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Development of a Monitoring System for Water Quality Using a Taste Sensor

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This paper describes the possibility of using a taste sensor which contains lipid membranes to detect pollutants and unusual tastes in water. First, it was shown that the taste sensor can distinguish between normal river water and river water contaminated by 1 ppm free cyanide and 1 ppm of a cyano complex. Second, the taste sensor was shown to be able to distinguish between normal tap water and tap water with an unusual taste due to 50 ppm poly aluminum chloride. The results using the taste sensor correlated well with sensory tests. The taste sensor is expected to be a more powerful method than sensory tests for real-time systems for monitoring water quality.

1. Introduction

When toxic substances in drains flow into a river, they cause environmental destruction. It is very important to detect toxic substances at the early stages in river water and factory drains. In monitoring water quality in river and factory drains, it is necessary to measure pollutants in real time before these substances spread widely. However, a real-time measurement is sometimes very difficult because the detection of some toxic substances in river water and also factory drains requires a time-consuming process due to the large number of substances that need to be analyzed. Some chemical analysis systems, such as absorption spectrophotometers, gas chromatograph-mass spectrometers, high-performance liquid-chromatographic systems and atomic absorption spectrometers,(1) are very high performance and can selectively detect these substances at the ppm or ppb level. However, these measurements take time, require technical skill and are costly.

Although a sensing system employing living fish has been devised,(2,3) there are some problems in reliability, maintenance and evaluation of water quality because the fish are living things. There are many papers and reports about multichannel taste sensors by Toko, Hayashi, Ikezaki(4–7) and others. The taste-sensor system using lipid/polymer membranes illustrates the concept of global selectivity(8) that implies the ability to classify enormous numbers of chemical substances into several groups, as typically found in the perception of taste in biological systems. This is a very different concept from that of conventional chemical sensors, which selectively detect specific chemical substances such as glucose or amino acids. A schematic of a taste sensor is shown in Fig. 1. The receptor membranes of the taste sensor are fabricated using a polymer to fix the lipids which play an important role in taste detection; the electric potential of the lipid membranes changes when the tastes are adsorbed. Instead of taste cells with different characteristics, lipids with different response characteristics were selected as membrane materials to obtain taste sensors with different properties. Taste discrimination was carried out by recognizing the signals obtained from arrays of taste sensors in the form of patterns.

The concept of a monitoring system using a taste sensor is shown in the graphical images in Figs. 2 and 3. This monitoring system distinguishes an unusual state from a usual state by processing the output signals of taste-sensors (multichannel lipid membrane sensors) and discriminating roughly metallic ions, pollutants, high acid, high alkali, and so on. It is possible to directly measure the influence of pollutants on living organisms using a sensor that has similar response mechanisms as biological systems. Concerning the feasibility of a taste sensor for water quality, we previously reported the sensitivity to metallic ions, cyanide and so on.(9) Furthermore, we improved the sensitivity of lipid membrane sensors for free cyanide and cyano complexes.(10) In this paper, we describe the possibility of using the taste-sensor system for the detection of contamination in river water and tap water.

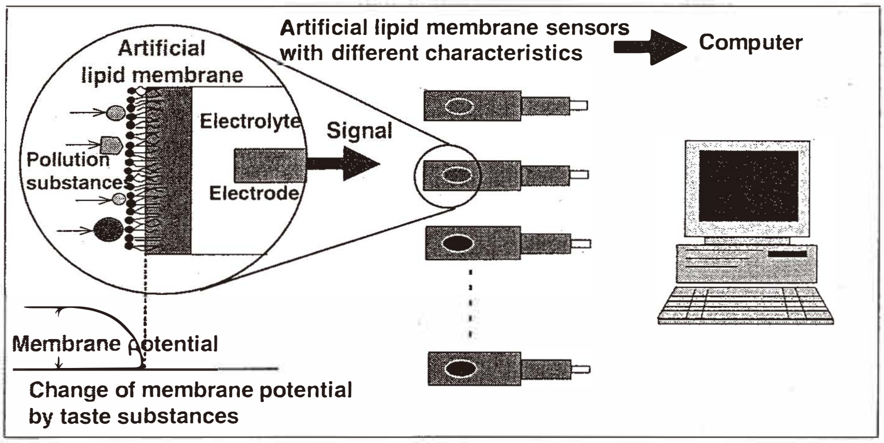

Fig. 1. Principles of a taste-sensing system, SA402.

