Highly Sensitive Nitrate-Sensing Materials for Ion-Selective Field-Effect Transistors for Single-Drop Rain Analysis

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Our objective is to obtain superior nitrate-sensitive materials in nitrate-sensitive membranes, which are composed of anion exchangers, systematically designed trialkylmethylammonium nitrates (TXMA-NO_3) and plasticizers, which are liquid solvents, systematically designed 2-nitrophenylalkylether (NPXE) and conventional poly(vinyl chloride) (PVC) as a sensing membrane matrix. In the nitrate-sensitive membrane, a highly hydrophobic anion exchanger, such as trihexadecylmethylammonium nitrate (THDMA-NO_3) improved its sensitivity, in particular, its linear response range for low concentrations, due to the decrease in elution of the corresponding nitrate from the nitrate-sensing membrane based on the plasticized PVC. However, trioctadecylmethylammonium nitrate decreased the lifetime of the nitrate-sensing membrane due to its immiscibility in the nitrate-sensitive plasticized PVC membrane. Among the plasticizers, NPXE, 2-nitrophenyltetradecylether (NPTDE) showed better miscibility in the PVC membrane and itself to be a superior plasticizer, and it also improved the lifetime of prototype checkers based on nitrate Ion-selective field-effect transistors (ISFETs) due to the better adhesion of the plasticized PVC membrane onto the gate insulator of the ISFET device. In the optimized nitrate-sensitive membrane, THDMA-NO_3, NPTDE and PVC gave a good performance as the nitrate FET checker for the single-drop analysis of rainwater by direct potentiometry.

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1. Introduction

The importance of global environmental problems, such as the acid rain as well as the global warming, has been recognized worldwide. The chemical properties of rain droplets will clarify the chemical processes of acid rain and also its affect on ecosystems. The most important chemical species in acid rain are hydrogen, nitrate and sulfate ions, because the acidification is caused by nitrogen oxides, NOx, and sulfur oxides, SOx, exhausted from mobile and stationary sources. In rainwater analysis, conventional analytical methods based on ion chromatography and pH glass electrodes in analytical laboratories are time-consuming.[1]

Several researchers have investigated single-raindrop analysis using various advanced methods.[2] Tenberken *et al*.[3] proposed single-raindrop analysis by capillary electrophoresis (CE). They developed a microinjection system for CE by applying a vacuum at the opposite end of a separation column. Kasahara *et al*.[4] proposed single-drop analysis by microparticle-induced X-ray emission (PIXE) analysis. They developed a sampling method involving freezing.

Ion-selective field-effect transistors (ISFETs) are miniaturized chemical sensors integrated with ion-selective electrodes (ISEs) and metal-oxide field-effect transistors (MOSFETs).[5–8] Since ISFETs have several advantages, such as miniaturization, high input impedance and low output impedance, they have attracted much attention for the on-site monitoring of acid rain.[9–16] In material design studies on ion-sensor materials, the ISFET specificity of high input impedance and low output impedance have resulted in the research and development of new sensor materials.

Although several authors including our group have studied nitrate ISFETs,[15–30] it is difficult to develop the highly sensitive ISFETs for sub-ppm (mg L^{-1}) concentration levels using conventional sensing materials to obtain accurate results in terms of sensitivity, selectivity and stability.

Concerning the sensitivity of nitrate ISFETs, we reported a fundamental study on 3 kinds of nitrate ISEs based on copper(I) cuproin complexes, such as bis(neocuproin)-copper(I) nitrate [Cu(ncp)$_2$]NO$_3$, bis(cuproin)-copper(I) nitrate [Cu(cp)$_2$]NO$_3$ and bis(bathocuproin)-copper(I) nitrate [Cu(bcp)$_2$]NO$_3$ as nitrate-sensing materials. As highly sensitive nitrate ISFETs, Hara *et al*. proposed bis(bathocuproin)-copper(I) nitrate to obtain high sensitivity and suggested that the nitrate ISFETs may be acceptable for rainwater analysis.[16]

Concerning the selectivity of nitrate ISFETs, several researchers have reported an improvement in the selectivity to chloride using a plasticizer with a high dielectric constant.[25–30] Among the proposed nitrate ISFETs, we used 2-nitrophenyldodecylether (NPDDE) as a highly viscous plasticizer (solid at room temperature) and PVC as a membrane matrix for nitrate ISFETs, and we obtained relatively good selectivity to chloride for single-drop rain analysis.

