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Evaluation of water quality and pollution using multichannel sensors

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Abstract

We studied and discussed the characteristics and the application of a multichannel electrode type sensor. It was based on eight membranes using various lipids as an effective and a simple potentiometric sensor for detecting water quality.

The response of the sensor was calibrated using a standard solution, adjusted as an artificial river water. Especially, we researched the response patterns of the sensor to the river water at Kitakyushu in Japan. In general, cations increase the membrane potential of negatively charged membranes, while anions decrease that of positively charged membranes. The water quality of the upper stream was clearly distinguished from the water quality of the other sites. The original data obtained with the sensor were expressed on an eight-dimensional space, so they were visualized on the two-dimensional plane using principal component analysis. That is, the water quality of the upper stream was the same, and the quality of middle and down stream was different. The multichannel sensor system will contribute to control water quality and water pollution. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Water quality; Pollution; Multichannel sensor; River water

1. Introduction

At present, chemical analysis is mainly carried out by gas and liquid chromatographic methods. However, this has many problems such as the complex procedures required for measuring chemicals, and large and expensive instruments. In particular, monitoring by a chemical sensor is more and more necessary for health-risk assessment of water quality in aquatic environments [1]. On the other hand, taste-originating chemicals can be measured with a multichannel lipid-membrane sensor, which responds to different taste qualities by each unique pattern of sensor output signals [2–4]. The lipid membranes are useful materials for transforming a quality information of various solution samples to electric signals. The multichannel sensor utilizes lipid membranes as a transducer of taste substances and the computer as a data analyser. The transducer plays the role of transforming taste information generated by chemical substances to electric potential changes.

In this study, we discuss the characteristics and the application of a multichannel electrode type sensor. It was based on eight membranes using various lipids as a simple potentiometric sensor system for detecting river water quality.

2. Materials and methods

2.1. Fabrication of the multichannel electrode

We fabricated a multichannel electrode as a transducer following the methods of Hayashi et al. [2]. The electrode was 40 mm wide, 20 mm thick and 100 mm long. The channel was approximately 10-mm circle, with a channel depletion mode device.

The sensor with a multichannel electrode was similar to the previously reported one [5], as mentioned below. The lipids are abbreviated as follows: dioctyl phosphate, C; trioctylmethylammonium chloride, T; oleyl amine, N; decyl alcohol, DA; oleic acid, OA. Hybrid lipid membranes such as C:T = 9:1, C:T = 3:7, and C:T = 5:5, implying a

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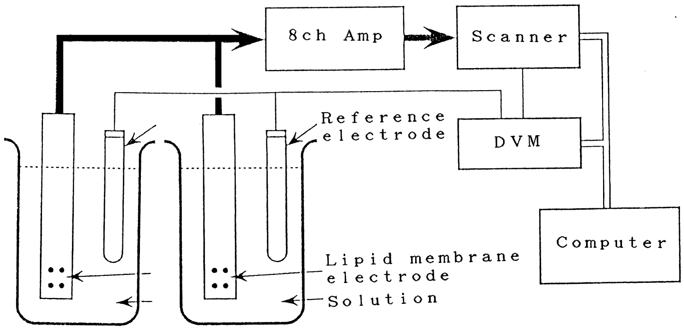

Fig. 1. Schematic diagram of multichannel electrode system.