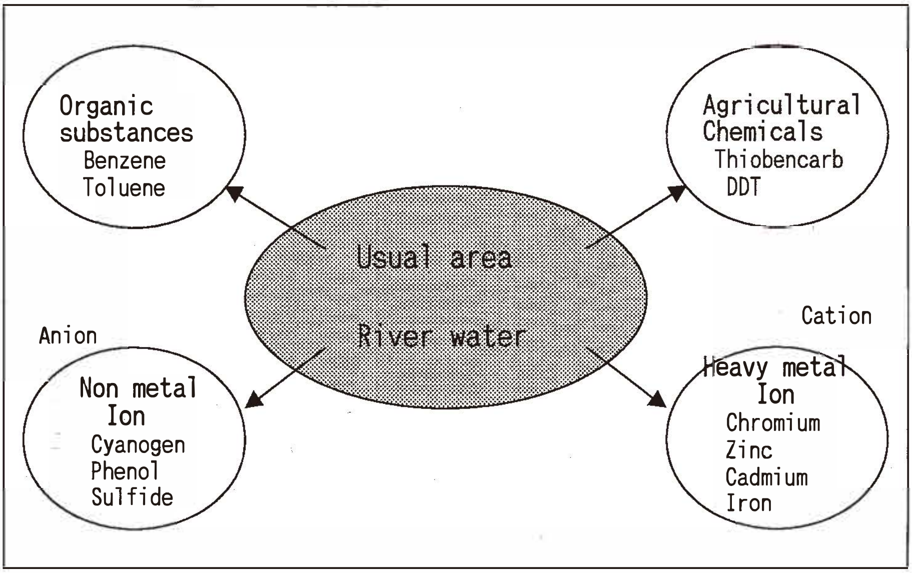

Fig. 2. Schematic of a water monitoring system to detect toxic substances.

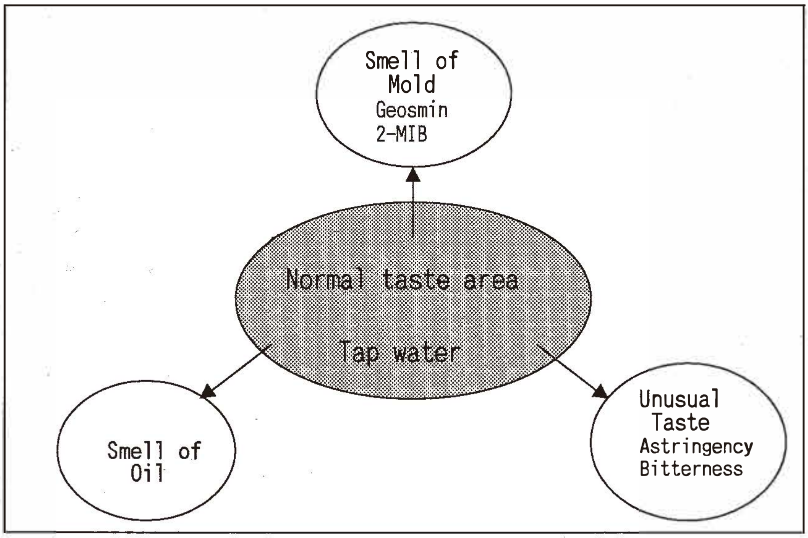

Fig. 3. Schematic of a tap-water monitoring system to detect unusual taste.

Cyanide and poly aluminum chloride (PAC) were chosen as examples of contaminating substances. The former is for the contamination of river water and the latter for tap water. Cyanide sometimes causes very severe problems in rivers at the outlet of factory drains and is one of the most dangerous pollutants. PAC is used as a coagulant in water treatment facilities and makes suspended substances precipitate easily. Sometimes it causes an unusual taste in tap water due to over-use.

