

**USE OF COMBINED ION-EXCLUSION
AND CATION-EXCHANGE CHROMATOGRAPHY
TO STUDY PHOTOOXIDATION
OF IONIC NITROGEN COMPOUNDS
ON A TITANIUM DIOXIDE PHOTOCATALYST**

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SUMMARY

Combined ion-exclusion and cation-exchange chromatography (IEC/CEC) on a weakly acidic cation-exchange resin in the H⁺-form (TSKgel Super IC-A/C) has been used as an advanced method for evaluation of the photooxidation of ionic nitrogen compounds, for example triethanolamine, trimethylamine, and urea, on a TiO₂ photocatalyst. Formation of NH₄⁺ and NO₃⁻ from each nitrogen compound by photooxidation on the catalyst during UV irradiation was successfully monitored by use of IEC/CEC under optimized mobile-phase conditions (6 mM tartaric acid and 3 mM 18-crown-6). It was found that the products formed depended on whether or not a molecule contained a hydroxylated nitrogen moiety or other hydroxyl group.

INTRODUCTION

Advanced oxidation processes have recently become a serious alternative to conventional water-purification methods. Purification of water containing organic and inorganic micro pollutants by use of a TiO₂ photocatalyst is one of several promising advanced oxidation processes for environmental remediation. In particular, ionic nitrogen compounds (NH₄⁺, NO₂⁻, NO₃⁻, or amines) causing eutrophication of aquatic environments have been the focus of numerous investigations in recent years [1–6]. The nitrogen compounds are converted to NH₄⁺ and NO₃⁻ on the surface of the photocatalyst via a photooxidative pathway. Monitoring of NH₄⁺ and NO₃⁻

produced by the photocatalytic reaction is, therefore, very important for understanding the photooxidation process. As far as we are aware, however, simultaneous monitoring of NH_4^+ and NO_3^- formed by photocatalytic decomposition of nitrogen species has not been reported.

As has been reported elsewhere [7–14], combined ion-exclusion and cation-exchange chromatography (IEC/CEC) has been recognized as an effective means of simultaneous determination of anions and cations after a single sample injection into the separation column. IEC/CEC is based on a combination of separation processes—ion-exclusion for the anions and cation-exchange for cations [14]. It has been used for simultaneous determination of common inorganic anions (SO_4^{2-} , Cl^- , and NO_3^-) and cations (Na^+ , K^+ , NH_4^+ , Mg^{2+} , and Ca^{2+}) in environmental water including rain, lake, underground, and river waters. In this study IEC/CEC was used for simultaneous determination of NH_4^+ and NO_3^- produced in the photooxidation process. In this paper we report results obtained from use of the IEC/CEC to study the photooxidation process for several typical ionic nitrogen compounds.

EXPERIMENTAL

Ion Chromatography

Ion chromatography was performed with a Tosoh IC-2001 instrument equipped with a vacuum degasser, pump, column oven, autosampler, and conductimetric detector (Tokyo, Japan). The injection volume was 30 μL . Separations were performed on a 150 mm \times 7.8 mm i.d. column packed with 3- μm particles of a polymethacrylate-based, weakly acidic, cation-exchange resin in the H^+ -form, Tosoh TSKgel Super IC-A/C, capacity 0.1 meq mL^{-1} . The column was equilibrated with mobile phase for 30 min before chromatography.

All reagents were analytical grade, purchased from Wako (Osaka, Japan) and standard solutions were prepared by dissolution in distilled and deionized water as necessary.

Photocatalytic Oxidation

The flow-type photocatalytic oxidation reactor used in this study is shown in Fig. 1. Solutions of triethanolamine (TEA), urea, and trimethylamine (TMA), used to evaluate the photooxidative performance of the TiO_2 photocatalyst, were prepared in distilled and deionized water. An aqueous

solution of the species being tested (0.1 mM, 400-mL) was placed in the tank. TiO₂ photocatalyst-coated glass beads (2.5 mm diameter, 50 g), synthesized specially by Photocatalytic Materials, were placed in the flow-type photocatalytic reactor, JIS TRZ 0018 (333 mm × 63 mm × 32 mm). The TiO₂ photocatalyst was evaluated using a commercial UV lamp (National FL20S-BLB) with a spectral maximum peak at approximately 350 nm. The catalyst was irradiated at room temperature for 1 h before beginning the photocatalytic reaction. A test sample solution was circulated from the tank to the reactor by means of a peristaltic pump (Cole-Parmer Master Flex 7518-10) at 300 mL min⁻¹. A 5-mL sample of solution after treatment with the photocatalyst was collected from the tank after circulation. The concentrations of NH₄⁺, NO₃⁻, and organic nitrogen in the solution collected were determined simultaneously by IEC/CEC after filtration through a 0.2 μm pore-size membrane filter.