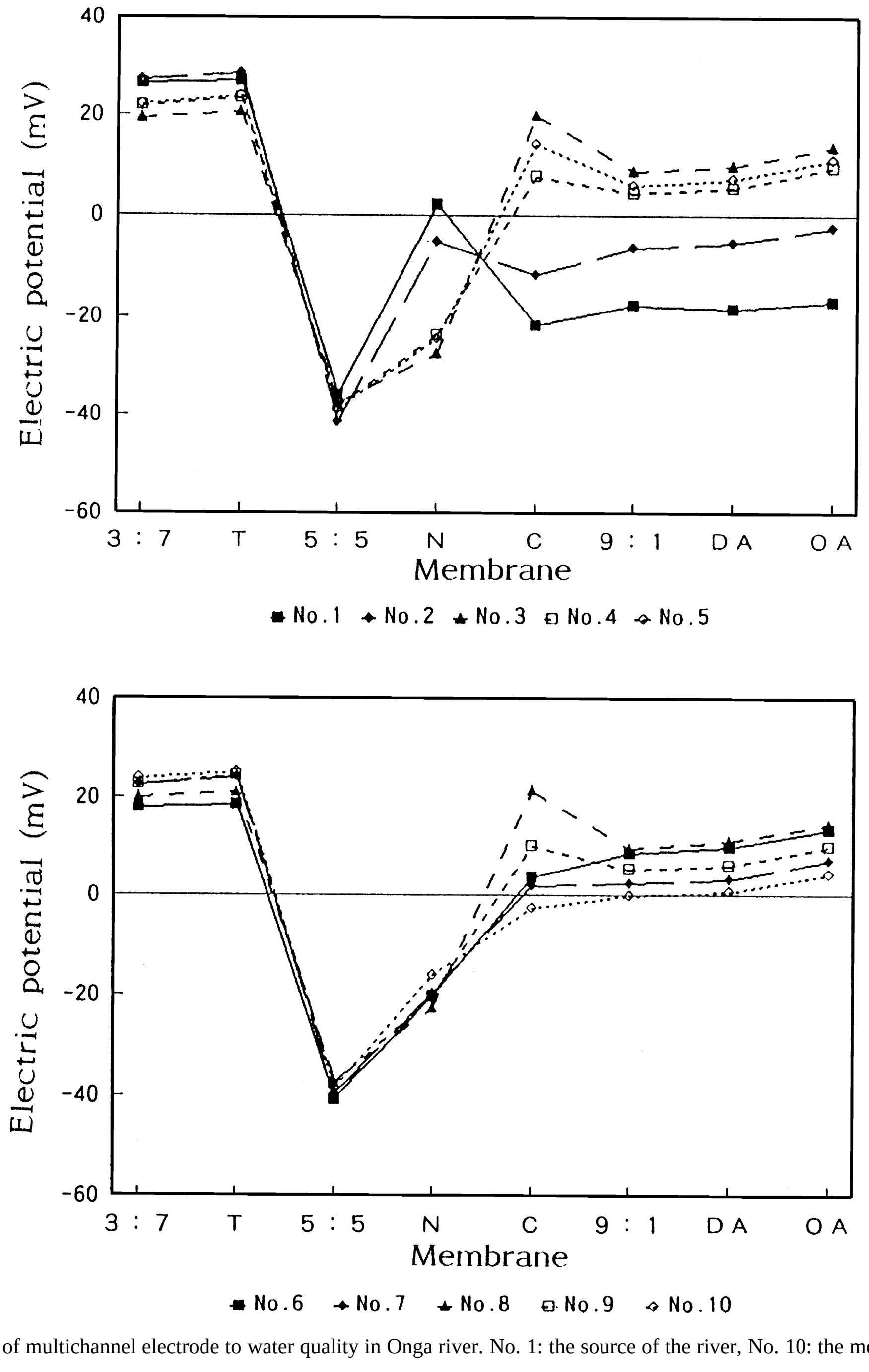

Fig. 2. Response of multichannel electrode to water quality in Onga river. No. 1: the source of the river, No. 10: the mouth of the river.

mixture of two lipids with the ratio of molar concentration, were also used. Each lipid was mixed with 800 mg polyvinyl chloride and 1.0 ml dioctyl phenylphosphonate (plasticizer), which was transparent, colorless and soft film of 150–200 μm thickness. The same lipid membranes were used for half a year throughout the present work.

