

Measurement of Aroma of Soup Using Potentiometric Gas Sensor

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A potentiometric type electrode based on an oxidation-reduction reaction has been developed for gas measurement by attaching a permeable membrane to a conventional composite electrode, and this electrode has been applied to the measurement of soup aroma. Using an ammonia gas electrode and a hydrogen sulfide gas electrode together with the oxidation-reduction gas electrode system, we have inspected the basic responses of such plural sensor systems with regard to the indicator components of an aroma derived from the process of cooking soup. These sensors showed characteristic responses for pyrazines, furans, sulfides, aldehydes and ketones that are important components in the aroma of soup. When applied to the measurement of aromas of consomme and chicken soups, the system was able to detect characteristic signals from individual sensors with regard to the different kinds of soups. The response of the oxidation-reduction sensor was larger than that of others regarding the diurnal quality change of soup. A deterioration of soup quality with the elapse of time was able to be identified by a method of principal component analysis using the signals of three sensors.

1. Introduction

In the food industry, concerning food quality control, the evaluation of aromas generated from food substances has been carried out by expert smellers called 'panelists'. But as their evaluation of aromas is susceptible to environmental conditions such as temperature and humidity as well as their own physical condition, appropriate devices have been required for a more objective evaluation. To date, several studies of aromatic substances using oxide semiconductor sensors and quartz-resonator sensors have been reported,⁽¹⁻¹³⁾

but the oxide semiconductor sensors have to be operated in the high temperature range of 300°C to 400°C and the measuring circuit of the quartz-resonator sensors is complicated. A potentiometric gas electrode is operated at room temperature and the measuring circuit is simple. Therefore, in this study we examined the practical possibilities of a sensor system based on a potentiometric gas electrode, for use in sensing soup aroma.

Generally, compounds containing oxygen, nitrogen and sulfur seem to be particularly important aroma substances derived from common cooking processes.^(1,4) Also it has been reported^(1,2) that pyrazines, furans, sulfides, aldehydes and ketones are important components of soup aroma. Hence, since methyl disulfides and pyrazines are also contained as sulfide and nitride in soup aroma, respectively, a hydrogen sulfide gas electrode and an ammonia gas electrode seem to be appropriate sensors for them. On the other hand, for foods containing unsaturated fatty acids and aldehydes, which are substances suitable for an oxidation-reduction system, an oxidation-reduction gas electrode was developed and added as one of the sensors for the measurement of aroma. The sensor used in this study has been developed for gas measurement by attaching a permeable membrane to a conventional conjugated electrode on the basis of the method for redox titration. The oxidation-reduction gas sensor seems to be effective in detecting the oxidation-reduction gases which are related to the spoilage of food.

The usage of gas electrodes does not seem to have been discussed for aroma sensing. The present procedure is convenient as it enables measurement at room temperature. The main objective of the current study is to discuss the utilities of the above sensory system, for example, in sorting types of soups, identifying deterioration of soup quality with elapse of time, etc., through trials of probing the aroma components of soup using the above system.

2. Experimental

2.1 Gas samples

The currently used samples^(1,2) consist of the components given in Table 1. These components are derived from conventional culinary heating processes, and have been chosen as relevant indicator components of an aroma sensor for soup in food quality control.

2.2 Structure of sensor

Three types of potentiometric gas sensors were used, i.e., oxidation-reduction type/OR-sensor, ammonia type/ NH_3 -sensor and hydrogen sulfide type/ H_2S -sensor. The OR-sensor is newly developed for our purpose and the NH_3 and H_2S sensors are commercially available (DKK Co., Tokyo, Japan) apparatuses.

