Nitrate-Selective Field-Effect Transistors Based Acid-Rain Checker using Phosphate Esters as Plasticizer

Summary

Highly sensitive nitrate-selective field-effect transistors (nitrate ISFETs) were prepared by casting the FET gate insulator surface with 5 kinds of phosphate-ester based plasticizers, a nitrate-sensing material based on trihexadecylmethylammonium nitrate and PVC matrix. The nitrate ISFETs with trioctylphosphate showed a linear response from $10^{-4.5}$ mol dm$^{-3}$ to 1 mol dm$^{-3}$. Using the most suitable nitrate-sensing membrane, we have prepared a prototype nitrate-checker composed of a nitrate ISFET and silver/silver chloride reference electrode and have demonstrated its preliminary application to real samples of rain water. We could obtain relatively good agreement of the values of nitrate concentration observed by the nitrate checker and conventional ion-chromatography and fairly good correlation coefficient between the both methods with 0.97.

Keywords: nitrate ISFETs, acid-rain monitoring, phosphate-ester based plasticizer, prototype nitrate-checker

1 INTRODUCTION

Acid rain has become one of the global environmental problems. And acid fog has also become one of the local environmental problems, especially in the local areas near big cities. The important chemical species in acid rain or fog are nitrate and sulfate because the acidification is caused by nitrogen oxides and sulfur oxides exhausted from mobile and stationary sources. Especially, it is well-known that in Japan, the concentration of nitrate in rain water is relatively higher than that of sulfate because of exhaust from cars [1].

Conventional analytical methods for acid rain such as ion-chromatography for these ions are time-consuming. On the other hand, ion-selective field-effect transistors (ISFETs) are the most promising method for convenient monitoring-checker of components in acid rain [2-4]. To detect mg dm$^{-3}$ (ppm) level nitrate in rain water, we have investigated highly sensitive nitrate ISFETs using specially designed nitrate-sensing materials as well as highly stable membrane materials [5-11]. We have obtained one of the problems that nitrate ISFETs require some improvements in selectivity.

In order to obtain highly selective nitrate ISFETs, we chose phosphate esters as an alternative plasticizer (membrane solvent). Recently, Reinholdt et al. reported influence of plasticizer on the selectivity of nitrate ISFETs [12]. And he concluded that the most suitable plasticizer for nitrate-selective CHEMFETs is one of the phosphate esters.

In this paper, we prepared 5 kinds of nitrate-selective electrodes (nitrate ISEs) based on phosphate esters and investigated their sensor characteristics. And then using the most suitable nitrate-sensing membrane, we have prepared a prototype nitrate-checker and have demonstrated its preliminary application to real rain water.

2 EXPERIMENTAL

2.1 Reagent

A newly designed trihexadecylmethylammonium chloride (THDMA-Cl) was obtained from Dojin Research Laboratories Co., Ltd. (Kumamoto). All reagents were of analytical grade and used without purification. Phosphate-ester based plasticizers, as shown in Fig. 1, were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo). Other chemicals were purchased from Wako Pure Chemical Industries, Ltd. (Osaka). As a specially designed nitrate-sensing material, trihexadecylmethylammonium nitrate (THDMA-NO3) was obtained from the corresponding THDMA-Cl by the conventional ion-exchange method [11].

\[
\begin{align*}
\text{OR} & \quad \text{R} = \text{C}_2\text{H}_5 : \text{TEP} \\
\text{RO} & \quad \text{R} = \text{C}_3\text{H}_7 : \text{TBP} \\
\text{P} & \quad \text{R} = \text{C}_6\text{H}_{17} : \text{TOP} \\
\text{OR} & \quad \text{R} = \text{C}_6\text{H}_5 : \text{TPP} \\
\text{OR} & \quad \text{R} = \text{C}_7\text{H}_7 : \text{TCP}
\end{align*}
\]

Figure 1 Chemical structures of phosphate-ester based plasticizers.