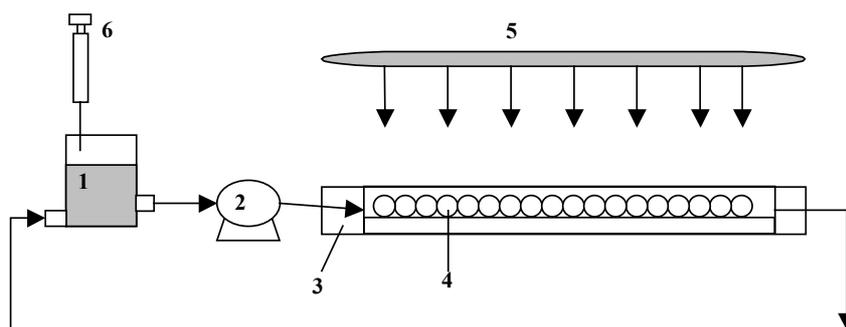


Fig. 1

Schematic diagram of the flow-type photocatalytic reactor. 1, sample tank; 2, peristaltic pump; 3, photocatalytic reactor; 4, photocatalyst; 5, UV lamp; 6, sampling site

RESULTS AND DISCUSSION

Optimization of Simultaneous Ion-Exclusion and Cation-Exchange Chromatography

Optimized conditions for simultaneous IEC/CEC determination of the anions and cations using a mobile phase containing tartaric acid and 18-crown-6 were studied by measurement of retention times, detection sensitivity, and mobile phase conductivity. As shown in Fig. 2, the retention

times of the anions were slightly increased by increasing the concentration of tartaric acid, as expected from the ion-exclusion/penetration effect, i.e. increased penetration of the resin-phase by the anions owing to neutralization of carboxyl-groups in the resin with increasing concentration of hydrogen ions in the tartaric acid mobile phase. In contrast, the retention times of the cations were substantially reduced as the concentration of tartaric acid was increased, as expected from the cation-exchange effect, i.e. reduced cation-exchange of cations with the carboxyl groups with increasing hydrogen ion content of the mobile phase.

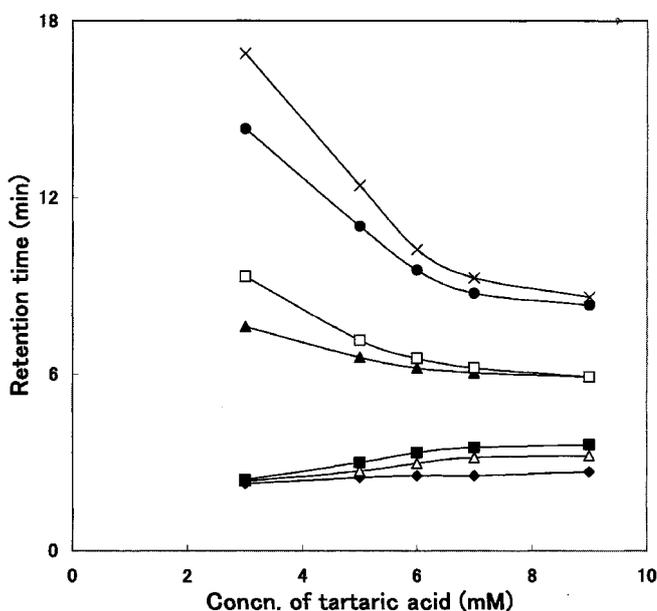


Fig. 2

Effect of tartaric acid concentration in the mobile phase on the retention times of anions and cations in simultaneous ion-exclusion/cation-exchange chromatography. The column (150 mm × 7.8 mm i.d.) was packed with 3- μ m-particles of TSKgel Super-IC-A/C with 0.1 meq mL⁻¹ capacity. The column temperature was 40°C, the injection volume 30 μ L, and the flow rate 1 mL min⁻¹. ◆, SO₄²⁻; Δ, Cl⁻; ■, NO₃⁻; ▲, Na⁺; □, NH₄⁺/K⁺; ●, Mg²⁺; ×, Ca²⁺

The background conductance of the mobile phase increased as the concentration of tartaric acid was increased (for example, 531 μ S cm⁻¹ for 5 mM tartaric acid and 1044 μ S cm⁻¹ for 9 mM tartaric acid). Because increasing the concentration of tartaric acid in the mobile phase reduced the

conductivity response of the detected anions and cations, the lowest possible mobile phase concentration of tartaric acid was required to obtain high detection sensitivity. The optimum concentration of tartaric acid was found to be 6 mM.

