Aroma Discrimination by Pattern Recognition Analysis of Responses from Semiconductor Gas Sensor Array

Tetsuo Aishima

Research and Development Division, Kikkoman Corporation, 399 Noda, Noda-shi, Chiba-ken 278, Japan

A semiconductor gas sensor array was applied to discriminating coffee aromas, essential oils, and volatile compounds with different functional groups. To standardize sample introduction and to remove excess ethanol from volatile mixtures, headspace concentration utilizing a porous polymer trap was incorporated into the sensing system. Distinctive differences were not observed among response patterns of samples due to the nonselectivity of semiconductor gas sensors. Pattern recognition techniques such as discriminant analysis and cluster analysis were applied to the normalized response patterns. Two ground coffees, *Coffea arabica* and *C. robusta*, and freeze-dried and spray-dried commercial instant coffees were clearly separated by cluster analysis and linear discriminant analysis. A combination of three sensors was sufficient to perfectly discriminate the four coffee samples. Two clusters corresponding to a citrus group and other fruits were shown by cluster analysis of essential oils. Clustering of compounds was partly based on their chemical structure.

INTRODUCTION

Aroma analysis by using capillary gas chromatography (GC) is an established methodology in food analysis. Chemometric pattern recognition techniques have been frequently applied to discriminating and to assigning food samples on the basis of their GC patterns for quality assurance purposes. However, GC analysis is not suitable to continuously monitor aroma quality in production process due to its inherent batchwise and differential (not integral) properties. Before pattern recognition analysis is applied to integrate information useful for sample assignment on a computer, intensive works are needed to feed a data matrix of GC profiles into a computer due to complicated GC patterns in food aromas.

However, the mammalian olfactory system can discriminate aromas without separating mixtures into individual compounds. Signals sent from receptor cells at the olfactory system seem to be decoded at the brain by using a kind of pattern recognition (Moulton, 1963). Recently several attempts of constructing aroma-sensing systems, i.e., the so-called "artificial nose" (Persaud and Pelosi, 1985), have been made by utilizing various gas sensors. Metal oxide semiconductor sensors (Persaud and Dodd, 1982; Oishi et al., 1988; Abe et al., 1989; Weimer et al., 1990), surface-acoustic wave (SAW) sensors (Rose-Pehrsson et al., 1988) and quartz-resonator sensors (Ema et al., 1989) seem potential methods. Although every sensor has its own advantages and disadvantages, there are not such sensors that can show perfect selectivity to specific compounds or a group of compounds. Pattern recognition of the responses from a multisensor array was incorporated into every analytical procedure due to the nonselectivity of gas sensors. However, until now, most efforts have been focused on detecting specific gases or hazardous compounds on the basis of their response patterns (Abe et al., 1989; Rose-Pehrsson et al., 1988; Weimar et al., 1990). From the viewpoint of aroma analysis, discriminating a particular gas mixture from other mixtures is essential.

As the first step for developing a simple aroma-monitoring system, pattern recognition analysis for responses to food aromas from a gas sensor array was attempted by using gas sensors. Although selectivity is not necessarily high, an array composed of six semiconductor gas sensors was applied to this study due to their durability, high sensitivity for most reducing compounds, and insensitivity to water vapor (*Figaro Gas Sensor for Industrial Use*, 1985). A semiautomatic headspace concentrator was incorporated into the sensing system to standardize the aroma introduction process and to remove excess ethanol from headspace volatiles of samples. Pattern recognition techniques were applied to discriminate the resulting response patterns from the sensor array.

EXPERIMENTAL PROCEDURES

Gas-Sensing System. The whole scheme of the gas sensing system is shown in Figure 1. TGS semiconductor gas sensors were courtesy of Figaro Sensor Inc. (Minoo, Osaka, Japan). All sensors used are commercially available. Although distinctive selectivity has not been materialized, properties of gas sensors are somewhat controlled by doping trace amounts of noble metals. The properties of the six gas sensors used for making a sensor array are shown in Table I (*Figaro Gas Sensor for Industrial Use*, 1985). One sensor array was installed in the three-necked 5-L sample flask, and another array was used as reference sensors. The circuit voltage for all sensors was kept at ca. 2 V. Heater temperature was kept around 350 °C during the sensing period. The resistance decreased when reducing gas, i.e., aroma compounds, contacted at the surface of the gas sensors. Amplified differences between sample sensors and reference sensors were recorded both by recorders and by an IBM PC through an A/D converter. After each measurement was finished, the flask was ventilated with air purified through charcoal and silica gel columns until responses decreased to the blank level.