Concerning the stability of nitrate ISFETs, we reported the durability of the Urushi ISFETs[23] over 1 month in order to resolve the poor adhesion of the ion-sensing membrane to the gate of the FET device, as described in detail in this journal.[8] Because Urushi is a natural latex used for lacquerware and the Urushi membrane including with

the ion-sensor material must be hardened for 10 days before use, other artificial polymers are expected to be more suitable for the ion-sensor matrix materials. The most promising material is poly(vinyl chloride) (PVC). However, in general, ISFETs with an organic ion-sensing material on the gate of the ISFET device have a short lifetime due to the poor adhesion between the ion-sensing membrane and the gate of the ISFET device. We reported relatively durable nitrate ISFETs with a 7 week lifetime using highly viscous nitrate-sensing materials[15] and also preliminary ISFET-based nitrate checkers for single-drop acid-rain analysis for the first time in the world.[27] We demonstrated the preliminary device using rain samples; however, it was found that we must improve the selectivity.

In this paper, we carried out a fundamental study on the design of sensor materials for use in nitrate ISFETs such as ion-sensing materials, anion exchangers, liquid membrane solvents (plasticizers) using systematically designed materials. Here we will systematically report results for various ion-sensor materials that can be used to obtain highly sensitive, selective and stable ISFETs and their successful application to the single-drop analysis of rainwater using direct potentiometry.

2.   Materials and Methods

2.1   *Materials*

As a conventional nitrate-sensing material, trioctylmethylammonium nitrate (TOMA-NO_3) was prepared from the corresponding quaternary ammonium chloride (Dojindo Laboratories) by the conventional ion-exchange method.[20] As a highly sensitive nitrate-sensing material, tridodecylmethylammonium nitrate (TDDMA-NO_3) was also prepared from the corresponding chloride (Polysciences, Inc.).[15] As designed nitrate-sensing materials, tritetradecylmethylammonium nitrate (TTDMA-NO_3), trihexadecylmethylammonium nitrate (THDMA-NO_3) and trioctadecylmethylammonium nitrate (TODMA-NO_3) were also prepared from the corresponding quaternary ammonium chlorides, which were synthesized and purified at Dojindo Laboratories. The chemical structure of trialkylmethylammonium nitrate (TXMA-NO_3) is shown in Fig. 1(a).

As a conventional liquid membrane solvent (plasticizer) in PVC, 2-nitrophenyloctylether (NPOE) was purchased from Dojindo Laboratories. As designed plasticizers, 2-nitrophenyldecylether (NPDE), 2-nitrophenyldodecylether (NPDDE), 2-nitrophenyltetradecylether (NPTDE), 2-nitrophenylhexadecylether (NPHDE) and 2-nitrophenyleicosanylether (NPECE), all synthesized at Dojindo Laboratories, were used. The chemical structure of 2-nitrophenylalkylether (NPXE) is also shown in Fig. 1(b).