2.2a OR sensor

The OR-sensor used is developed on the basis of the redox reaction, and is applicable to gas sensing. The structure is shown in Fig.1. It is a composite type sensor, consisting of a permeable membrane, a reference electrode of silver-silver chloride, a detection electrode of gold and an inner solution dissolving a couple of oxidant-reductants. This structure allowed the measurement of variations in potential due to the reaction between the inner

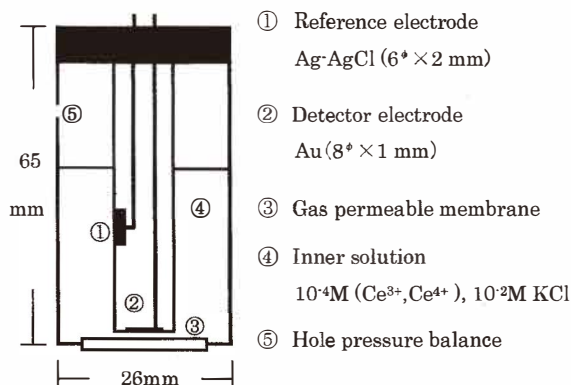


Fig. 1. Structure of an oxidation reduction gas sensor.

Table 1
Molecules used for aroma components of soup.

Molecule	Abbreviation
2-Methylpyrazine (C ₄ N ₂ H ₃ CH ₃)	MP
2-n-Pentylfuran (H ₄ C ₃ O(CH ₂) ₄ CH ₃)	PF
Dimethyl disulfide (CH ₃ S) ₂	DMDS
Acetone (CH ₃ COCH ₃)	AT
Capronaldehyde (CH ₃ (CH ₂) ₄ CHO)	CA

liquid and the gaseous sample permeated into the electrode through the membrane. The gas permeable membrane of 0.22 μm pore diameter is made of Teflon; it is a body not permeable by liquid and thus preserves the inner solution. The clearance between the surface of the detector electrode and the gas permeable membrane is 0.1 mm.

In the present sensor, the kinds of metal ions and their degrees of concentration used in the inner solution play an important part. Hence the inner solution was decided on as follows. Cerium (Ce⁴⁺, Ce³⁺) and iron (Fe³⁺, Fe²⁺) were examined as metal ions for the sample shown in Table 1. Consequently, due to the difference in responsiveness between (Ce⁴⁺, Ce³⁺) and (Fe³⁺, Fe²⁺) and the probing of their concentrations, a mixture solution of equimolecular amounts of Ce⁴⁺ and Ce³⁺ is selected, and their concentrations were prepared such that they were 10⁻⁴ M in a 0.25 M H₂SO₄ solution.

2.2b Ammonia and hydrogen sulfide sensors

These sensors are NH₃- and H₂S-electrodes, commercially available sensors, and their fundamental structures are the same as that of the OR-sensor. The inner solution of each electrode is prepared in the following manner. For the NH₃-sensor a 10⁻² M NH₄Cl solution is used, and for the H₂S-sensor a 10⁻² M KCl/tris-buffer solution (pH 10) is used. Each solution contains 70% ethyl glycol in order to prevent their vaporization.

2.3 Experimental apparatus and measurement

2.3a Experimental apparatus

The experimental apparatus introduced in this study consists mainly of gas sensors and their connections. The total experimental setup is shown as a schematic in Fig. 2, where a sensor cell made of Teflon is fixed inside a thermostat together with a receptacle for the sample of gas to be tested. The air and sample are passed through a tube having a diameter of 2 mm and introduced to the sensor cell. Electric potential signals generated at the sensors are digitized and transmitted to the computer. Experimental temperature was kept constant at 30°C. Values measured from each sensor are the potential differences within a definite time subsequent to the setting of the sample, and the process is as follows. Dry air was at first passed into the sensor cell and once the potential value reached a constant at every each sensor, the gas sample was passed in. Both the dry air and the gas sample were made to flow through the sensor cell at a constant rate of 40 ml/min.

2.3b Preparation of samples

Data of aroma component concentrations were obtained in the process as follows. An adequate amount of sample solution was dropped into a polyethylene bag and sealed with 5000 ml of dry air; the bag was left for one day at 35°C, then cooled to 30°C before being ready to use in the experiment. Among the samples, vaporized acetone (AT) is used by placing 0.5 ml (ca. 4 g) of it in 5000 ml of dry air, because it has a low boiling point and high diffusibility. Another sample of dimethyldisulfide (DMDS) is obtained in the form of 1/50