2.2 Preparation of nitrate ISEs

Nitrate-selective electrodes (nitrate ISEs) were prepared as follows. Nitrate-sensitive membranes were prepared by casting with a tetrahydrofuran (THF) solution of 5 wt.% of THDMA-
NO₃ as a nitrate-sensing material, 65 wt.% of a phosphoric ester based plasticizer as a membrane solvent and 30 wt.% of poly(vinyl chloride) (PVC, n=1000) as a matrix material onto the ISE chip of an ISE kit (7960-0.65W; DKK Corp, Tokyo). The resulting ISE chips were allowed to dry overnight. After soaking in 10⁻³ mol dm⁻³ KNO₃ standard solution overnight (conditioning), the nitrate ISEs were prepared by attaching the chip onto the electrode body of an ISE kit filling internal solution of 10⁻² mol dm⁻³ KNO₃.

2.3 Preparation of prototype nitrate-checker

Prototype nitrate-checkers were prepared by casting the THF solution containing the most suitable nitrate-sensitive PVC membrane materials onto the ISFET device of a pH checker (pH Boy-P2; Shindengen Electric Mfg. Co., Ltd., Tokyo). One of the photographs for the prepared nitrate-checker is shown in Fig. 2. The resulting nitrate-checkers were also allowed to dry overnight [11].

2.4 Apparatus

After conditioning of the prepared nitrate ISEs, potential responses of nitrate ISEs were measured versus a silver/silver chloride double-junction reference electrode (4083; DKK Corp., Ag/AgCl electrode with an inner chamber filled with sat. KCl and an outer chamber filled with 0.1 mol dm⁻³ lithium acetate) by soaking in the stirred KNO₃ test solutions from low to high concentration. The recorder output of the sensor response was introduced into a computing integrator (SDP-100; Nippon Denshi Kagaku Co. Ltd., Kyoto) via an ion-meter (Ionanalyzer 801/digital pH; Orion Research Corp., Boston).

2.5 Rain-water analysis

The samples of rain water were taken by an automated rain-sampling apparatus (Raingoround AR-8; Horiba Mfg. Co., Ltd., Kyoto) at our laboratory. After soaking of the prepared prototype nitrate-checker in 10⁻³ mol dm⁻³ KNO₃ solution overnight, we measured the nitrate concentrations of rain-water samples in each millimeter by the checker using a direct potentiometry and ion-chromatography (IC-7000; Yokogawa Electric Mfg. Co., Ltd., Tokyo).

3 RESULTS AND DISCUSSION

3.1 Sensitivity of nitrate ISEs

The prepared nitrate ISEs showed fairly stable responses within several seconds except for TEP and TCP based ISEs, as shown in Fig. 3. The most sensitive TOP based ISEs showed a linear response range from 10⁻⁴.5 mol dm⁻³ to 1 mol dm⁻³ with -56 mV per decade change of activity. The selectivity characteristics of the prepared nitrate ISEs are summarized in Table 1. In phosphoric alkylesters, the superior nitrate ISEs are obtained as follows; TOP > TBP > TEP. These results suggest that the superior nitrate ISEs will be obtained using more hydrophobic phosphoric alkylester. Since the sensitivity will be determined by leaching of a nitrate-sensing material from the nitrate-sensitive membrane [9], these behavior could be explained a nitrate-sensing material as well as a plasticizer is co-leaching from nitrate-sensing membrane. Therefore, the sensitivity could be determined in accordance with hydrophobicity of plasticizers. From this results, the studies on improving the sensitivity of nitrate sensors using a designed hydrophobic phosphate alkylester based plasticizers are now under investigation.

Concerning phosphate phenylesters such as TPP and TCP, it is difficult to discuss the behavior due to our few data.

3.2 Selectivity of nitrate ISEs

As shown in Fig. 4, the selectivity coefficients were evaluated with the conventional mixed solution method [13]. The selectivity coefficients calculated with the conventional

![Figure 3: Sensor response of nitrate ISEs based on several phosphate esters.](image)

![Figure 2: Photograph of prototype nitrate-checker based on nitrate ISFET and reference electrode.](image)

