Water quality monitoring system for determination of ionic nutrients by ion-exclusion chromatography with spectrophotometric detection on cation- and anion-exchange resin columns using water eluent

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Abstract A unified ion-exclusion chromatography (IEC) system for monitoring anionic and cationic nutrients like NH$_4^+$, NO$_3^-$, NO$_2^-$, phosphate ion$^-$ silicate ion and HCO$_3^-$ was developed and applied to several environmental waters. The IEC system consisted of four IEC methodologies including the IEC with ultraviolet (UV) detection at 210 nm for determining NH$_4^+$ on anion-exchange separation column in OH$^-$ form connected with anion-exchange UV-conversion column in I$^-$ form in tandem, the IEC with UV-detection at 210 nm for determining simultaneously NO$_3^-$ and NO$_2^-$ on cation-exchange separation column in H$^+$ form, the IEC with UV-detection at 210 nm for determining HCO$_3^-$ on cation-exchange separation column in H$^+$ form connected with anion-exchange UV-conversion column in I$^-$ form in tandem, and the IEC with visible-detection based on molybdenum-blue reaction for determining simultaneously silicate and phosphate ions on cation-exchange separation column in H$^+$ form. These IEC systems were combined through three manually driven 6-port column selection valves to select each separation column to determine selectively the ionic nutrients. Using this sequential water quality monitoring system, the analytical performances such as calibration linearity, reproducibility, detection limit and recovery were also tested under the optimized chromatographic conditions. This novel water quality monitoring system has been applied successfully for the determination of the ionic eutrophication components in sub-urban river waters.

Key words ion-exclusion chromatography, IEC, anionic and cationic nutrients, column selection valve, water eluent

CLC number O658 Document code A Article IC 1000-8711 201207-0721-07

In recent years the eutrophication has been recognized to be a serious aquatic environmental issue. The eutrophication phenomenon is caused by the increase of the concentrations of the ionic nutrients such as NH$_4^+$, NO$_3^-$, NO$_2^-$, silicate ion, phosphate ion and HCO$_3^-$ alkalinity inorganic carbon source in environmental waters. These ionic nutrients increase in environmental water because of the increasing human activities such as agriculture, industrial production, urbanization etc.

Generally NH$_4^+$, NO$_3^-$, NO$_2^-$, silicate ion, phosphate ion and HCO$_3^-$ could be determined individually by official analytical methods 1, 2. However these methods are often complicated, non-simultaneous/sequential determination and time...

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Foundation item This study was financially supported from TOSOH Corporation and Fellowships Program for Young Scientists of the Japan Society for the Promotion of Science on FY2011.

Received date 2012-02-22
consuming. Therefore the development of a convenient and highly sensitive technique for the simultaneous/sequential determination of these ionic nutrients is very important for estimating and evaluating the eutrophication effects.

In this study a new convenient water quality monitoring system for sequential determination of anionic and cationic eutrophication components by ion-exclusion chromatography with spectrophotometric detection on cation- and anion-exchange resin columns in parallel using water as the common eluent was developed.

The system is consisted of the 4 ion-exclusion chromatographic IEC methodologies including the IEC with ultraviolet UV-detection at 210 nm for determining NH₄⁺ on anion-exchange separation column in OH⁻ form connected with anion-exchange UV-conversion column in I⁻ form in tandem the IEC with UV-detection at 210 nm for determining simultaneously NO₃⁻ and NO₂⁻ on cation-exchange separation column in H⁺ form the IEC with UV-detection at 210 nm for determining HCO₃⁻ on cation-exchange separation column in H⁺ form connected with anion-exchange UV-conversion column in I⁻ form in tandem and the IEC with visible-detection based on molybdenum-blue reaction for determining simultaneously silicate and phosphate ions on cation-exchange separation column in H⁺ form using water eluent alone

These IEC systems were combined through three manually-driven 6-port column selection valves to select the suitable separation column for determining the ionic eutrophication components. The fluctuation of the anions’ and cations’ concentrations due to the influx of the treated water emitted from a biological sewage treatment plant was evaluated in terms of the biological activity by applying the monitoring system.

1 Experimental

1.1 instrumentation

The monitoring system consisted of an eluent delivering pump a sample injector a sample injector a sample injector IC-2001 an oven for each column and reaction coil Toish CO-8020 and two spectrophotometric detectors set at 210 and 700 nm Toish UV-8020. Reactant mixture 50 mmol/L sulfuric acid-10 mmol/L sodium molybdate for determination of phosphate and silicate was delivered by an HPLC pump Toish DP-8020. Reducing agent 50 mmol/L ascobic acid was delivered by an HPLC pump Shimadzu LC-10AD. The flow line was made from polyetheretherketone tube 0.25 mm I. D. Two reaction coils 6.0 m x 0.25 mm I. D. were made from polytetrafluoroethylene tube. The apparatus was controlled by an IC workstation Toish IC-WS Data Processor. To switch the separation and conversion columns three 6-port column selection valves Toish UV-8020 were used.