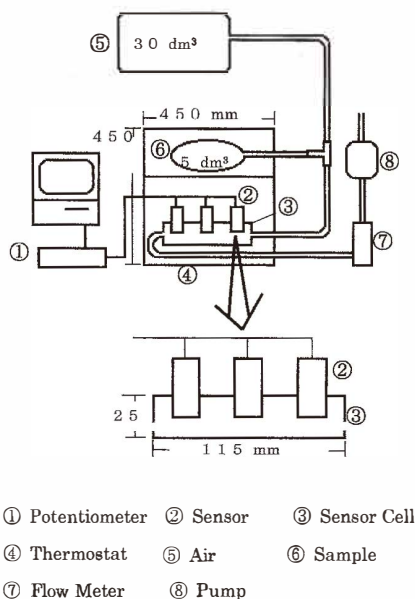


Fig. 2. Experimental apparatus.

dilution of the original concentration in 5000 ml of dry air. These concentrations, quantified by means of gas chromatography, are shown in Table 2, where the units show weights contained in a volume of 1 ml.

3. Results and Discussion

A series of measurements for the aroma components shown in Table 2 was attempted in order to examine the expected utility of the proposed sensor system with three alterable gas sensor electrodes. By measuring the potential differences among the reactions, the data obtained can be considered more significant when they indicate a stronger characteristic of each component. The present device comprised of electrodes, due to its potential to provide both positive and negative values of potential change, can show markedly different values of potential change according to the type of component, and hence seems to be effective as an aroma sensor.

3.1 Time response of OR-sensor

The measurement is carried out by the following process. First, the dry air was passed into the sensor cell at a rate of 40 ml/min. After the potential reached a constant, a vapor carrying aroma components was passed in at the same rate, and then the respective electric potentials were measured. An example is illustrated in Fig. 3, wherein the potential difference in response of the OR-sensor to samples DMDS and CA is shown relative to time for response; ordinates and abscissas show potential differences and response time, respectively. The time consumed for changes in potential as it stabilizes to a constant is shorter for DMDS than for CA samples. Due to such differences in response mode and depending on the kind of substance tested, all adopted experimental values are taken from the electric potential measured after a fixed time of ten min. subsequent to the setting of the sample. Likewise, rates of recovery of potential are longer for larger potential differences and shorter for smaller potential differences.

3.2 Measurement of aroma component substances

Potential differences measured at each sensor for aroma component samples are shown in Table 3. The experiments are repeated three times under the same conditions, for averages of the resulting data to be used. Each substance discussed above has been proved to be capable of such measurement by sensors. Notably, the OR-sensor shows a stronger

Table 2
Concentration of samples used for aroma components.

Molecule	Concentration/ $\mu\text{g/ml}$ (air)
MP	33.0
PF	7.5
DMDS	1.1
AT	80.0
CA	16.0

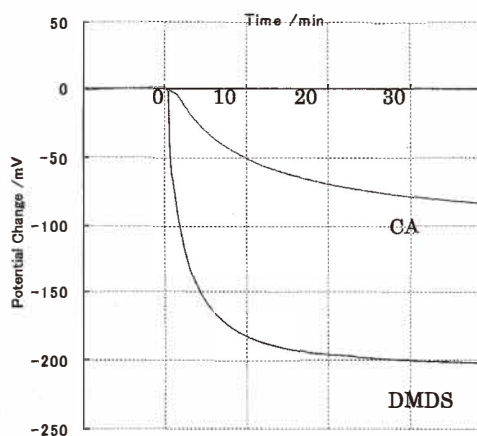


Fig. 3. Response curves for DMDS and CA by OR-sensor.

Table 3

Changes in potential of aroma component substances measured by each sensor. /mV.

Sensor	MP	PF	DMDS	AT	CA
Oxidation-reduction (OR)	-15	-48	-185	-20	-51
Hydrogen sulfide (H ₂ S)	-30	-11	-64	0	-9
Ammonia (NH ₃)	-15	14	41	15	31

response than the other sensors. Clearly, with differences depending on the kind as well as concentration of samples, different types of responses (changes in potential) could be measured. But the present fact shows that gas electrodes have been proven to be able to serve in detecting substances such as the components of soup aroma and this implies their practical potentiality as sensors for the quality control of food. In particular, as shown in Table 3, the response of 2-methylpyrazine (MP) to the NH₃ sensor is negative, in contrast to the other substances. In view of its merits, including its capacity for response with either sign, the currently introduced device offers greater efficiency in discriminating among aromas.