Addition of 18-crown-6 to the mobile phase very effectively improved peak resolution between the monovalent cations. K^+ , especially, can form a very stable metal-in-hole type complex with 18-crown-6, because the size of the internal cavity of 18-crown-6 fits the size of K^+ . Complete separation of the monovalent cations was achieved by addition of 3 mM 18-crown-6 to the mobile phase. The optimum elution conditions were found to be 6 mM tartaric acid and 3 mM 18-crown-6. Under these conditions NH_4^+ and NO_3^- could be determined simultaneously, as shown in Fig. 3.

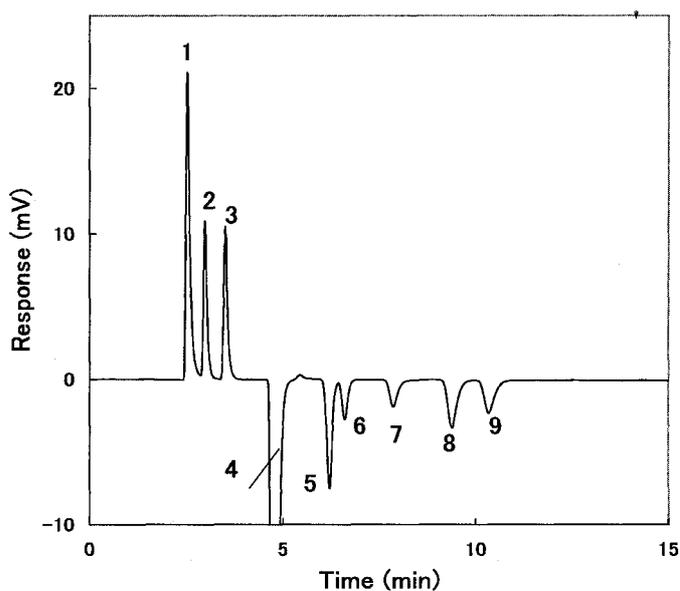


Fig. 3

Simultaneous ion-exclusion and cation-exchange chromatogram obtained from the anions and cations by elution with 6 mM tartaric acid and 3 mM 18-crown-6. Other conditions as for Fig. 2. Peaks: 1, SO_4^{2-} ; 2, Cl^- ; 3, NO_3^- ; 4, elution dip; 5, Na^+ ; 6, NH_4^+ ; 7, K^+ ; 8, Mg^{2+} ; 9, Ca^{2+}

Analytical Performance

Calibration graphs were constructed by plotting peak area against concentration of anion or cation under the optimum conditions. Linear plots

were obtained in the concentration ranges 0.01–5 mM for anions ($r^2 = 0.9999$ for SO_4^{2-} , 0.9990 for Cl^- , and 0.9998 for NO_3^-) and 0.01–5 mM for cations ($r^2 = 0.9999$ for Na^+ , 0.9990 for NH_4^+ , 0.9989 for K^+ , 0.9995 for Mg^{2+} , and 0.9991 for Ca^{2+}). Detection limits ($S/N = 3$) ranged from 0.14 to 0.30 μM for anions and from 0.18 to 0.61 μM for cations.

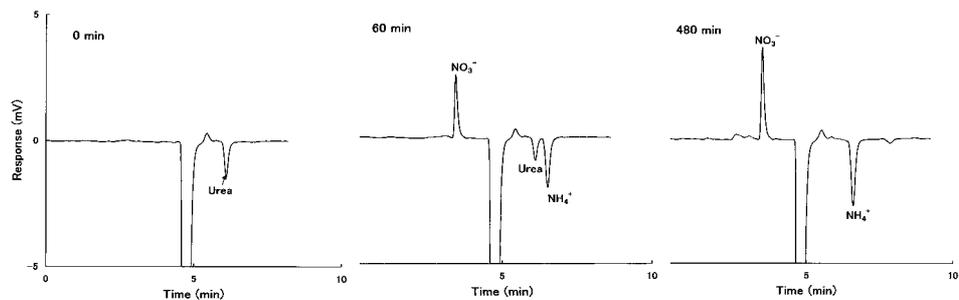
In replicate chromatographic analyses ($n = 15$) relative standard deviations of retention times of analyte samples under the optimum condition were 0.1–0.3%; those for peak area were 1.1–2.6%. Day-to-day reproducibility over 7 days was also high (0.2–0.5% for retention time and 1.3–3.3% for peak area).