As a membrane matrix, poly(vinyl chloride) (PVC, *n*=1000) was purchased from Kishida Chemical Co., Ltd., and was used without purification. Tetrahydrofuran (THF, Nacalai Tesque, Inc.) was used as a volatile solvent to dissolve the nitrate-sensing material, plasticizer and PVC for casting the nitrate-sensing membrane. The other chemicals were of analytical grade and were used without purification. KNO_3 and other standard solutions were prepared with deionized and distilled water.
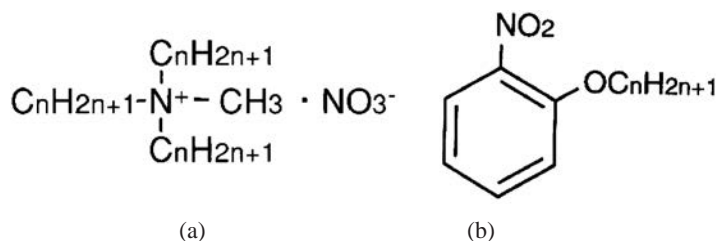
Fig. 1.   Chemical structures of designed nitrate-sensing materials (n = 8, 12,14,16 and 18) on left side (a) and designed plasticizers (n = 8, 10, 12, 14 and 20) on right side (b).

2.2   *Preparation of nitrate-selective electrode*

Nitrate-ion-selective electrodes (NO_3^--ISEs) used to evaluate for the sensor response of the nitrate-sensitive membrane, were prepared using DKK ISE kits (7900-0.65P; DKK-TOA Corp.) by the following procedure. After forming a THF solution of the nitrate-sensing membrane containing 5 wt% of nitrate-sensing material, 65 wt% of plasticizer and 30 wt% of membrane matrix, PVC was completely dissolved in the solution at room temperature. A Teflon membrane in the ISE kit was then immersed in the THF solution for *ca.* 2 min. The immersed Teflon membrane was placed on the small well of the tip of the blank cap in the ISE kit using tweezers. After the volatile THF solution of the Teflon membrane was completely evaporated in a draft chamber, the nitrate-sensing membrane (*ca.* 1 mm thickness) was obtained by casting onto the small well of the tip several times using a glass pipette in the draft chamber. The resulting sensing membrane was allowed to dry overnight. The cap with the sensing membrane was immersed in a conditioning solution of 10^{-2} M KNO_3 for one day. The cap was filled with 10^{-2} M KNO_3+10^{-2} M KCl as an internal solution and connected with the ISE kit body which is based on an Ag/AgCl+Ag_2S internal electrode. The preparation processes of the nitrate ISE was carried out in a dried laboratory at room temperature.

2.3   *Preparation of ISFET-based nitrate checker*

Prototype nitrate checkers were prepared by casting the above-mentioned THF solution onto the gate part of the ISFET device in a pH checker (pH Boy-P2; Shindengen Electric Mfg. Co., Ltd.) in almost the same manner as for the preparation of NO_3^--ISE. The thickness of the nitrate-sensing membrane was *ca.* 0.2 mm. The resulting nitrate checkers were allowed to dry overnight.

2.4   *Apparatus*

After the conditioning, which involves immersing the prepared nitrate ISEs into 10^{-3} M KNO_3 solution overnight to establish electrochemical equilibrium, sensor responses were evaluated on the basis of the potential difference of the nitrate ISE versus a Ag/AgCl double-junction reference electrode (DKK-TOA Corp.) using a pH meter (HM-60S, DKK-TOA). The reference electrode had an inner chamber filled with saturated KCl

solution and an outer chamber containing 0.1 M lithium acetate. The measurement of the sensor responses of the prepared nitrate ISE was carried out automatically using an automatic turntable sample-changer system (TTT-1, DKK-TOA Corp.) and a personal-computer-based data-processing system.

The samples of rainwater were taken using an automated rainwater sampling apparatus (Raingoround AR-8; Horiba Mfg. Co., Ltd.) at the Kansai Center of the National Institute of Advanced Industrial Science and Technology (AIST). After conditioning the prototype nitrate-checker overnight using 10^{-3} M KNO_3 solution, the nitrate concentrations in rainwater samples per millimeter were measured using the prepared checker by a direct potentiometric method and measured by the conventional method[1] using ion chromatography (IC-7000; Yokogawa Electric Mfg. Co., Ltd.).