Next, relations between the difference in concentration and the changes in potential are investigated. DMDS and CA are chosen as samples, and diluted by the dry air to have a concentration that is 1/2 of the original shown in Table 2. Thus, from the data obtained and the changes in potential listed in Table 3, the plotted relations in Fig. 4 are provided. Here, the plotted points refer to potential changes relative to the concentration values. Abscissas C(1) and C(1/2) respectively refer to the concentrations in Table 2 and their 1/2 values. The graphic symbols represent the sensors, and the measured samples are shown in parentheses. A comparison of the two cases reveals an overall correspondence of the concentrations of the substances to the potential changes. This is suggestive of the utility of the present device for an aroma sensor. The OR-sensor in particular seems to be superior to other sensors in view of the rate of slopes.

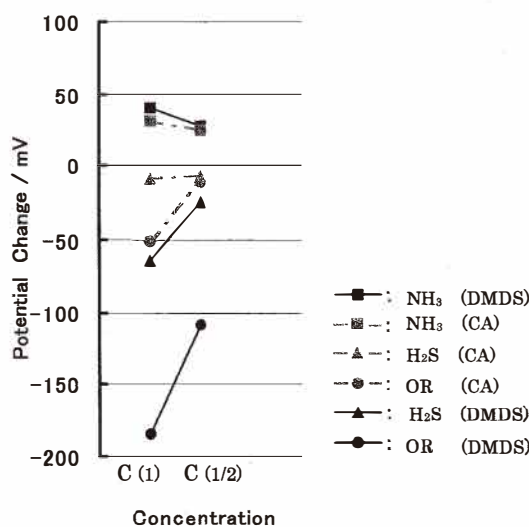


Fig. 4. Relation between changes in potential and concentrations of aroma components.

3.3 Discrimination among soups depending on aroma

The discrimination among kinds of soups in terms of their aromas by three kinds of gas sensors was attempted. With respect to the corresponding samples, commercially available consomme/CS and chicken/TS types of soup have been used. Testing samples are the gas that was emitted from a suspension of 10 g soup cubes in 150 ml of water, after their being left for 6 h at 30°C in a pack of 5 l of dry air. Regarding the test procedure, samples CS and TS were kept at 30°C in the thermostat for one, five and nine days after their being unsealed, respectively, and thus are designated 1D-, 5D- and 9D-samples. They were measured to determine the changes in potential, and the result is shown in Fig. 5. Considering that these soup samples contain significant amounts of water, such water contents are also examined with the result that only in the NH₃ sensor a slight response occurs.

First, the potential differences of the 1D-samples for both CS and TS are checked. The response of the OR-sensor is stronger for TS than CS, but for the H₂S-sensor the response is very small for both samples, and at the NH₃-sensor there is an appreciable response to CS and a negligible response to TS. Hence, the difference in experimental values in terms of potential for the two 1D samples suggests the kind of soup. The gas electrode type method introduced here seems to be effective in discerning soup quality.

Next, the changes of potential with the elapse of time for samples 1D- through 9D- are checked. Concerning the CS samples, potential changes increase sharply for the OR-sensor for 5D-samples and remain practically unaltered thereafter. For the NH₃-sensor only small changes in potential are seen in the 1D- through 9D-samples. For the H₂S-sensor, potential