River water from the Onga river and the Murasaki river at Kitakyushu in Japan was collected at 10 sites on July 30 and eight sites on October 26, 1997, respectively. These water samples were stored in deionized polyethylene bottles (500 ml).

2.2. Measurement of the potential by the sensor

The construction of the measuring system in Fig. 1 is as follows: Ag/AgCl electrode in 100 mM KCl solution membrane reference electrode in the standard solution. Inorganic ions in a sample solution may change the mem-

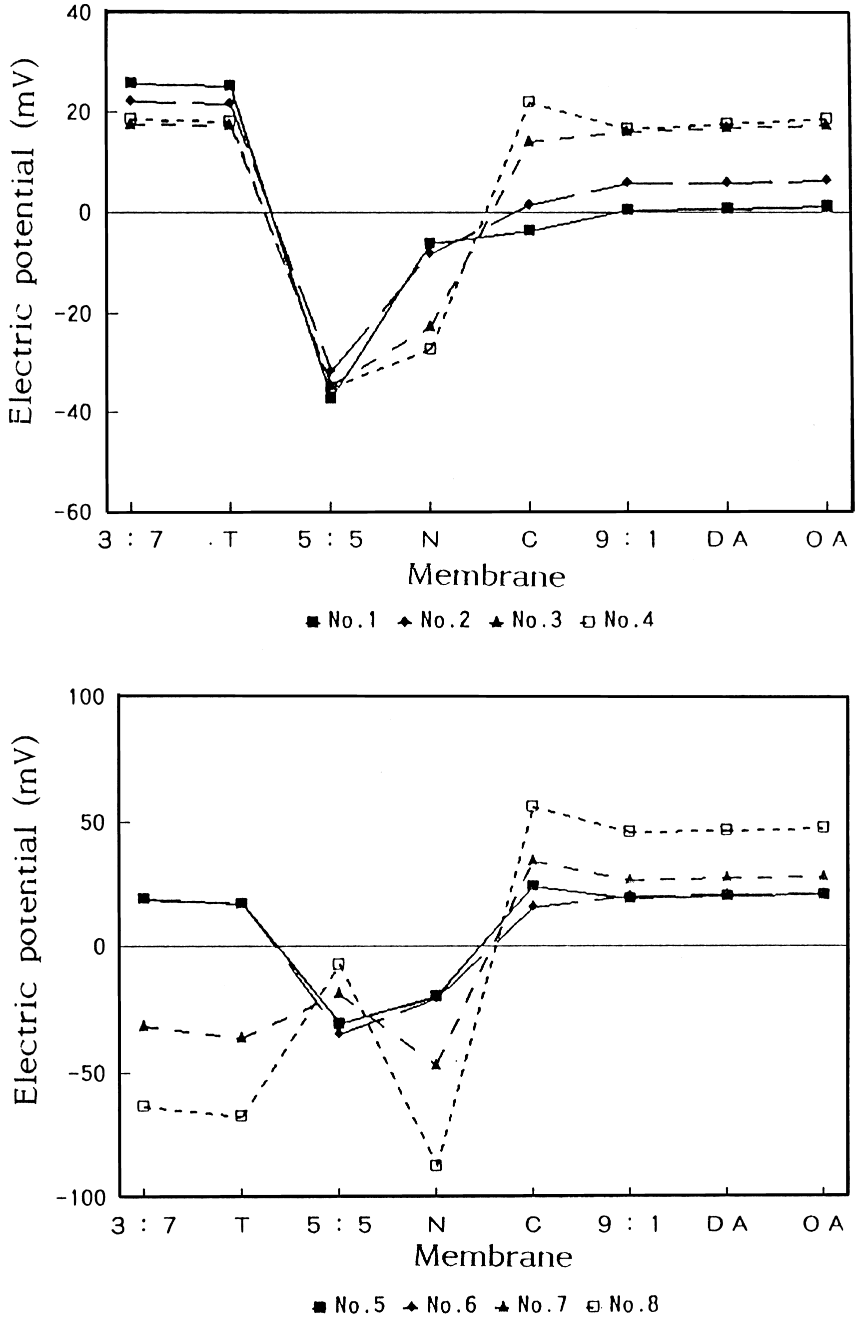

Fig. 3. Response of multichannel electrode to water quality in Murasaki river. No. 1: the source of the river (Musubutci dam), No. 8: the mouth of the river.