Materials. Coffee beans (*Coffea arabica* and *Coffea robusta*) were courtesy of Tokyo Allied Coffee Roasting Co., Ltd. (Tokyo, Japan). Spray-dried and freeze-dried instant coffees were purchased from a local market. Essential oils dissolved in ethanol were courtesy of Soda Aromatic Co. Ltd. (Tokyo, Japan). Compounds purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan), were used without further purification.

Sample Treatment for Sensing. A Tekmar LSC 2000 semiautomatic headspace concentrator was used for the pretreatment of sample aroma. The conditions for sample treatment were fixed for every sample. Sample aroma was purged with N_2 gas for 15 min at 40 mL/min at room temperature (ca. 25 °C). The volatiles trapped on a mixture (ca. 150 mg) of Tenax TA and silica gel were dry-purged with N_2 gas for 35 min at 40 mL/min. Aroma desorption from the trap was performed at 180 °C for 4 min. The desorbed aroma was introduced into the flask with N_2 gas at 40 mL/min through a fused silica capillary column (0.53 mm i.d.) transfer line heated at 100 °C. The tip of the transfer

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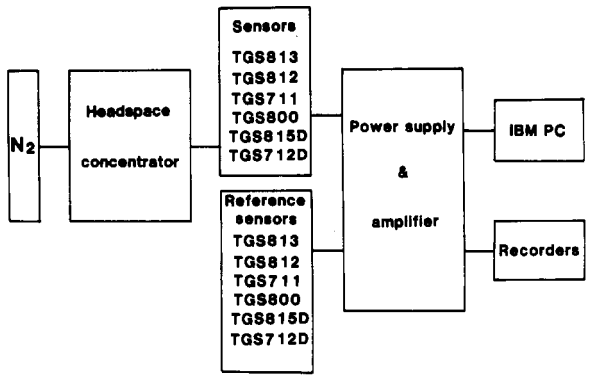

Figure 1. Diagram of aroma-sensing system with gas sensor array.

Table I. Six Semiconductor Gas Sensors Used for a Gas-Sensing Array

no.	sensor	circuit voltage	heater voltage	objective gases
1	TGS812	1.7	4.4	alcohols, organic solvents
2	TGS813	1.8	4.4	general combustive gases
3	TGS711	2.2	5.4	carbon monoxide
4	TGS800	1.5	4.4	general gases
5	TGS815D	1.8	4.4	general combustive gases
6	TGS712D	1.7	4.4	carbon monoxide

line was only inserted into the flask through a septum during the desorption step and then extracted. The purging was started immediately after 5 g of a coffee sample was put into the sample flask. Repeated measurements were performed by renewing samples. In essential oils and volatile compounds, an arbitrary amount (1–5 μL) was spotted on a strip (0.7 × 3.0 cm) of filter paper by using a microsyringe. The strip of spotted filter paper was inserted into the flask, and the purging was started immediately.

Aroma Extraction. Aroma extraction of 5 g of a coffee sample in 500 mL of water was performed by using a conventional simultaneous distillation–extraction method for 2 h with 15 mL of dichloromethane containing 280 ppm of vanillin as the internal standard for GC analysis. The extract was concentrated to ca. 50 μL with a Kuderna-Danish concentrator and a following purge with a N_2 gas stream.

Gas Chromatographic Analysis. One microliter of the concentrate was injected into a Shimadzu GC-9A gas chromatograph equipped with FID detectors. A fused silica capillary column (30 m × 0.25 mm i.d.) coated with Supelcowax 10 (0.25 μm, Supelco Inc., Bellefonte, PA) was used. A split-type injection was used, and the split ratio was 60:1. The linear velocity of helium carrier gas was 24 cm/s. The column temperature was programmed from 50 to 220 °C at 3 °C/min. The temperatures of the detector and injection port were kept at 250 °C.