Application of IEC/CEC to Photooxidation of Nitrogen Compounds on a TiO_2 Photocatalyst

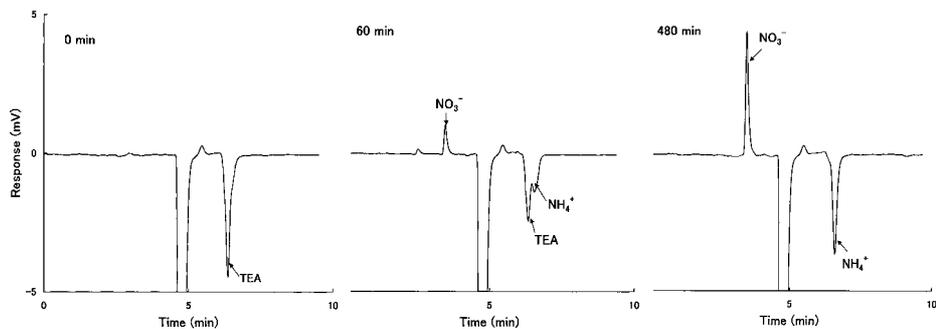
Formation of NH_4^+ and NO_3^- by decomposition of the organic nitrogen compounds on a TiO_2 photocatalyst with a UV irradiation time of 8 h was monitored using IEC/CEC. As shown in Fig. 4, peaks corresponding to urea and triethanolamine (TEA) eluted before that of NH_4^+ ; in contrast, the trimethylamine (TMA) peak eluted after that for NH_4^+ . The concentrations of the starting compounds were reduced by photooxidation, by amounts depending on irradiation time, with formation of NH_4^+ and NO_3^- . TEA and urea were clearly converted to both NH_4^+ and NO_3^- whereas TMA was predominantly converted to NH_4^+ rather than NO_3^- , as shown in Fig. 4.

The mechanisms of formation of NH_4^+ and NO_3^- by photooxidation of each ionic nitrogen compound have been discussed by many authors [1–6]. It has been inferred that in the decomposition of nitrogen compounds adsorbed on the surface of the photocatalyst under alkaline conditions the rate of C–N bond cleavage in a molecule is faster than that of either the C–C or C–H bonds in hydrocarbon groups [1–4]. Figure 5 shows the dependence on irradiation time of the decrease in concentration of compounds with C–N bonds. It has been suggested that nitrogen compounds with an hydroxylated nitrogen moiety are predominantly converted to NO_3^- [3]. Figure 5 shows that urea, with hydroxylated nitrogen, was more readily converted into NO_3^- than TMA, which has no hydroxylated nitrogen. Similarly, TEA, with hydroxyl groups was also efficiently converted into NO_3^- , possibly because the presence of the hydroxyl group supports production of NO_3^- .

Urea



TEA



TMA

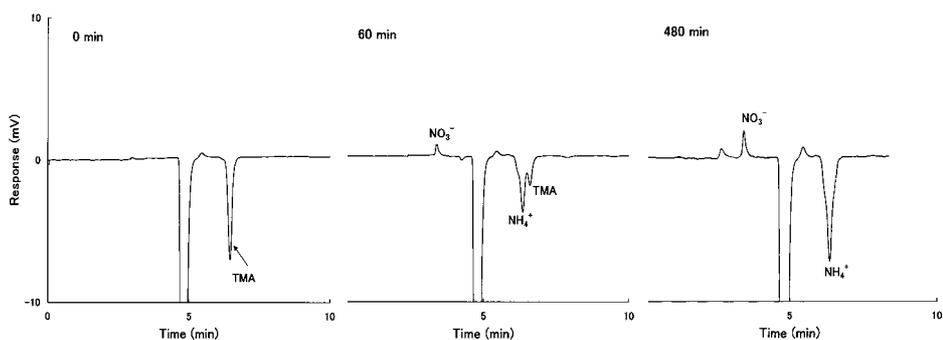


Fig. 4

Combined ion-exclusion and cation-exchange chromatograms obtained from nitrogen compounds after UV irradiation for different times in the presence of a TiO_2 photocatalyst. The test compounds were urea (top), TEA (middle), and TMA (bottom). The concentration of nitrogen in the tested sample was 0.1 mM. The amount of TiO_2 photocatalyst was 50 g in 400 mL 0.1 mM test solutions. The solution was circulated at 300 mL min^{-1} . IEC/CEC conditions were as for Fig. 3

