot shows a steep curve from components

Table I. Data set (extracted parameters) for PCA.

Samples	I_2/I_1	I_3/I_1	I_4/I_1	m_1	m_2	m_3	m_4
cinnamon1	0.461	0.036	0.254	-0.0892	-0.0808	-0.0840	-0.0966
cinnamon2	0.463	0.033	0.259	-0.0876	-0.0812	-0.0831	-0.0960
cinnamon3	0.475	0.032	0.260	-0.0869	-0.0821	-0.0820	-0.0966
oregano1	0.626	0.022	0.253	-0.0752	-0.0916	-0.0871	-0.0922
oregano2	0.706	0.021	0.255	-0.0728	-0.0928	-0.0882	-0.0914
oregano3	0.781	0.021	0.254	-0.0710	-0.0927	-0.0891	-0.0915
parsley1	0.543	0.024	0.252	-0.0772	-0.0849	-0.0828	-0.0901
parsley2	0.584	0.023	0.255	-0.0752	-0.0871	-0.0852	-0.0895
parsley3	0.630	0.022	0.256	-0.0735	-0.0887	-0.0861	-0.0894
garlic1	0.784	0.020	0.249	-0.0694	-0.0928	-0.0880	-0.0911
garlic2	0.841	0.020	0.250	-0.0686	-0.0917	-0.0888	-0.0913
garlic3	0.887	0.020	0.248	-0.0681	-0.0910	-0.0899	-0.0923
nutmeg1	0.858	0.021	0.264	-0.0708	-0.0887	-0.0891	-0.0903
nutmeg2	0.926	0.021	0.263	-0.0698	-0.0886	-0.0894	-0.0909
nutmeg3	0.989	0.020	0.261	-0.0689	-0.0881	-0.0920	-0.0915
rosemary1	0.587	0.023	0.259	-0.0766	-0.0902	-0.0882	-0.0921
rosemary2	0.624	0.023	0.260	-0.0751	-0.0904	-0.0874	-0.0910
rosemary3	0.658	0.022	0.261	-0.0743	-0.0912	-0.0885	-0.0912
yuzukosho1	0.554	0.023	0.248	-0.0775	-0.0899	-0.0872	-0.0940
yuzukosho2	0.604	0.022	0.248	-0.0745	-0.0910	-0.0883	-0.0923
yuzukosho3	0.661	0.021	0.248	-0.0727	-0.0938	-0.0888	-0.0930

number 1 to 3 and an almost flat line from 4 to 7 [Fig. 4(c)], indicating that principal components 1 to 3 cover most of the variability (94.39%). The eigenvalues are summarized in Table II.

4. Discussion

The present results show the identification of spices by *smell*. It is important to note that these results are not affected by undesired components such as the vapor of solution. Another important key to this odor identification is the feature extraction method. In this study, both static and dynamic information contribute to the discrimination of each spice. Static information, that is, the combination of relative intensity ratios ($I_2 : I_1 : I_3 : I_4$, or $I_2/I_1, I_3/I_1, I_4/I_1$) is strongly related to the affinity of the receptor materials to odor molecules. In general, a higher affinity leads to a higher signal intensity. For example, the MSS coated with hydrophilic polymer (PVP) exhibits a higher signal intensity for water vapor than that coated with hydrophobic polymer (PMMA). Thus, odors from different spices cause different signal intensity ratios ($I_1 : I_2 : I_3 : I_4$, or $I_2/I_1, I_3/I_1, I_4/I_1$) in accordance with the affinities of the receptor materials to the odor molecules. In contrast, the slopes of the linear fit to the decay curve (m_1, m_2, m_3, m_4) reflect the desorption dynamics of odor molecules from the receptor materials. According to the theoretical model for a cantilever coated with viscoelastic materials reported by Wenzel et al.,¹⁴ transient responses contain the dynamics of gas sorption/desorption as well as the viscoelastic behaviors of the receptor materials. Since the dynamic behavior of gas desorption from a polymer should be unique to the gas species, m can be utilized to identify the odors.