Pattern Recognition. Response heights from the blank level at 8, 16, and 24 min after sample introduction were measured and averaged. Responses of six sensors were logarithmically transformed to linearize them for the concentration of aroma. Then each transformed response was normalized as the ratio to the total of six sensor responses to eliminate effects of absolute amounts of volatiles on pattern recognition. Thus, each sample is expressed as a point in a six-dimensional vector space. Multivariate analysis, cluster analysis, and linear discriminant analysis (LDA) were performed by SPSS PC+ V3.0 programs (Norusis, 1988) on an IBM PS/55 5551T system.

RESULTS

Sensor Responses. Typical recorder responses from six TGS sensors to *C. arabica* are shown in Figure 2. Attenuation of recorders was arbitrarily adjusted to make every signal within the recording limits. After sample introduction into the flask, sensors soon started responding. The response patterns of some sensors declined after showing initial humps as typically shown by TGS813 in

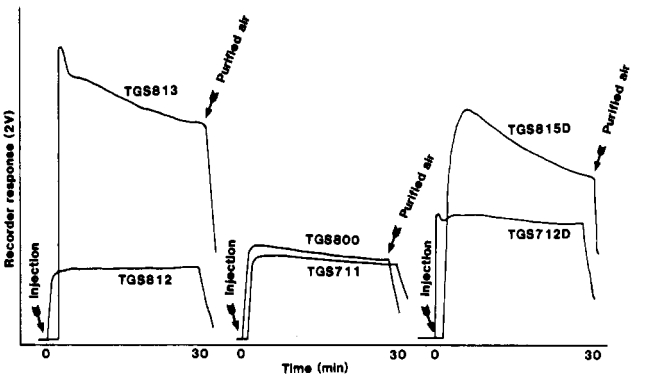

Figure 2. Responses of six TGS gas sensors for the aroma of *C. arabica*.

Table II. Correlation Coefficients of Sensor Responses for Coffee Samples

	sensor					
sensor	TGS-812	TGS-813	TGS-711	TGS-800	TGS-815D	TGS-712D
TGS812	1.000	0.966**	0.969**	0.965**	0.985**	0.990**
TGS813		1.000	0.904**	0.912**	0.983**	0.962**
TGS711			1.000	0.975**	0.954**	0.979**
TGS800				1.000	0.946**	0.983**
TGS815D					1.000	0.987**
TGS712D						1.000

**$P < 0.001$ ($n = 60$).

Figure 2. The humps were not included into the variables for the subsequent pattern recognition because the shapes of humps changed in repeated measurements even for the same sample. This inconsistency seems to derive from the injection conditions of sample volatiles as well as sensor properties. The direction of the tip of the transfer line was not strictly controlled when desorbed volatiles were introduced into the flask; the humps did not seem to reflect quality of sample aroma. Some other sensors showed stable plateau patterns as typically shown by TGS812 in Figure 2. All subsequent calculations were performed on the basis of the mean heights of responses measured at 8, 16, and 24 min after sample introduction.

The correlation coefficients for six sensors were calculated on the basis of 60 responses from coffee samples (Table II). All correlation coefficients were highly significant, and the highest correlation, 0.990, was found between TGS812 and TGS712D. Even the lowest combination was high, i.e., 0.904, for responses from TGS813 and TGS711. Thus, strong duplication of information in the responses from nonselective sensors was suggested.

Widely known GC profiles and total peak areas of flavors in a specific food indicate quality and quantity of their aromas, respectively. Some attempts utilizing pattern recognition analysis for discriminating coffee varieties have been successful (Liardon et al., 1984). Great differences in aroma quantities of ground coffees and instant coffees are clearly shown by their GC data (Figure 3). However, differences in their GC patterns were not so apparent as their quantity differences.