brane potential, and the electric signal from each membrane was converted to a digital code by a digital voltmeter through a high impedance amplifier and an eight-channel scanner, and recorded in a computer. The response of the sensor was calibrated with a standard solution. This solution was adjusted based on average values of river-water quality in Japan as an artificial river water containing Na^+ 5.1 mg/l, K^+ 1.0 mg/l, Mg^{2+} 2.0 mg/l, Ca^{2+} 6.3 mg/l, Cl^- 11.1 mg/l, SO_4^{2-} 8.3 mg/l, NO_3^- 19.2 mg/l.

3. Results and discussion

3.1. Response of the sensor using multichannel electrode

The characteristics of the sensor with eight membranes have been described in previous studies [5,6]. The membranes of C:T = 3:7, T, and N were positively charged, whereas those of C:T = 9:1, C and OA were negatively charged. The detection range of inorganic ions using the multichannel electrode was 0.01–3000 μM at room temperature. These chemical ions in water can be measured using the sensor, which responds to different water qualities by means of unique patterns of output signals for each water quality.

Fig. 2 shows response patterns of the sensor to the river water from 10 sites (No. 1–10) of the Onga river. The sample numbers are sequential along the river at intervals from 5 to 10 km. The river is about 60.7 km long and drains an area of 1030 km^2 extending from the headwaters in south Kitakyushu to Japan Sea. Samples were measured after confirmation that errors are less than ± 0.5 mV in the standard solution, hence each sample is clearly distinguished. In general, cations such as Ca^{2+}, Mg^{2+}, heavy metal ions and so on increase the membrane potential of negatively charged membranes, while anions decrease that of positively charged membranes. This result suggests that the water quality will be mainly analysed based on response patterns at the output voltage (about 0 to -100 mV) measured by N of positively charged membrane and

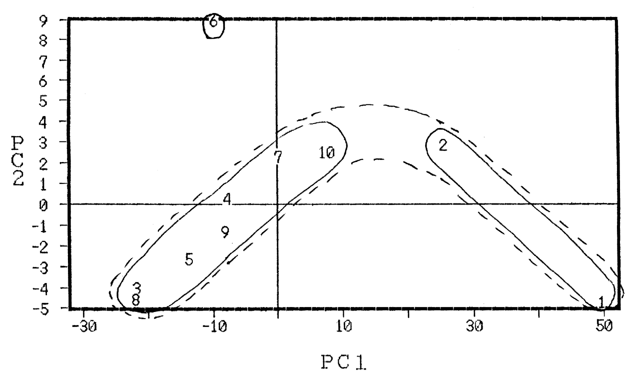

Fig. 4. Principal component analysis on Onga river.

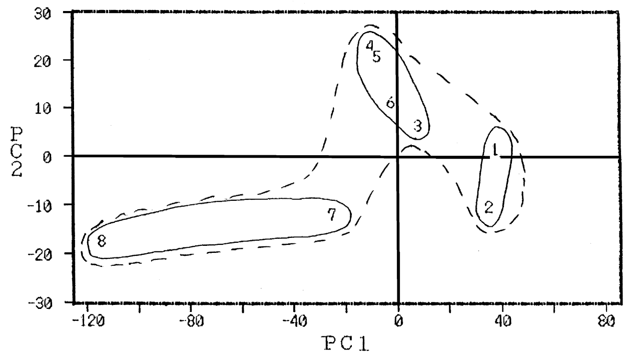

Fig. 5. Principal component analysis on Murasaki river.

negatively charged ones. Especially, this membrane is quite sensitive to alkalis because its hydrophilic portion is a protonated ammonium group. The samples No. 1 and 2 of the upper stream were clearly distinguished from the water quality of other sites. Step by step, the water quality downstream showed increased pollutants, as minerals.