1.2 Columns

The separation column for NO₃⁻ NO₂⁻ HCO₃⁻ phosphate ion and silicate ion was Toish TSKgel SuperIC-A/C 150 mm x 6 mm I. D. packed with polymethacrylate-based weakly acidic cation-exchange resin in the H⁺ form. The separation column for NH₄⁺ was Toish TSKgel DEAE-5PW 150 mm x 6 mm I. D. packed with polymethacrylate-based weakly basic anion exchange resin in the OH⁻ form. To convert counter anion of analyte cation into I⁻ form a Toish TSKgel SAX column 50 mm x 4.6 mm I. D. packed with polymethacrylate-based strongly basic anion exchange resin in the I⁻ form was used. These separation columns and UV-conversion columns were selected by using three 6-port column selection valves and were kept in the column oven operated at 40 °C.

1.3 Reagents

All reagents of analytical grade Wako Chemical Co. Japan were used as received. The sample stock solutions of NO₃⁻ NO₂⁻ HCO₃⁻ and NH₄⁺ were prepared at 0.1 mol/L. The sample stock solutions of phosphate ion 1000 mg/L of P⁻ and silicate ion 1000 mg/L of Si⁴⁺ were prepared with the commercial standard solutions. The mixture of sulfuric acid and sodium molybdate was prepared as a color-forming reactant for
the molybdenum-blue method. Ascorbic acid solution was prepared as a reducing agent and stored in a foil-wrapped polyethylene bottle. This solution was stable at least for 24 h. The ultra pure water > 18 MΩ cm Millipore Co. was used as the eluent and for the preparation of the solutions.

1.4 River waters
Kurose River 238.8 km² of the flow passage area 50.6 km of the river channel length flows through the center of Higashi-Hiroshima City Hiroshima Prefecture. The pollution from a sewage treatment plant contributes significantly to the river in the middle stream and the river flows into Seto Inland Sea 13 14. The river water samples n = 14 were collected from the upstream to the downstream of the Kurose River watershed on 25th September 2010. After filtration through a hydrophilic polytetrafluoroethylene syringe filter with 0.2 μm pore size DISMIC®-25HP Advan-tec Toyo Kaisha Ltd. the water samples were stored in a dark room at 5 °C until analysis.

2 Results and Discussion

2.1 Separation mechanism of IEC for ionic nutrients

2.1.1 Determination of HCO₃⁻
As shown in Fig. 1 the solid flow line was used for the determination of HCO₃⁻ which was separated from other anions as the corresponding acids H⁺-HCO₃⁻ on a weakly acidic cation-exchange resin column Column-A TSKgel SuperIC-A/C in the H⁺ form based on the ion-exclusion mechanism difference of the pKᵣ values. After separation H⁺-HCO₃⁻ was converted to H⁺- I⁻ on a strongly basic anion-exchange resin column Column-B TSKgel SAX in the I⁻ form by ion-exchange mechanism and was detected by a spectrophotometric detector set at 210 nm 3.

![Diagram](image-url) Fig. 1 Schematic diagram for the determination of HCO₃⁻ and its typical ion-exclusion chromatogram

Eluent water flow rate of the eluent delivering pump 0.4 mL/min. Column-A separation column TSKgel SuperIC-A/C 150 mm x 6 mm I.D. Column-B UV-conversion column TSKgel-SAX 40 mm x 6 mm I.D. Column temperature 40 °C.

2.1.2 Determination of NO₃⁻ and NO₂⁻
As shown in Fig. 2 the solid flow line was used
for the determination of NO\textsuperscript{3-} and NO\textsubscript{2} which were separated as the corresponding acids H\textsuperscript{+}-NO\textsubscript{3} and H\textsuperscript{+}-NO\textsubscript{2} on a weakly acidic cation-exchange resin column \(\text{Column-A} \) TSKgel SuperIC-A/C in the H\textsuperscript{+} form based on the ion-exclusion mechanism and were detected selectively by a spectrophotometric detector set at 210 nm \(3 - 7\) mm.

### 2.1.3 Simultaneous determination of phosphate and silicate ions

As shown in Fig. 2 the solid flow line was used for the determination of phosphate and silicate ions which were separated from other anions as the corresponding acids on a weakly acidic cation-exchange resin column \(\text{Column-A} \) TSKgel SuperIC-A/C in the H\textsuperscript{+} form based on the ion-exclusion mechanism. After the separation the reduced complexes of the molybdate with phosphate and silicate ions were formed based on molybdenum-blue reaction and these complexes were determined selectively by a spectrophotometric detector set at 700 nm \(8 - 12\) nm.