We examined the detection of these contaminants using a taste sensor. We also analyzed the possibility of discriminating between usual and unusual states of water quality. We report the experimental results for cyanide in river water and PAC in tap water.

2. Materials and Methods

2.1 *Measuring system*

A taste-sensing system SA402 (Anritsu Corp.) was used. This system consists of a section of multichannel sensors of lipid/polymer membranes, a reference electrode, an autosampler and a personal computer that analyzes the measured data. In this experiment, eight kinds of lipid/polymer membrane sensors were used. The difference in electrical potential between the multichannel sensors and the reference electrode was measured. A taste map was made by applying principal component analysis to the potential differences, and the results were shown visually as a distribution of taste.

2.2 *Multichannel lipid membrane sensor*

A lipid/polymer membrane was fitted on an electrode. There are many kinds of lipid/polymer membranes. The membranes used herein were made of polymer (polyvinyl chloride), plasticizer (dioctyl phenyl phosphonate) and lipid (shown in Table 1). The method of manufacturing these membranes is as follows.(11,12) First, polymer, plasticizer and lipid are mixed and solvated with tetrahydrofuran (THF). These mixtures are then dried on a glass plate set on a hot plate, the temperature of which is held at approximately 30°C. Finally, the film was cut into suitable sizes, and pasted on probes. The thickness of these transparent soft films is approximately 200 μm.

Table 1 is a list of lipids for each sensor and the positive or negative charge of the membrane. Ch1~ch4 sensors are negatively charged membranes and ch5~ch8 sensors are positively charged membranes.

The free cyanide and the cyano complex are anions in water. It can be assumed that the positively charged lipid membrane sensor has a high sensitivity for free cyanide and cyano complex. In the case of free cyanide, we used a positively charged membrane sensor as the ch7 sensor, and its charge was adjusted by mixing positively and negatively charged lipids. For the cyano complex, we used a similar sensor for the ch8 sensor, but its charge was adjusted by the addition of only one other positively charged lipid. These techniques are fairly complex. It is necessary to select specific lipids and adjust their concentration ratio. We previously reported the existence of an optimum concentration ratio for two specific kinds of lipids regarding sensitivity to free cyanide.(13)

On the other hand, PAC precipitates as minute particles, after which some fraction remains in solution as chloride and aluminum ions. To detect PAC, therefore, we used the typical sensors ch2~ch4, as listed in Table 1.

2.3 *Method*

Figure 4 shows a flow chart for measurement. Potassium chloride (10 mmol/l KCl) was used as the standard solution to stabilize the sensors initially because the conductivity of the samples (river water and tap water) and the standard solution was similar. We defined Vr as the sensor output for the standard solution before measuring the sample solution, Vr' as that for the standard solution after measuring the sample solution and Vs as that for the sample solution. We defined two values in this research: the first is (Vs–Vr'), which is the output signal due to the change in membrane potential caused by electrolytes; the second is (Vr'–Vr), which is the output signal symbolized by CPA(14) (Changed membrane Potential caused by Adsorption) caused by adsorbing pollutants.

Table 1
List of lipids for sensors.

Channel	Materials of sensor (lipid)	contains	charge
Ch1	Dioctyl phosphate	0.4 ml	—
Ch2	No added lipids	—	—
Ch3	Oleic acid	0.4 ml	—
Ch4	1-Decanol	0.4 ml	—
Ch5	Trioctyl methyl ammonium chloride	500 mg	+
Ch6	Oleyl amine	0.05 ml	+
Ch7	Dioctyl phosphate	0.19 ml	+
	+ Trioctyl methyl ammonium chloride	+ 200 mg	
Ch8	Dimethyl ditetradecyl ammonium bromide	50 mg	+

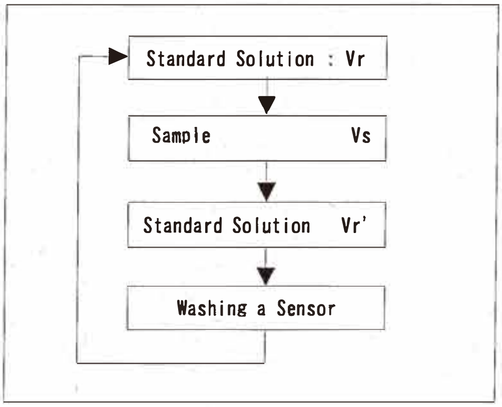

Fig. 4. Procedure of measurement for SA402.