<table>
<thead>
<tr>
<th>plasticizers</th>
<th>response range*</th>
<th>slope sensitivity**</th>
<th>remarks</th>
</tr>
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<tbody>
<tr>
<td>TEP</td>
<td>10⁻⁴ - 10⁻²</td>
<td>-26</td>
<td>unstable</td>
</tr>
<tr>
<td>TBP</td>
<td>10⁻⁴⁻⁻⁻ - 1</td>
<td>-49</td>
<td></td>
</tr>
<tr>
<td>TOP</td>
<td>10⁻⁴⁻⁻⁻ - 1</td>
<td>-56</td>
<td></td>
</tr>
<tr>
<td>TPP</td>
<td>10⁻⁴ - 1</td>
<td>-46</td>
<td></td>
</tr>
<tr>
<td>TCP</td>
<td>10⁻⁴ - 1</td>
<td>-47</td>
<td>unstable</td>
</tr>
</tbody>
</table>

* mol dm⁻³, ** mV per decade change of activity

Table 1. Sensitivity characteristics of nitrate ISEs.
graphical method are summarized in Table 2. The sequence of selectivity coefficients followed the typical Hofmeister’s series. For practical application, the influence of coexisting chloride and sulfate in rain water should be as small as possible. The logarithmic selectivity coefficient of the nitrate sensor for chloride (-2.3) is much better than that of our data reported in Ref. 11; ETH 2112 based ISFETs (-1.1) and almost the same as that reported in Ref. 12 (-2.5), Ref. 14 (-2.0) and Ref. 15 (-2.3). And that for sulfate (-3.4) is also much better than that of our ETH 2112 based ISFETs (-2.5), almost the same as that reported in Ref. 12 (-4.1), Ref. 14 (-3.8) and worse than that in Ref. 15 (-5.0). Concerning the carbonate dissolved in rain water from atmosphere, it will be explained that the prepared nitrate ISEs have little error from the dissolved carbonate, as discussed in detail elsewhere [16]. The required selectivity coefficients were calculated within 10% error from Nicolsky-Eisenman equation [4] and also listed in Table 2. The prepared nitrate ISFETs require some improvements using the membrane technology, such as control of membrane surface, as well as the sensing-material technology.

3.3 Stability of nitrate ISEs

The TOP based nitrate ISEs showed fairly stable responses, however, they have relatively short durability less than 2 weeks. The reason seems that the components of the sensing membrane, such as THDMA-NO₃, TOP and PVC, do not dissolve uniformly, because the TOP based nitrate-sensing membrane is not so transparent. We should improve stability using the membrane technology as well as the sensing-material technology.

3.4 Rain-water analysis

The prototype nitrate-checker based on TOP showed a linear response range from 10⁻⁴ to 1 mol dm⁻³ and showed logarithmic selectivity coefficients for chloride (-2.3) and sulfate (-3.4) which responses are almost the same as that of the corresponding nitrate ISEs.

We tried to measure each millimeter of rainfall with the direct potentiometry using the nitrate checker. A preliminary results showed about 6 ppm nitrate concentration in the initial millimeter and about 2 ppm in the following millimeters of a rainfall. The results are summarized in Fig. 5. It was observed that the values of nitrate concentration decreased with increasing millimeter of the rainfall. This phenomena is

![Figure 4 Sensor response of TOP based nitrate ISEs with interfering ions.](image)

![Figure 5 Nitrate concentrations using nitrate checker.](image)

![Figure 6 Correlation between nitrate concentrations by nitrate checker and ion-chromatography.](image)
similar to our previous data [11] and can be explained with the so-called washout effect [1]. We also measured each millimeter of the same rainfall using a conventional ion-chromatography. We could obtain relatively good agreement of the measured values of nitrate concentration. Between the TOP based checker and the conventional ion-chromatography at ppm level and then relatively good correlation (Y=1.2X-1.0; R=0.97) assuming the results have a linear correlation as shown in Fig. 6. We have already reported that we had only good correlation (Y=2.8X-4.0; R=0.99) using the ETH 2112 based nitrate-checker [11]. We are successful in demonstrating a convenient nitrate checker to measure a drop of rain water, however, it is clear that some improvements in its basic sensor characteristics are necessary.

4. CONCLUSIONS

We investigated highly selective nitrateISEs using 5 kinds of phosphate esters as an alternative plasticizer in order to improve selectivity of the sensor characteristics. Using the most suitable TOP based membrane, we prepared a proto-type nitrate-checker and tried to demonstrate its preliminary application to real samples of rain water. We could obtain relatively good agreement of the values of nitrate concentration at ppm level between the TOP based checker and the conventional ion-chromatography successfully.

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REFERENCES

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