2.5 *Evaluation of nitrate-sensitive membrane*

The prepared nitrate-sensitive membrane was evaluated using the Nicolsky-Eisenman equation based on the expanded Nernst equation as follows:

$$E = Eo + 2.303RT/Z_i F \log(a_i + K_{ij}^{\mathrm{pot}}(a_j)^{Z_i/Z_j}),$$

where E is the potential of the NO_3^--ISE, Eo is the standard potential of the NO_3^--ISE, Z_i and Z_j are the charges of the primary ion i (NO_3^-) and interfering ion j (Cl^-, SO_4^{2-}, NO_2^-, ClO_4^-), and a_i and a_j are the activities of ions i and j respectively. R, T and F have the usual meanings. According to the theoretical response at 25°C, the slope sensitivity of the NO_3^--ISE is –59.16 mV per decade change of the activity, a_i. a_i was calculated from the Debye-Hückel equation based on simple ionic-strength theory. K_{ij}^{pot} is the selectivity coefficient of the NO_3^--ISE in the presence of interfering ion, j. K_{ij}^{pot} was evaluated by the mixed-solution method,[31] and can be considered to be a reliable selectivity parameter. The values of K_{ij}^{pot} were calculated by the fixed-interference method (FIM). The potential responses were measured in the NO_3^- standard solutions in the presence of each interfering ion using 5.0×10^{-1} M NaCl, 5.0×10^{-1} M Na_2SO_4, 5×10^{-2} M $NaNO_2$, 5.0×10^{-5} M $NaClO_4$ and 5.0×10^{-5} M NaI.

3.   Results and Discussion

3.1 *Design of nitrate-sensing material*

In a previous paper, we obtained a significant improvement of the sensitivity and stability of nitrate ISFETs using the new hydrophobic nitrate-sensing materials, TDMA-NO_3 and TTDMA-NO_3.[15] In the case of TTDMA-NO_3, a linear response to 10^{-5} M was achieved. Thus, we designed a series of quaternary ammonium nitrate compounds with a long alkyl chain, such as TXMA-NO_3 (X = C_8, C_{12}, C_{14}, C_{16} and C_{18}), as shown in Fig. 1(a).

3.2   *Effects of hydrophobicity of nitrate-sensing material on sensor response*

Using the conventional NPOE and PVC, we systematically studied the sensitivity of nitrate-sensitive membranes based on the 5 TXMA-NO$_3$ compounds. The potential responses of the NO$_3^-$-ISEs based on TXMA-NO$_3$ are summarized in Fig. 2. It was clearly observed that the sensitivity of the NO$_3^-$-ISEs is dependent on the kinds of nitrate-sensing material. In case of the conventional nitrate-sensitive membrane consisting of TOMA-NO$_3$, NPOE and PVC, the NO$_3^-$-ISEs have a linear response range from 10$^{-4.0}$ M to 10$^{-0.3}$ M. As the carbon number in the alkyl chain in TXMA-NO$_3$ increased, superior low detection limits were obtained. The NO$_3^-$-ISE based on TODMA-NO$_3$ has a linear response range from 10$^{-5.5}$ M to 10$^{-0.3}$ M. The linear response range, particularly sensitivity to low concentrations improved in the following order:

$$\text{TODMA-NO}_3 \geq \text{THDMA-NO}_3 \geq \text{TTDMA-NO}_3 \geq$$
$$\text{TDMA-NO}_3 \gg \text{TOMA-NO}_3,$$