Means ($\bar{x}$), standard deviations (s), and coefficients of variations (CV = $100s/\bar{x}$) were calculated for response heights of 15 repeated measurements in every coffee sample as shown in Table III. All responses show a quantitatively similar tendency to the total volatiles obtained from GC analysis shown in Figure 3. CV decreased considerably by normalizing responses. Each response was normalized as the ratio to the total of six sensors, and the resulting patterns for four coffee samples are shown in Figure 4. Four response patterns are rather similar to one another,

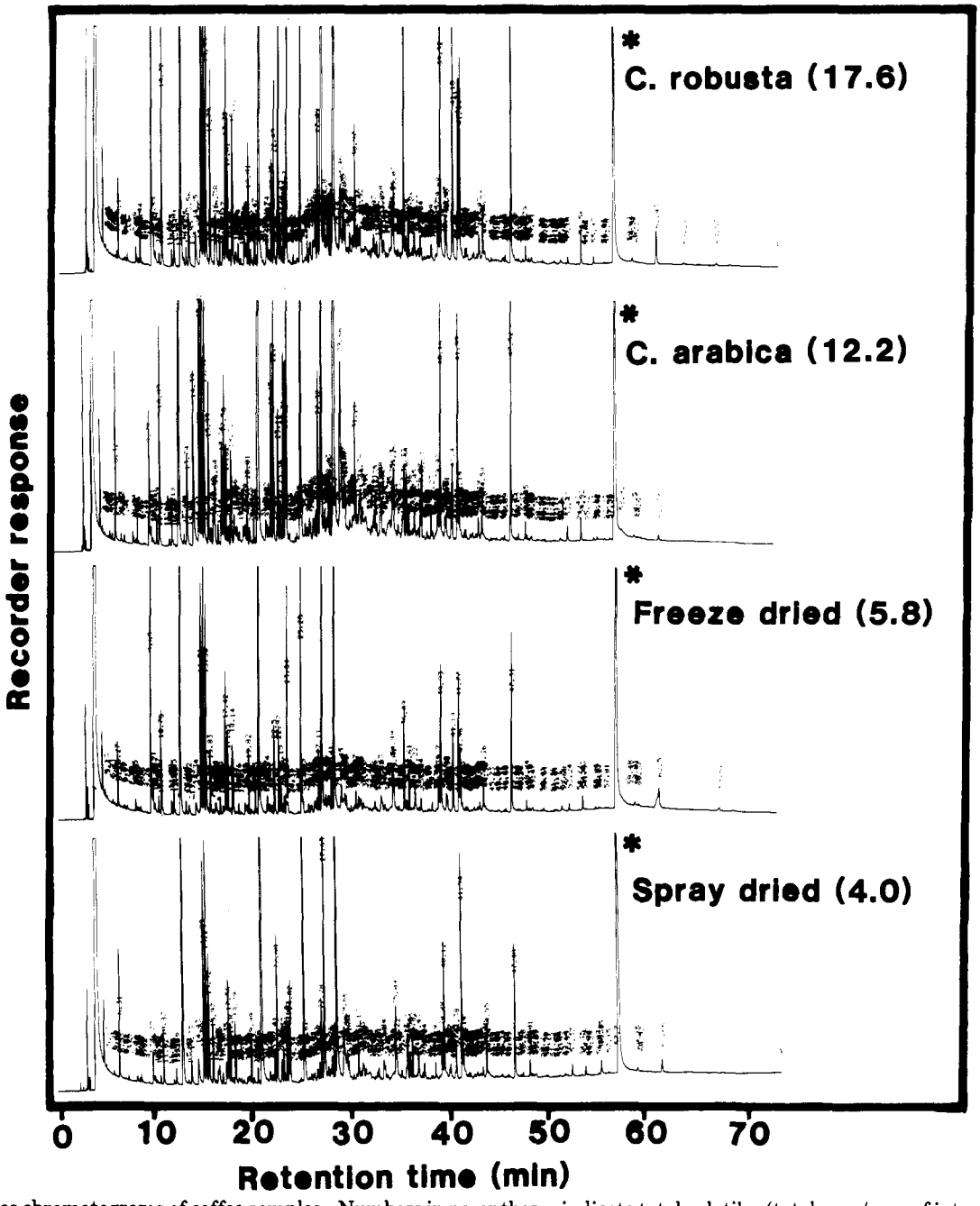

Figure 3. Gas chromatograms of coffee samples. Numbers in parentheses indicate total volatiles (total area/area of internal standard peak indicated by asterisk).

but as long as the repeatability is reliable enough, pattern recognition analysis can be applied to such a data set.