Fig. 3 shows response patterns of the sensor to the river water from eight sites (No. 1–8) of the Murasaki river. The sample numbers also are sequential along the river at intervals of about 2 km. The river is about 20 km long and drains an area of 101.4 km^2 extending from the headwaters in the city. This result also suggests that the water quality will be analysed based on response patterns at the output voltage, similar to the Onga river. The samples No. 7 and 8 of the down stream were clearly distinguished from the water quality of other sites. It was recognized from the abnormal changes of the response pattern that these sites in a section of 3 km from the river mouth were especially contaminated by an inflow of seawater. These results show that the pattern of the output voltage using the sensor system can distinguish from various rivers.

3.2. Principal component analysis

The water quality of aquatic environments was investigated using principal component analysis [7]. In the present case, the original data were expressed on an eight-dimensional space from eight kinds of membranes. Whereas principal component analysis is very effective to reduce dimensional space, its axes have no meaning. It is desirable to let the axes have chemical meanings. The evaluation of water quality in rivers is especially required from a total viewpoint. For this purpose we prepared the river waters as comparative solutions which were sampled from upper to down streams.

The original data obtained with the sensor were expressed on an eight-dimensional space, so they were visualized on the two-dimensional plane using principal component analysis, as illustrated in Figs. 4 and 5. The contribution rates were 94.4% and 3.5%, and 95.7% and 3.6% for PC1 and PC2, respectively. In Onga river, No. 4–8 and

9 and 10, are randomly distributed in Fig. 4. Contrary to these, No. 1, 2 and 3 are aligned from right to left in the same river. In Murasaki river, No. 1 and 2, 3–6, 7 and 8are aligned from right to left in Fig. 5. In the water quality of both rivers, the group of No. 1 and 2 was shown to be nonpolluted in the upper streams, as water resources. That is, the water quality of the upper stream (the group of No. 1 and 2 in both rivers) were the same, and the quality of middle and down stream (the group of No. 3–5 and 7–10, 6 in Onga riber, and the group of No.3–6 and No.7 and 8 in Murasaki river) were different in each group. However, the water quality of sample No. 6 in Fig. 4 may be especially disturbed by water quality from branch rivers. In general, these results show that cations and anions as pollutants originating from outside increase in the down rivers, while pollutants decrease in the upper streams. In addition, the distribution of the element of grouping will make a shape of a mountain. However, it may be difficult to discuss the change in each chemical concentration in this coexisting situation; individual water quality cannot be separated in a straightforward manner based on the response pattern. The sensor does not directly express chemicals, but its discrimination and risk management of water quality in rivers is superior, simple and quick compared to other types of sensing systems. They were visualized on the two-dimensional plane (PC1 and PC2) in Figs. 4 and 5 using principal component analysis, which was very effective for reducing dimensional space without losing information.

4. Conclusion

The development of practical sensors, such as the multichannel sensor, is an important topic for water-quality research. In this study, the responses of the multichannel sensor to river waters that contain various ions were investigated by taking the pattern for the standard solution. The analytical results were directly displayed response patterns by the output voltage of the sensor. Especially, it suggests that the water quality will be mainly analysed based on response patterns at the output voltage (about 0–100 mV) measured by N of positively charged membrane and negatively charged ones. These results also show that the pattern of the output voltage using the sensor system can distinguish from various rivers. Therefore, a map of the water quality in rivers based on the response of the sensor and the principal component analysis are useful for an estimation of water quality.

A new technique for detecting chemicals in aquatic environments is expected for a faster, simpler, safer, and inexpensive analysis. The multichannel sensor system will contribute to control water quality and water pollution.

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