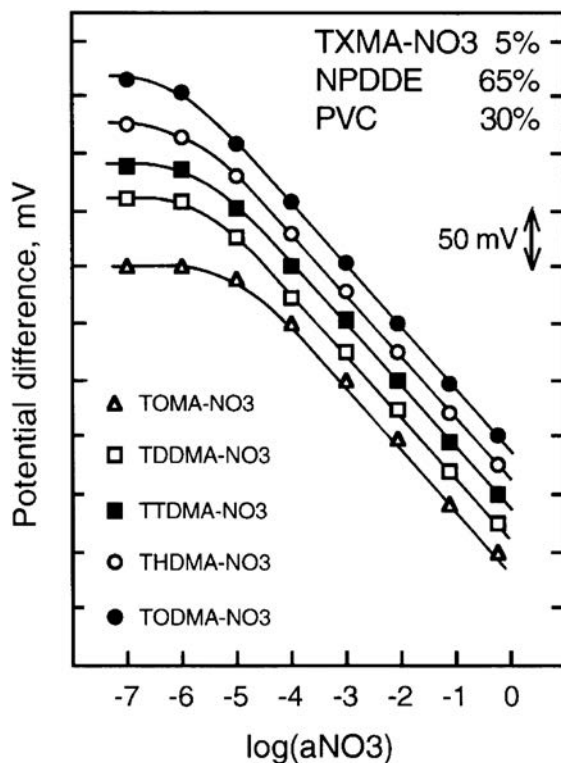and also the slope sensitivity was gradually improved as the following order;

Fig. 2.   Potential responses of NO$_3^-$-ISEs based on TXMA-NO$_3$ to activity of nitrate ion.

$$TODMA\text{-}NO_3 \geq THDMA\text{-}NO_3 \geq TTDMA\text{-}NO_3 \geq$$
$$TDMA\text{-}NO_3 \gg TOMA\text{-}NO_3$$

The improved low detection limit and slope sensitivity may be explained as a decrease in the elution of the nitrate-sensing material from the plasticizer NPOE in the PVC matrix to the solution due to the hydrophobicity of the nitrate-sensing material. The low detection limits might be ruled by the nitrate concentration derived from the elution of the nitrate ions (TXMA-NO$_3$) at the contact of the NO$_3^-$-ISE. Similarly, for Vitamin B$_1$ electrodes, sensitivity for low concentrations increases with the hydrophobicity of the cation exchanger.[32] It is also found that the low detection limits obtained using the silver halide (AgX) electrodes as an ion-sensing material based on solid-state ionics, may be explained by the solubility product of AgX, i.e., the Ag$^+$ or X$^-$ concentration caused by the elution of the AgX.[33]

Although the sensitivity to low concentrations increased using a hydrophobic nitrate-sensing material, the properties of the sensing membrane deteriorated from the viewpoint of uniformity and miscibility in the prepared membrane; therefore, in the case of TODMA-NO$_3$, the lifetime of the NO$_3^-$-ISEs was rather short (less than a few days) due to the heterogeneity of the nitrate-sensing membrane. The heterogeneous property might be mainly caused by the immiscibility of the TODMA-NO$_3$ and PVC using highly soluble NPOE, which has a relatively high dielectric constant, $\varepsilon = ca.$ 24 (25°C).

Instead of NPOE, using another plasticizer, tetraundecyl-α-hydroxy-4,4'-methylene-diphthalate (ETH 2112), we have already reported highly sensitive NO3-ISFETs based on THDMA-NO$_3$ and PVC; however, we could not obtain the stable electrochemical property of NO$_3^-$-ISEs as well as NO$_3^-$-ISFETs based on TODMA-NO$_3$ and PVC, and therefore we did not report this fact in the paper.[27]

In conclusion, THDMA-NO$_3$ was the most suitable nitrate-sensing material for practical application in the case of using NPOE and PVC as sensor materials.