Pattern Recognition of Coffee Samples. Cluster analysis was applied to the normalized data matrix of sensor responses. The resulting dendrogram shown in Figure 5 suggested clear separation of four groups. First, responses from four coffee samples fused into their exclusive clusters. Then each of the two ground coffee clusters and two instant coffee clusters fused into their larger clusters, respectively.

Stepwise LDA was applied to the data matrix of coffee samples by using Wilks' λ as a criterion for the variable selection. The summary of LDA shown in Table IV suggests that TGS812 is the most effective sensor to discriminate coffee aromas. By use of TGS812 alone, 78% correct sample classification was attained. When information from TGS813 was added at step 2, correct classification was improved to 96.7%. Perfectly correct classification was attained by adding TGS800 and TGS815D into the set of discriminant variables at steps 3 and 4, respectively. Thus, only three or four sensors are sufficient to discriminate two ground coffees and two instant coffees. Canonical scores were calculated on the basis of responses from TGS812, TGS813, TGS800, and TGS815D and are shown in Figure 6. Clear separation of four groups is observed in the resulting scatter plot. However, the existence of two groups corresponding to the ground coffees and instant coffees is also indicated.

Essential Oils and Compounds. The diversity in response patterns for both essential oils and compounds was more apparent due to their inherent differences in components and chemical structure. Responses of 14 different essential oils were analyzed by cluster analysis (Figure 7). Two large clusters, i.e., citrus and other fruits, are observed. Two essential oils of peach and of apple do not make their exclusive clusters. As is well-known, there is not any statistical criterion to assess the appropriateness in the clustering obtained from conventional cluster

Table III. Basic Statistics of Sensor Responses to Coffee Samples

coffee	sensor TGS-812	TGS-813	TGS-711	TGS-800	TGS-815D	TGS-712D
C. arabica (n = 15)						
mean	157.8	129.4	736.0	363.1	224.5	581.4
SD	25.4	20.3	123.0	65.2	32.0	91.4
CV, %	16.1	15.7	16.8	17.9	14.3	15.7
C. robusta (n = 15)						
mean	179.1	183.8	705.2	399.1	273.2	667.2
SD	19.4	30.0	65.1	58.4	33.6	70.0
CV, %	10.8	16.3	9.2	14.6	12.3	10.5
freeze-dried (n = 15)						
mean	65.3	47.1	253.9	173.8	78.0	224.2
SD	6.4	4.1	27.3	28.8	6.9	22.1
CV, %	9.7	8.7	10.8	10.8	8.9	9.9
spray-dried (n = 15)						
mean	45.5	37.9	168.9	111.4	56.3	161.3
SD	7.0	5.4	32.9	23.8	9.3	26.7
CV, %	15.3	14.2	19.5	21.4	16.6	16.5

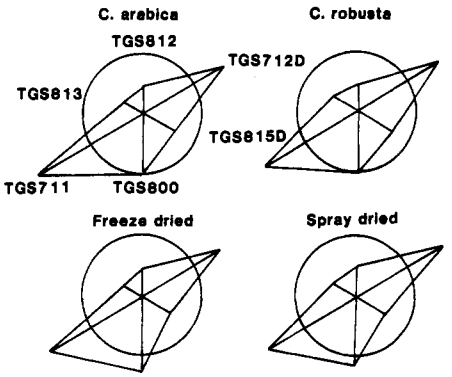

Figure 4. Radar charts of six gas sensors for coffee aromas.