3. Results and Discussion

In this study, we used cyanide as one of the toxic substances in river water and PAC as a substance causing an unusual taste in tap water. We examined the possibility of applying the sensors to a monitoring system of water quality in these two cases.

3.1 *Detection of cyanide as a toxic substance in river water*

We investigated the possibility of detecting cyanide as a toxic substance in river water. First, Fig. 5 shows the response of eight kinds of sensors to cyanide. Among the positively charged membrane sensors, ch7 mainly responds to free cyanide and ch8 responds to cyano complex. Negatively charged membrane sensors in ch1~ch4 are insensitive. Therefore, it can be expected that free cyanide and cyano complexes can be discriminated among various toxic substances in river water using these sensors and data processing.

Six kinds of river water were sampled (three times at a two-week interval in two rivers: the Sagami River and the Sakawa River). We assume that these six samples of river water were usual. Free and complex cyanide were added to the six samples of river water in nine steps which are listed as No. 2~No. 10 in Table 2. Fifty-four (nine steps for six samples of river water) examples of unusual river water were composed.

We examined the possibility of discriminating between the region of usual taste and the region of unusual taste in the taste map using the sensors. Cyanide exists as free cyanide ions (CN^-) or hydrogen cyanide (HCN) or cyano complex ions in solution as a function of pH. Sample solutions were adjusted to pH=12 using KOH solution so that

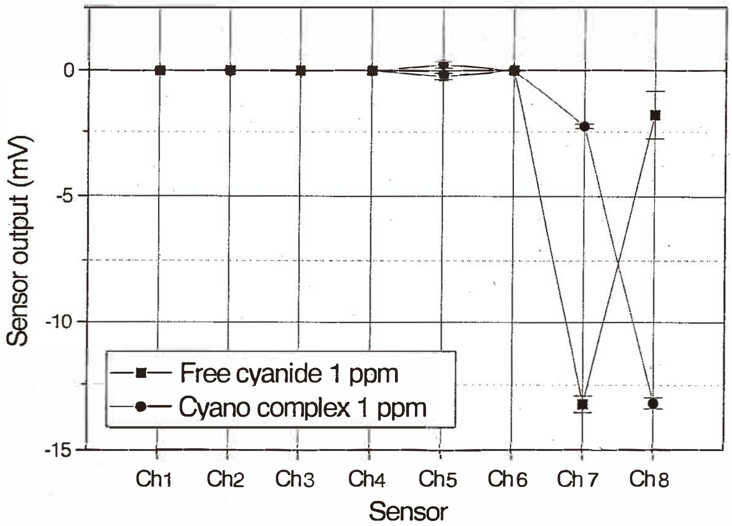

Fig. 5. The responses of eight kinds of sensors to cyanide.

HCN would be converted to CN^- and some metal ions might be precipitated as their hydroxides. The CN^- and cyano complex ions at pH=12 are stable in solution. Potassium cyanide (KCN) and potassium ferrocyanide ($K_4Fe(CN)_6$) were used as reagents.

These samples were measured using the set of sensors listed in Table 1. Figure 6 shows the result of principal component analysis of the sensor outputs. The horizontal axis shows the first principal component (PC1) and the vertical axis shows the second principal component (PC2). Solid circles represent the data points from the 60 samples of river water (6 usual and 54 unusual) samples. The concentrations of free cyanide and cyano complex ions are shown in parentheses. For example, the term (10:1) indicates a

Table 2
Concentration of cyanide added to six samples of river water (collected three times in two rivers).