3.2 *Design of plasticizers*

In a previous paper,[27] we reported the preliminary application of highly sensitive nitrate ISFETs to acid-rain monitoring. In the paper, we successfully demonstrated a prototype ISFET-based nitrate checker using a relatively hydrophobic liquid membrane solvent, ETH 2112; however, we pointed out that it is clear that some improvements in its selectivity are necessary. The calculated target values of the selectivity coefficients K_{ij}^{pot} are less than $10^{-2.3}$ in Cl$^-$ and $10^{-2.0}$ in SO$_4^{2-}$ as discussed in detail in the reference paper.[34]

We summarize the logarithms of selectivity coefficients for Cl$^-$ and SO$_4^{2-}$ in Table 1, which were obtained from our published paper. Table 1 shows the logarithmic selectivity coefficients for common interfering anions. The observed selectivity coefficients were in agreement with the Hofmeister series, which is correlated with the hydration energies of the anions, and the selectivity profile was correlated with the dielectric constant, which determines the universal selectivity characteristics in ion exchanger based ISEs or ISFETs.

Table 1
Effect of plasticizers on logarithms of selectivity coefficients of NO_3^--ISEs based on THDMA-NO_3.

ion/plasticizer	ETH 2112[*]	TOP[**]	NPOE[***]
Cl^-	−1.1	−2.3	−2.0
SO_4^{2-}	−2.5	−3.4	−4.4
NO_2^-	−0.6	−1.5	−1.4
I^-	0.5	0.7	1.4
ClO_4^-	1.4	1.0	2.6

[*]ref. 27, estimated dielectric constant is much less than 4.9; [**]ref. 30, dielectric constant is 4.9; [***]this study, dielectric constant is 24.

Using NPOE, which has a high dielectric constant, we obtained acceptable selectivity for application to acid-rain analysis. Moreover, Pérez *et al.*[35] reported that as the dielectric constant of the plasticizer increases the lifetime of the NO_3^--ISE increases in spite of unexpected good adhesion due to its low viscosity as discussed in detail.[15–16] Thus, we designed a series of long alkylchain ethers for NPXE (X = C_8, C_{12}, C_{14}, C_{16} and C_{20}) in the same manner as for the nitrate-sensing material.

4.3 *Effects of hydrophobicity of plasticizer on sensor response*

Using the most sensitive nitrate-sensing material, THDMA-NO_3 and conventional PVC, we systematically studied the sensitivity of nitrate-sensitive membranes based on the 5 plasticizers. The potential responses of NO_3^--ISEs based on NPXE are summarized in Fig. 3. Unlike the case of TXMA-NO_3, it was observed that the NO_3^--ISEs are independent of the type of plasticizer. We also systematically studied the selectivity of 4 NO_3^--ISEs using the mixed-solution method. The selectivity coefficients are summarized in Table 2. As shown in Table 2, we obtained similar selectivities. This may explain the almost the same similar properties of the nitrate-sensitive membranes due to the similar dielectric constant of the NPXEs.

Using the NPXEs (X = C_8, C_{10}, C_{12} and C_{14}), we obtained acceptable selectivity for application to acid-rain analysis. We expect that highly viscous plasticizer will be suitable for applying the NO3-ISFET from the viewpoint of the adhesion of the plasticized PVC membrane to the gate (tantalum oxide) of the ISFET. However, in the case of NPECE, we could not obtain stable electrochemical characteristics because of the heterogeneity of the nitrate-sensing membrane. The heterogeneous property might be mainly caused by the immiscibility of THDMA-NO_3, NPECE and PVC. We also observed a relatively heterogeneous membrane using NPHDE. In conclusion, NPTDE is the most suitable plasticizer for practical application in the case of THDMA-NO3 and PVC as sensor materials.
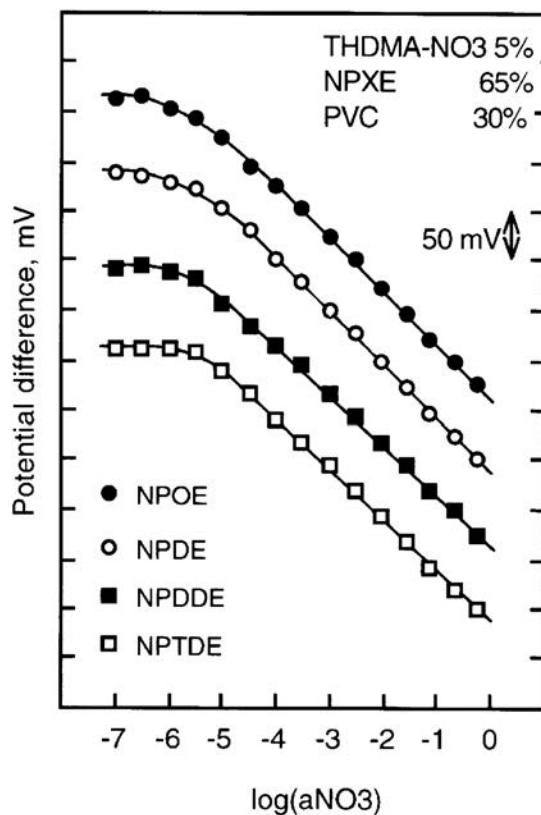
Fig. 3.   Potential responses of NO_3^--ISEs based on NPXE to activity of nitrate ion.