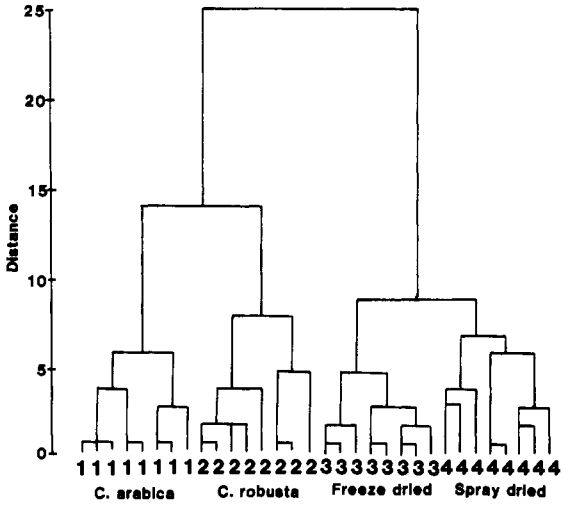

Figure 5. Clustering of coffee samples based on responses from six sensors.

analysis, but at least classification of citrus and other fruits seems to be acceptable on the basis of their aroma characteristics.

Next, a similar approach was applied for different volatile chemicals. Differences in sensory properties of single compounds are usually very conspicuous according to their chemical structure. Successful discrimination of volatile compounds based on multisensor systems has already been reported (Persaud and Dodd, 1982; Abe et al., 1989). In this study cluster analysis was applied to the data matrix obtained from the arbitrarily selected 24

Table IV. Summary of Stepwise Linear Discriminant Analysis Applied for Sensor Responses to Coffee Samples

step no.	entered	F	Wilks' λ (significance)	correct % (wrong/total)
1	TGS812	226.0	0.076 (0.000)	78.3 (13/60)
2	TGS813	52.7	0.020 (0.000)	96.7 (2/60)
3	TGS800	8.8	0.013 (0.000)	100 (0/60)
4	TGS815D	2.9	0.011 (0.000)	100 (0/60)
5	TGS712D	1.3	0.011 (0.000)	98.3 (1/60)

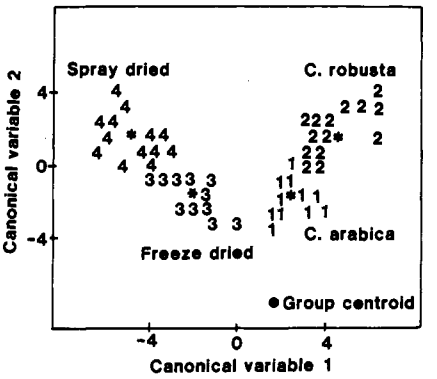

Figure 6. Canonical plot of coffee samples based on responses of TGS812, TGS813, TGS800, and TGS815D sensors.

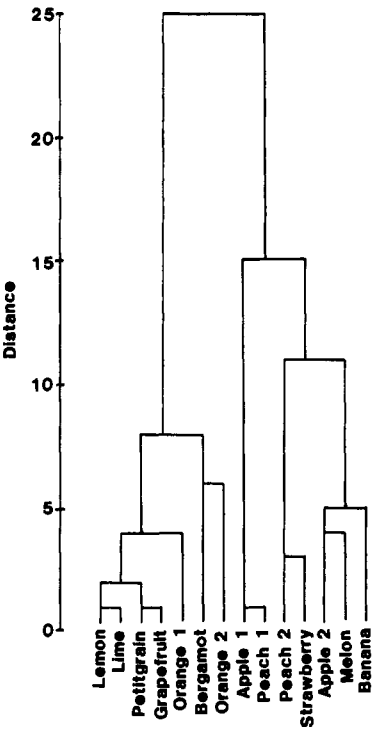

Figure 7. Clustering of essential oils based on responses from six sensors.

compounds as shown in Figure 8. Some of the structurally similar compounds, such as pyrazines, terpenes, terpene alcohols, and aliphatic alcohols, made their clusters. However, whole clustering cannot necessarily be explained in terms of chemical structure or aroma characteristics of samples.

Other combinations of semiconductor gas sensors are now being tested for aroma sensing in our laboratory. In the near future more logical clustering results may be obtained by finding more appropriate combinations of gas sensors.