As the features extracted in this study correlate with the chemical interactions between receptor materials and odor molecules, the scatter plot should reflect the chemical characteristics of the odor molecules. Table III shows the main

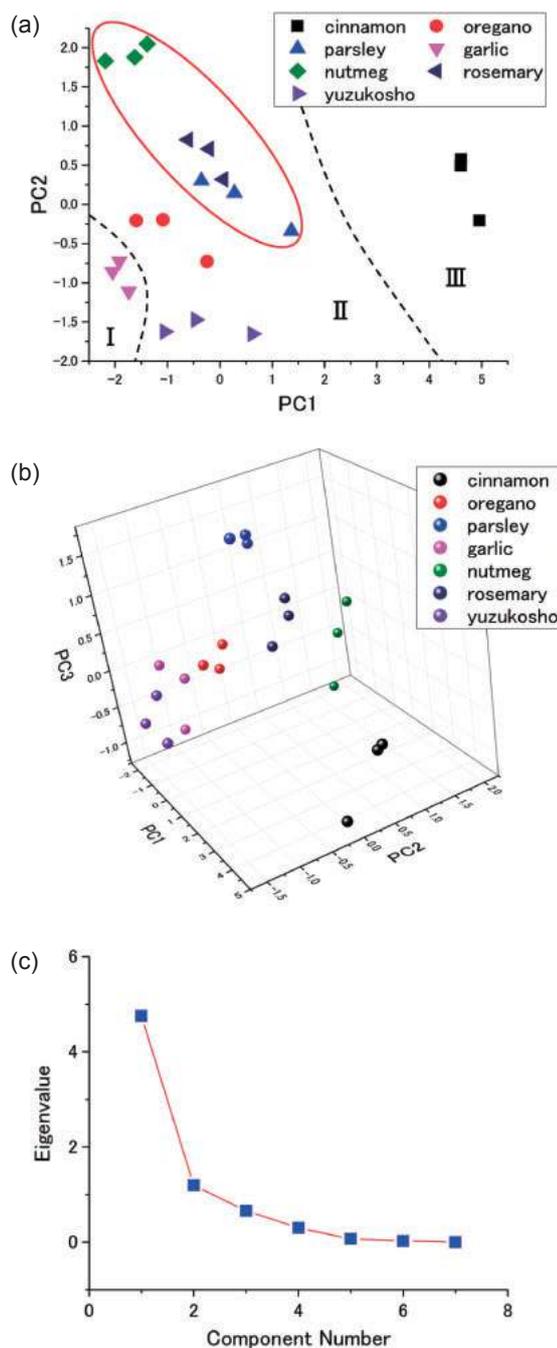


Fig. 4. (Color) (a) 2D- and (b) 3D-scatter plots of the component scores. (c) Scree plot of eigenvalues.

Table II. Eigenvalues from PCA.

Component	Eigenvalues	% of variance	Cumulative %
1	4.7552	67.93	67.93
2	1.19233	17.03	84.96
3	0.65953	9.42	94.39
4	0.29893	4.27	98.66
5	0.06726	0.96	99.62
6	0.02539	0.36	99.98
7	0.00135	0.02	100.00

volatile organic compounds in each spice.^{15–28} On the basis of the chemical species, spices are roughly categorized into three groups as shown in Fig. 4(a). Among these groups,

Table III. Major volatile organic compounds in vapors of spices.

Spices	Major components
Cinnamon ^{15,16}	cinnamaldehyde
Oregano ¹⁷	carvacrol ^{b)} , cymene ^{a)}
Parsley ^{18,19)}	1,3,8- <i>p</i> -menthatriene ^{a)} , pinene ^{a)} , phellandrene ^{a)}
Garlic ²⁴⁾	allicin, 2-propene-1-thiol, diallyl disulphide
Nutmeg ^{20,28)}	pinene ^{a)} , sabinene ^{a)} , myristicin
Rosemary	pinene ^{a)} , camphor ^{b)} , camphene ^{a)} , 1,8-cineole ^{b)}
<i>Yuzu</i> ^{25,27)} (<i>Citrus junos</i> Sieb. ex Tanaka)	limonene ^{a)} , terpinene ^{a)}
Peppers ^{21,23)}	caryophyllene ^{a)} , carene ^{a)} , limonene ^{a)}

a) terpenes, b) terpenoids

group II is composed of spices containing mainly terpenes and terpenoids in their vapors. Terpenes are natural organic compounds that can be built up from units of isoprene (C_5H_8). Terpenoids are regarded as derivatives of terpenes and contain oxygen-containing functional groups such as hydroxyl and carbonyl groups. It is found that spices that contain terpenes and terpenoids appear in close proximity in the scatter plot. In particular, spices marked with a circle in Fig. 4(a) contain pinene ($C_{10}H_{16}$), a kind of terpene with a bicyclic structure. Although spices in groups I (garlic) and III (cinnamon) also contain a certain amount of terpenes, the major components of their vapors are not terpenes but organosulfur compounds and aromatic aldehydes, respectively.