4.4   *Rainwater analysis using prototype nitrate checker*

Using the optimized nitrate-sensitive membrane composed of THDMA-NO_3, NPTDE and PVC, we prepared a prototype nitrate-checker based on the pH-ISEFT checker, as described in detail in the experimental section. The prototype nitrate checker showed a linear response in the range from $10^{-5.5}$ M (0.20 ppm) to $10^{-0.3}$ M, as shown in Fig. 4. The lifetime of the checker was over 2 weeks. We tried to measure nitrate ion concentration per millimeter of rainwater by direct potentiometry using the nitrate checker, and the results are shown in Fig. 5. In the rainwater, we observed a concentration of about 6 ppm (10^{-4} M) in the initial millimeter and about 2 ppm (10^{-5} M) in the following millimeters. The results of the nitrate concentration in this rainwater indicate the washout effect,[1] which may be caused by local air pollution, where the rain initially fell.

We also studied the relationship between results obtained using our proposed nitrate checker and those obtained by the conventional method. Figure 6 shows the correlation

Table 2
Logarithms of selectivity coefficient of NO_3^--ISEs based on NPXEs.

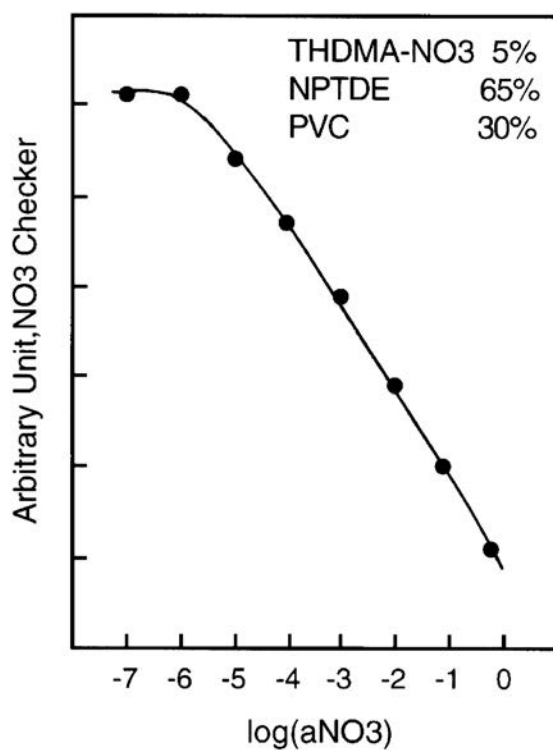| ion/plasticizer	NPOE	NPDE	NPDDE	NPTDE
Cl^-	–2.0	–2.1	–2.2	–2.2
SO_4^{2-}	–4.4	–4.5	–4.6	–4.7
NO_2^-	–1.4	–1.2	–1.3	–1.1
I^-	1.4	1.1	0.9	1.4
ClO_4^-	2.6	2.5	2.6	2.7