DISCUSSION

Some research groups have already reported successful results on discriminating particular compounds in gas

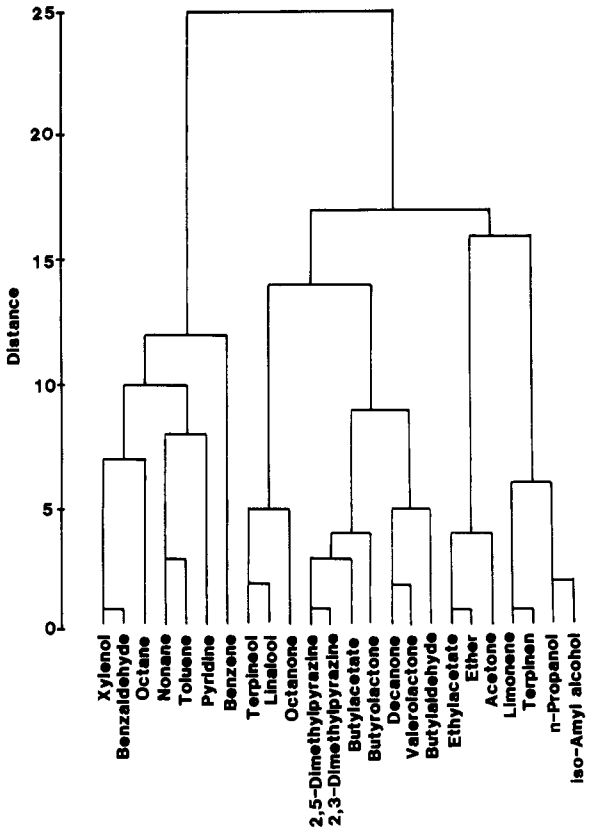

Figure 8. Clustering of compounds based on responses from six sensors.

mixtures. Ema et al. (1989) succeeded in aroma discrimination of liquors using a six quartz-resonator sensor array and neural-network pattern recognition. However, subtraction of sensor signals to the same content of ethanol from the responses to liquors was needed to attain good classification. By incorporating the concentrating step utilizing porous polymers, we can easily avoid effects of ethanol vapor from essential oils and examine whether response patterns from semiconductor gas sensors can really be discriminated statistically. However, of course, we cannot construct an on-line aroma-monitoring system as long as porous polymers are used. So far, it seems very difficult to develop sensors that are selectively insensitive only to ethanol vapor. Ethanol is the most abundant volatile compound in many foods and is also artificially added as a preservative for foods.

Although ordinary gas sensors are nonselective in nature, there are four possible ways to increase selectivity to semiconductor gas sensors: the use of catalysts and promoters, the use of temperature control, the use of specific surface additives, and the use of filters (Morrison, 1987). Incorporating concentration with porous polymers corresponds to the use of filters. Incorporating pattern recognition may be needed for aroma discrimination as long as required selectivity cannot be materialized in gas sensors.

As clearly shown in LDA, aroma discrimination based on sensor responses is much simpler than those using GC data matrix. Of course, from such discrimination, we cannot obtain detailed information concerning aroma compounds, such as which compounds contribute to the discrimination. At this point predicting the future of an aroma-sensing system is not easy, but applying semiconductor gas sensors to constructing an artificial nose seems a potential methodology because of their advantages over other sensors, i.e., long durability, insensitivity to moisture, and economy (*Figaro Gas Sensor for Industrial Use*, 1985).

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Registry No. Xylenol, 1300-71-6; benzaldehyde, 100-52-7; octane, 111-65-9; nonane, 111-84-2; toluene, 108-88-3; pyridine, 110-86-1; benzene, 71-43-2; terpineol, 8000-41-7; linalool, 78-70-6; octanone, 27457-18-7; 2,5-dimethylpyrazine, 123-32-0; 2,3-dimethylpyrazine, 5910-89-4; butylacetate, 123-86-4; butyrolactone, 96-48-0; decanone, 29221-56-5; valerolactone, 108-29-2; butylaldehyde, 123-72-8; ethylacetate, 141-78-6; ether, 60-29-7; acetone, 67-64-1; limonene, 138-8; terpinen, 8013-00-1; *n*-propanol, 71-23-8; iso-amyl alcohol, 123-51-3.