Finally, we discuss a strategy for improving smell identification. As most of the spices contain mainly terpenes and terpenoids, using receptor materials with high chemical affinity to such hydrocarbons would improve the sensitivity. It is expected that hydrophobic materials will be more sensitive to such hydrocarbons rather than hydrophilic materials.^{29–31} In addition to using receptor materials with high affinity to target molecules, the increase in the number of channels can improve the performance of smell identification. Even with a sensor chip having many channels, however, it is important to choose reasonable combinations of receptor materials on the basis of the expected variation in the features with an appropriate extraction protocol.

5. Conclusions

We successfully identified seven spices by smell using polymer-coated MSS. By using both static and dynamic information extracted from the sensing signals, odors were identified through PCA, which reflects the chemical composition of the vapors. We demonstrated the identification of samples by *pure* smell and showed a feature extraction protocol that can identify odors on the basis of their chemical characteristics. Considering the compact measurement system realized by MSS, this study will be an important step towards realizing a mobile artificial olfactory system.

Acknowledgments

This research was supported by the Grant-in-Aid for Young Scientists (B) 16K21602 MEXT, Japan; the Grant-in-Aid for Scientific Research (B) 15H03588, MEXT, Japan; TEPCO Memorial Foundation; and the World Premier International Research Center Initiative (WPI) on Materials Nanoarchitectonics (MANA).

- 1) J. Gutiérrez and M. C. Horrillo, *Talanta* **124**, 95 (2014).
- 2) K. Mori and H. Sakano, *Annu. Rev. Neurosci.* **34**, 467 (2011).
- 3) S. Firestein, *Nature* **413**, 211 (2001).
- 4) H.-J. Kim and J.-H. Lee, *Sens. Actuators B* **192**, 607 (2014).
- 5) H. Yoon, *Nanomaterials* **3**, 524 (2013).
- 6) B. Lee, S. Roh, and J. Park, *Opt. Fiber Technol.* **15**, 209 (2009).
- 7) A. D. Wilson and M. Baietto, *Sensors* **11**, 1105 (2011).
- 8) B. Wyszynski and T. Nakamoto, *IEEE Trans. Electr. Electron. Eng.* **4**, 334 (2009).
- 9) C. Di Natale, E. Martinelli, R. Paolesse, A. D'Amico, D. Filippini, and I. Lundström, *PLoS ONE* **3**, e3139 (2008).
- 10) N. F. Martínez, P. M. Kosaka, J. Tamayo, J. Ramírez, O. Ahumada, J. Mertens, T. D. Hien, C. V. Rijn, and M. Calleja, *Rev. Sci. Instrum.* **81**, 125109 (2010).
- 11) H. P. Lang, J. P. Ramseyer, W. Grange, T. Braun, D. Schmid, P. Hunziker, C. Jung, M. Hegner, and C. Gerber, *J. Phys.: Conf. Ser.* **61**, 663 (2007).
- 12) G. Yoshikawa, T. Akiyama, S. Gautsch, P. Vettiger, and H. Rohrer, *Nano Lett.* **11**, 1044 (2011).
- 13) G. Yoshikawa, T. Akiyama, F. Loizeau, K. Shiba, S. Gautsch, T. Nakayama, P. Vettiger, N. Rooij, and M. Aono, *Sensors* **12**, 15873 (2012).
- 14) M. J. Wenzel, F. Josse, S. M. Heinrich, E. Yaz, and P. G. Datskos, *J. Appl. Phys.* **103**, 064913 (2008).
- 15) D. Gunawardena, N. Karunaweera, S. Lee, F. van Der Kooy, D. G. Harman, R. Raju, L. Bennett, E. Gyengesi, N. J. Sucher, and G. Munch, *Food Funct.* **6**, 910 (2015).
- 16) F. Golmohammad, M. H. Eikani, and H. M. Maymandi, *Procedia Eng.* **42**, 247 (2012).
- 17) I. L. J. Milovanović, A. Č. Mišan, M. B. Sakač, I. S. Čabarkapa, B. M. Šarić, J. J. Matic, and P. T. Jovanov, *Food Feed Res.* **36**, 75 (2009).
- 18) W. Mangkoltriluk, G. Szrednicki, and J. Craske, *Pol. J. Food Nutr. Sci.* **14**, 63 (2005).
- 19) L. S. E. Bruno Kolb, *Static Headspace–Gas Chromatography: Theory and Practice* (Wiley, New York, 2006) 2nd ed., p. 276.
- 20) E. A. Bejnarowicz and E. R. Kirch, *J. Pharm. Sci.* **52**, 988 (1963).
- 21) T. Hasselstrom, E. J. Hewitt, K. S. Konigsbacher, and J. J. Ritter, *J. Agric. Food Chem.* **5**, 53 (1957).
- 22) M. Jalali-Heravi, R. S. Moazeni, and H. Sereshti, *J. Chromatogr. A* **1218**, 2569 (2011).
- 23) H. H. Jeleń and A. Gracka, *J. Chromatogr. A* **1418**, 200 (2015).
- 24) I. Laakso, T. Seppänen-Laakso, R. Hiltunen, B. Müller, H. Jansen, and K. Knobloch, *Planta Med.* **55**, 257 (1989).
- 25) N. T. Lan-Phi, T. Shimamura, H. Ukeda, and M. Sawamura, *Food Chem.* **115**, 1042 (2009).
- 26) D. Meziane-Assami, V. Tomao, K. Ruiz, B. Y. Meklati, and F. Chemat, *Food Anal. Methods* **6**, 282 (2013).
- 27) N. Miyazawa, N. Tomita, Y. Kurobayashi, A. Nakanishi, Y. Ohkubo, T. Maeda, and A. Fujita, *J. Agric. Food Chem.* **57**, 1990 (2009).
- 28) H. P. Schenk and D. Lamparsky, *J. Chromatogr. A* **204**, 391 (1981).
- 29) Although PMMA is the only hydrophobic polymer, the PMMA-coated