### 2.1.4 Determination of NH\textsubscript{4}\textsuperscript{+}

As shown in Fig. 3 the solid flow line was used for the determination of NH\textsubscript{4}\textsuperscript{+} which was separated from other cations as the corresponding bases \(\text{NH}_{4}^{+}\cdot\text{OH}^{-}\) on a weakly basic anion-exchange resin column \(\text{Column-C} \) TSKgel DEAE-5PW in the OH\textsuperscript{-} form based on the ion-exclusion mechanism difference of the pK\textsubscript{a} values of the bases. NH\textsubscript{4}\textsuperscript{+}\cdot\text{OH}^{-} was converted to NH\textsubscript{4}\textsuperscript{+}\cdot\text{I}^{-} on a strongly basic anion-exchange resin column \(\text{Column-D} \) TSKgel SAX in the I\textsuperscript{-} form by the ion-exchange mechanism and was detected by a spectrophotometric detector set at 210 nm \(3 - 6\) mm.

### 2.2 Analytical performance

Under the present optimized chromatographic
conditions the calibration curves of peak areas to the concentrations were linear in the range of $0.001 - 1.000 \text{ mmol/L}$, correlation coefficient $r^2 = 0.987$ for $\text{NH}_4^+$, $0.990$ for $\text{NO}_3^-$, $r^2 = 0.999$ for $\text{NO}_2$. When adding $0.50 \text{ mmol/L}$ of $\text{NH}_4^+$ and $0.050 - 1.000 \text{ mmol/L}$ $\text{NO}_3^-$, the detection limits of the analyte ions were calculated at a signal/noise of $3\sigma$ for $\text{NH}_4^+$ at $10 \mu\text{mol/L}$, $\text{NO}_3^-$ at $24 \mu\text{mol/L}$, and $\text{HCO}_3^-$ at $44 \mu\text{mol/L}$. The relative standard deviations of the repeated chromatographic runs were in the range of 0.36% to 1.06% for these anions and cations.

### 2.3 Application to environmental water samples

The present IEC system was applied to the sequential determination of eutrophication components in the river water samples. As shown in Fig. 4, good IEC chromatograms of eutrophication components in the river water samples were obtained. When adding $0.50 \text{ mmol/L}$ of $\text{NH}_4^+$ and $0.050 - 1.000 \text{ mmol/L}$ of $\text{NO}_2$, the recoveries were in the range of 97.0% to 99.9%.

Fig. 5 shows the fluctuation of the concentrations of the eutrophication components in the river water.

$\text{NH}_4^+$ was not detectable at the sampling points 1 to 6. The concentration of $\text{NH}_4^+$ dramatically increased after the discharge from a biological sewage treatment plant located between sampling points 6 and 7 near the downtown site of Higashi-Hiroshima under the aerobic condition. Then the $\text{NH}_4^+$ concentration decreased at the sampling points 7 to 14 due to the biological nitrification reaction occurred under aerobic condition to form $\text{NO}_3^-$. 

![Diagram](image-url)
NO$_3^-$ the intermediate of biological nitrification reaction was undetectable. As shown in this result NH$_4^+$ was biologically oxidized to NO$_3^-$ rapidly and NO$_3^-$ was preset at very low concentration in the river water. Additionally it was reported that a slight amount of NO$_2^-$ was oxidized to NO$_3^-$ by H$^+$ derived from ion exchange resin in the separation column in previous paper. Therefore NO$_2^-$ was undetectable in these river water samples. In the future to reduce the effect of oxidation of NO$_2^-$ to NO$_3^-$ we will test the short weakly cation exchange resin column for separation column.

The concentration of NO$_3^-$ gradually increased from the upstream to the downstream sampling points 1 to 6 where the area was more urbanized. Especially the concentration of NO$_3^-$ dramatically increased after the discharge from the biological sewage treatment plant. It indicated that the discharge from the treatment plant was a significant source of inorganic nitrogen in the river watershed. The gradual decrease of NO$_3^-$ concentration after the treatment plant was due to the dilution effect of the river water.

The concentration of HCO$_3^-$ gradually increased from the upstream to the downstream sampling points 1 to 6 due to the effect of human activity. Then it decreased fairly toward the treatment plant as the inorganic-carbon source of nitrification reaction. The considerable decrease after the
treatment plant was due to the occurring of the biological nitrification. The concentration of HCO$_3^-$ increased after the treatment plant. The concentration of the phosphate ion increased drastically toward the treatment plant sampling points 1 to 7. The remarkable decrease of the phosphate ion concentration after the treatment plant sampling points 8 to 14 was due to the biological assimilation reaction to form biomass in the downstream of the river.

The concentration of the silicate ion was almost unchanged through the whole watershed of the river. It can be inferred that the silicate ion is insusceptible to human activity such as the discharge from a household or a waste treatment plant.

As a result the present monitoring system can be successfully applied for evaluating the water quality of the river watershed in terms of the eutrophication.

3 Conclusions

Using the IEC system equipped with 3 column selection valves and ultraviolet/visible detectors, the sequential/simultaneous and selective water quality monitoring of ionic nutrients such as NH$_4^+$, NO$_3^-$, NO$_2^-$, HCO$_3^-$, silicate and phosphate ions was achieved using water alone as the eluent. The water quality evaluation for eutrophication in sub-urban river watershed is possible by applying the IEC-water quality monitoring system.

References

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