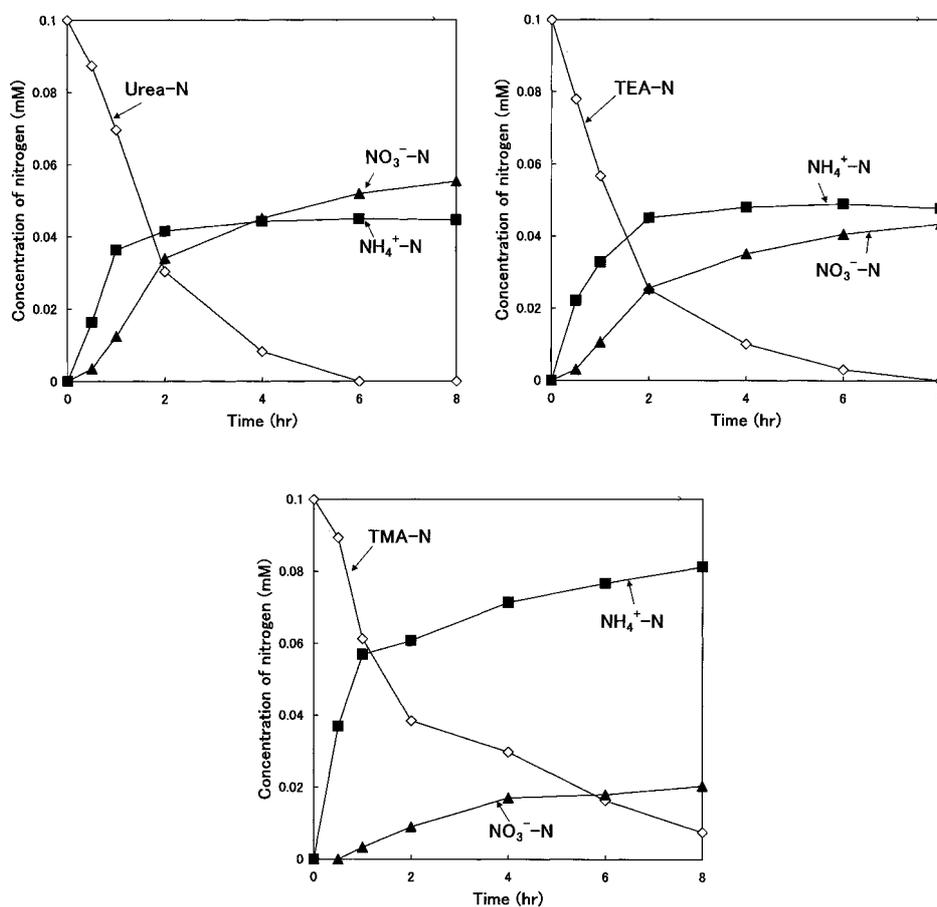


Fig. 5

Time-dependence of changes in the concentrations of organic nitrogen compounds, NH_4^+ and NO_3^- , as nitrogen, on UV irradiation. The conditions used for photodegradation and IEC/CEC separation were the same as for Fig. 4

The efficiencies of conversion into NH_4^+ and NO_3^- , calculated as the concentrations of nitrogen atoms produced by photooxidation of the three nitrogen compounds for 8 h (initial nitrogen atom concentration, C_0 , = 0.1 mM) are listed in Table I. Because of incomplete decomposition of the compounds and their intermediates, conversion efficiency was below 100%. Determination of the intermediates arising from the samples tested, e.g. methylamine and dimethylamine from TMA, will enable more detailed understanding of the photooxidation process in water.

Table I

Efficiency of conversion of nitrogen atoms into NH_4^+ and NO_3^- by photodegradation of urea, triethanolamine, and trimethylamine

Sample	Conversion (%) after 8 h		
	NH_4^+	NO_3^-	Total
Urea	42	54	96
Triethanolamine	44	39	83
Trimethylamine	77	17	94

CONCLUSION

By use of simultaneous IEC/CEC anions and cations formed by photooxidation of inorganic and organic nitrogen compounds in the presence of a TiO_2 photocatalyst have been successfully monitored. As a result, the process of photocatalytic decomposition of organic nitrogen was found to depend on their chemical structure. In future work the methods developed here will be applied to compounds with different atoms and structure.

ACKNOWLEDGMENT

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