MSS (Ch3) shows a lower intensity of sensing signals than MSS coated with hydrophilic polymers (PVP and PAA). This is due to the thickness of the receptor layers; the optimized thickness differs depending on the Young's modulus of the receptor materials.^{30,31)}

- 30) G. Yoshikawa, C. J. Y. Lee, and K. Shiba, *J. Nanosci. Nanotechnol.* **14**, 2908 (2014).
- 31) G. Yoshikawa, *Appl. Phys. Lett.* **98**, 173502 (2011).



Gaku Imamura received his M.S. and Ph.D. in Science from the University of Tokyo, Japan, in 2010 and 2013, respectively. He was a project assistant professor at the Graduate School of Frontier Sciences, the University of Tokyo, from 2013 to 2014. He was a postdoctoral researcher at the WPI Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS) from 2015 to 2016. He is now ICYS-MANA researcher at NIMS. His research interests lie in the field of chemical sensors, particularly in nanomechanical sensors. Currently he is developing an analysis method for sensor signals.



Kota Shiba received his M.S. and Ph.D. degree from Waseda University, Japan, in March 2009 and March 2012, respectively. Then, he moved to National Institute for Materials Science (NIMS) in April 2012 as a postdoctoral researcher. He was selected as an ICYS-MANA researcher at NIMS in September 2014. Since August 2016, he is a MANA scientist at NIMS as a member of the newly developed nanomechanical sensor group. His research interests include design and applications of nanomaterials, physical/chemical sensors, etc.



Genki Yoshikawa received his M.S. and Ph.D. in Science from the University of Tokyo, Japan, in 2001 and 2004, respectively. He was Assistant Professor at Institute for Materials Research (IMR), Tohoku University, Japan (2005–2008), Visiting Scientist at Department of Physics, University of Basel, Switzerland (2007–2009), ICYS-MANA Researcher (2009–2011), Independent Scientist (2011–2016), and currently Group Leader (2016–present) at WPI-MANA, NIMS, Japan. Since 2015, he is also Associate Professor of Joint Graduate School in University of Tsukuba. He received the 23rd Tsukuba Encouragement Prize and nano tech 2015 Research Project Award in 2013 and 2015, respectively.