Step	Free cyanide (ppm)	Complex cyanide (ppm)	State
1	0.0	0.0	usual
2	0.1	0.1	unusual
3	1.0	0.1	unusual
4	10.0	0.1	unusual
5	0.1	1.0	unusual
6	1.0	1.0	unusual
7	10.0	1.0	unusual
8	0.1	10.0	unusual
9	1.0	10.0	unusual
10	10.0	10.0	unusual

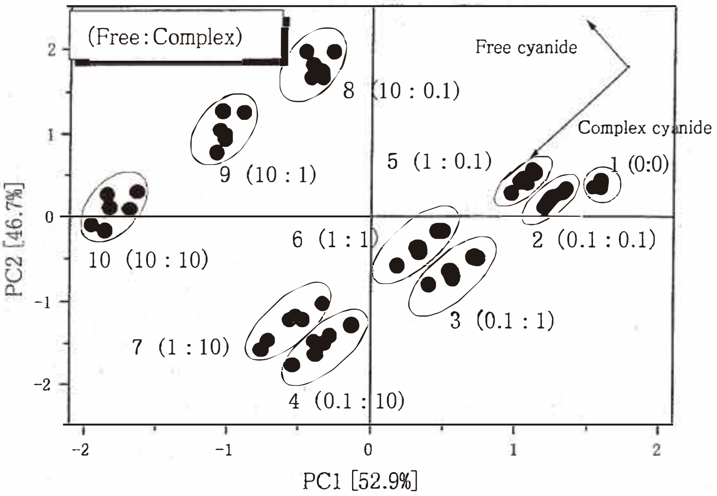

Fig. 6. Results of principal component analysis (cyanide in river water).

sample that contains 10 ppm free cyanide ions and 1 ppm cyano complex ions. This result implies that it is possible to distinguish between free cyanide and cyano complex in river water. The data points move in the direction of the arrows due to the changing cyanide concentration. The data points for free cyanide and cyano complex move in different directions. The variation in the data points for each river for the same concentration of cyanide or cyano complex also is fairly small. Closed circles identify the area where the same cyanide concentrations were added to six samples of river water. It is possible to distinguish each concentration (0.1 ppm, 1 ppm, 10 ppm) of cyanide in spite of the differences in the river water. It is also possible to discriminate the usual river water that has no free cyanide and the river water that contains 1 ppm free cyanide. It is also possible to detect the cyano complex below a concentration of 1.0 ppm in river water.

3.2 *Detection of PAC as a substance imparting an unusual taste to tap water*

We investigated the possibility of detecting an unusual taste caused by PAC in tap water. PAC is used as a coagulant and produces suspended materials in river water. The amount of PAC used is determined according to the turbidity of the water. It is difficult to adjust the quantity of PAC to achieve normal water quality when the turbidity of river water rises suddenly because of rain. A panel in a water supply facility tastes tap-water but sometimes judges incorrectly. The PAC causes an unusual taste in tap water when it is overused. Tap water is supplied widely as drinking water. We attempted to detect this unusual taste using the taste sensing system. Figure 7 shows the characteristics of the sensors for PAC, where sensors ch2~ch4 are sensitive to PAC; specifically, the sensitivity

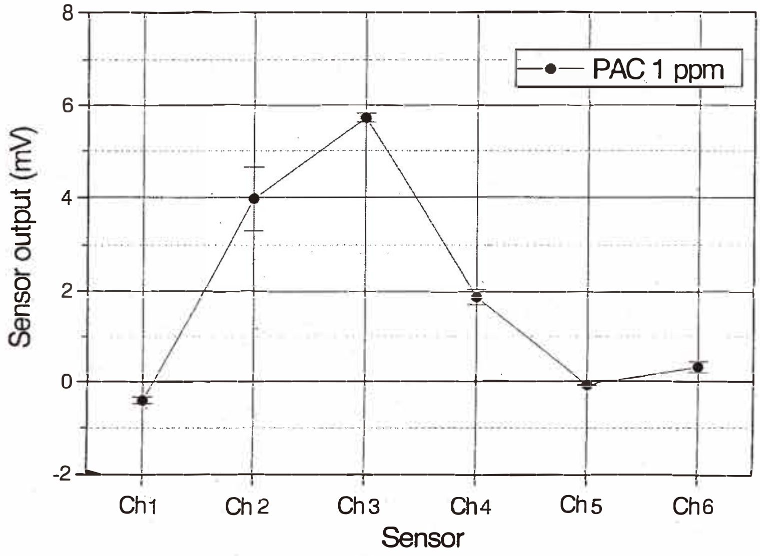

Fig. 7. The responses of six kinds of sensors to PAC.