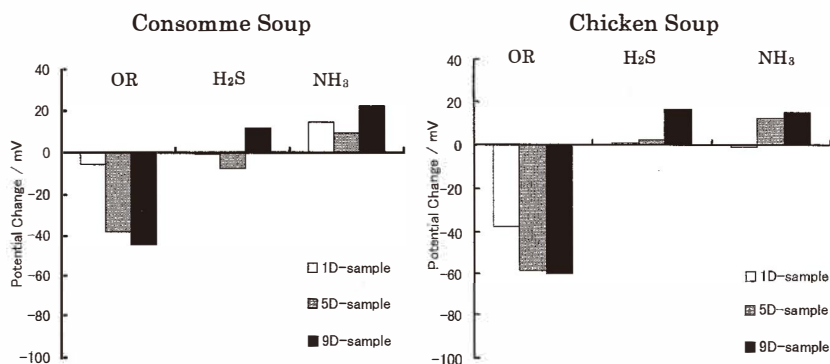


Fig. 5. Changes in potential measured on each sensor with elapse of time for two types of soups.

changes increase with the elapse of time. For the TS samples, for the OR-sensor the potential changes until reaching the 5D samples and remains practically unchanged thereafter. The potential changes increase for the NH₃-sensor for 5D-samples and does not alter thereafter. Also for the H₂S sensor, daily increases are noted, and the tendency is roughly the same as that for the CS samples.

Three subjects (men in their twenties) evaluated the quality change of soup aromas by smelling the 1D- through 9D-samples, and judged them on the criterion of no spoilage or spoilage. The 1D-samples of both CS and TS were judged as having no spoilage by all subjects. Concerning 5D-samples, a subject judged both samples as having no spoilage. Two subjects judged that both samples had spoiled a little and the spoilage of the TS sample was stronger than that of the CS sample. All subjects judged both 9D-samples as having spoilage. Because the responses of sensors showed the tendency to increase regarding the diurnal quality change of soup, it was found that the response of sensors roughly corresponded to the sensory evaluation.

From the above observations, it is known that for different kinds of samples, as well as the preservation conditions, the potential changes are different. Therefore, it can be suggested that the usage of the potentiometric gas sensor is reasonably applicable for food quality control.

On the other hand, the obtained data carry multidimensional information, because they were measured by three devices. Therefore, we have performed a principal component analysis, in order to interpret the data given by measurement of the soups. The results of this analysis are summarized in Fig. 6. The figure is plotted with the first principal component as abscissa and the second principal component as ordinate, respectively. The symbols of circles and squares in the figure represent the consomme and chicken soups, respectively. From the figure, CS and TS samples can be separated into the groups, which suggests that the types of soups may be discerned by plotting and their diurnal quality changes can be similarly discerned.

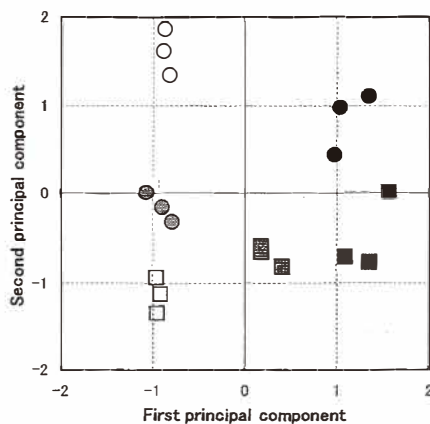


Fig. 6. Discrimination between soups using principal component analysis: symbols \circ , \bullet , \bullet represent 1D-, 5D-, 9D-samples of consommé soup, and \square , \blacksquare , \blacksquare represent 1D-, 5D-, 9D-samples of chicken soup, respectively.

4. Conclusions

We have attempted to develop a gas sensor of potentiometric type by applying an oxidation-reduction system. Using ammonia- and hydrogen sulfide gas electrodes together with an oxidation-reduction gas electrode system, we have inspected the basic responses of such a composite sensor system with regard to the indicator components of soup aromas derived from a conventional culinary heating process. These sensors showed characteristic responses for the soup aroma components. In particular, the oxidation-reduction sensor showed stronger responses than the other sensors and was effective in discerning among aroma components.

When applied to the measurement of soup aroma, the system was able to detect characteristic signals from individual sensors with regard to the kinds of soups and their diurnal quality changes. The response of the oxidation-reduction sensor was larger than that of others regarding the diurnal quality change of soup and its effectiveness has been confirmed in discerning the diurnal quality change. Thus, it can be postulated that the system of potentiometric gas sensors may enable pertinent quality control in a convenient and reliable manner.

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