Fig. 4.   Sensor response of prototype NO_3^- checker based on NO_3^--ISFET using THDMA-NO_3, NPTDE and PVC to activity of nittrate ion.

between the observed values of nitrate concentration using the proposed nitrate checker and by conventional ion chromatography.   We obtained excellent agreement of the absolute values at ppm level ($Y = 0.96\,X - 1.30$, $r = 0.999$).
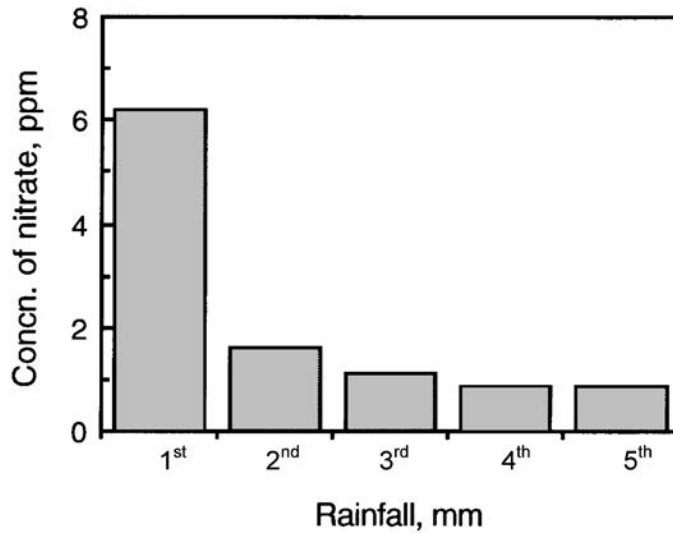
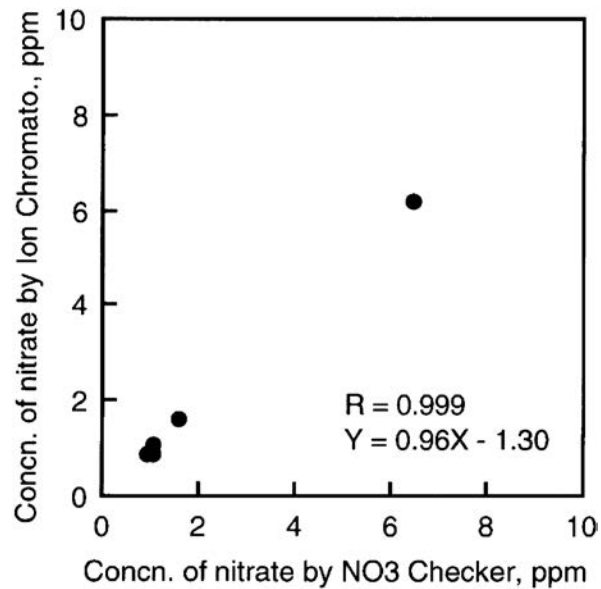Fig. 5.   Nitrate concentrations in rainwater using prototype NO_3^- checker.

Fig. 6.   Concentration between nitrate concentration obtained using protoypee of No_3^- checker and by ion chromatography.

5.   Conclusions

We systematically investigated nitrate-sensing materials, consisting of a quaternary ammonium nitrate (TXMA-NO$_3$) and a plasticizer, 2-nitrophenylalkylether (NPXE), using a conventional PVC matrix. Generally, we found that hydrophobic sensor materials are superior in sensitivity and stability; however, the immiscibility of the nitrate-sensing materials in a heterogeneous nitrate-sensing membrane deteriorates and becomes unstable for sensor responses using the most hydrophobic sensor materials, TODMA-NO$_3$ and NPECE. Using an optimized nitrate-sensing membrane, we were successful in demonstrating the usefulness of the nitrate checker for single-drop analysis using direct potentiometry.

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