of ch3 is higher than the others. We expect that it is able to discriminate between the unusual taste caused by excess PAC in tap water and the normal taste.

We measured nine samples of tap water that were collected at the Isehara filtration plant every three hours and three tap water samples that contained added PAC at levels of 10, 50 and 100 ppm. The measurement time was approximately 5 min for each sample. Figure 8 shows the result of principal component analysis, which indicates that it is able to discriminate clearly between a sample with 50 ppm PAC added and a non-PAC sample. The variations in data points among non-PAC samples are clearly small in comparison with those of samples containing PAC (10 ppm~50 ppm).

According to sensory tests, the sample with 10 ppm PAC tasted normal, whereas the sample with 50 ppm PAC had a slightly unusual taste, i.e., an acrid taste. The results of this experiment using the taste sensing system demonstrate that the sensitivity of the taste sensor is similar to that of the sensory test. It is therefore possible that the taste-sensing system may be successfully applied to monitoring unusual tastes in tap water. We believe that the taste-sensing system is very effective and more powerful for the real-time monitoring of tap water than bioassay methods and sensory tests.

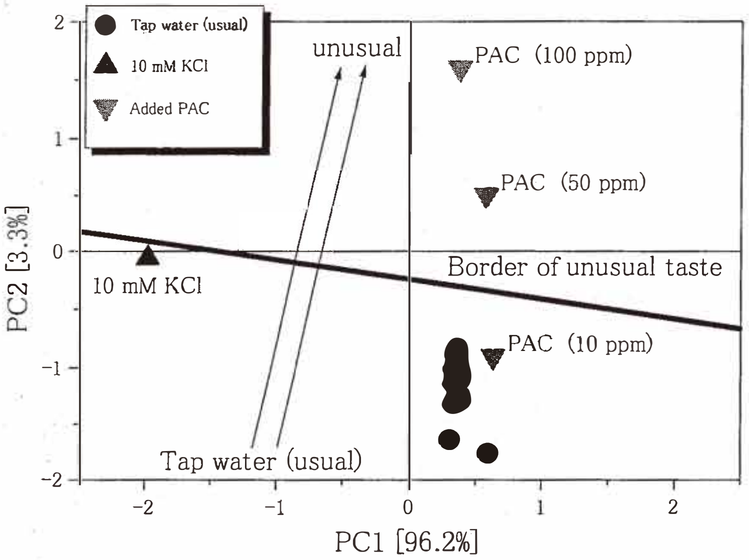

Fig. 8. Results of principal component analysis (PAC added to tap water).

4. Conclusion

We investigated the possibility of detecting pollutants and unusual tastes in water using a taste sensor.

First, we applied the taste sensor to the detection of cyanide in river water. The results indicate that the taste sensor can distinguish between usual river water and contaminated river water at levels of 1 ppm free cyanide and 1 ppm cyano complex. It was found that the taste sensor has great potential to monitor cyanide in river water in real time. The taste sensor, in combination with an autosampling system, is expected to be more powerful, more stable and more inexpensie than a real-time monitoring system, using bioassay methods.

Next, we applied the taste sensor to the detection of PAC in tap water. The results indicate that the taste sensor can distinguish between normal tap water and contaminated tap water at levels of 50 ppm PAC. It was found that the taste sensor correlated well with the sensory test and has great potential for the real-time monitoring of PAC in tap water. The taste sensor is expected to be more powerful, more stable and more effective than sensory tests.

We are now investigating applications for other types of contamination and will proceed with the development of real-time monitoring systems using taste sensors.

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