Water quality monitoring of Jialing-River in Chongqing using advanced ion chromatographic system

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Abstract The water quality monitoring operation to evaluate the water quality of polluted river is an extremely important task for the river-watershed management/control based on the environmental policy. In this study, the novel simple and convenient water quality monitoring of Jialing-River in Chongqing, China was carried out using an advanced ion chromatography (IC) consisting of ion-exclusion/cation-exchange chromatography (IEC/CEC) with conductivity detection for determining simultaneously the common anions such as SO4\(^{2-}\), Cl\(^{-}\) and NO3\(^{-}\) and the cations such as Na\(^{+}\), NH\(_4\)\(^{+}\), K\(^{+}\), Mg\(^{2+}\) and Ca\(^{2+}\) the ion-exclusion chromatography (IEC) with visible detection for determining simultaneously the nutrient components such as phosphate and silicate ions and the IEC with the enhanced conductivity detection using a post column of K\(^{+}\)-form cation-exchange resin for determining HCO\(_3\)-alkalinity as an inorganic-carbon source for biomass synthesis in biological reaction process under the aerobic conditions. According to the ionic balance theory between the total equivalent concentrations of anions and cations the water quality evaluation of the Jialing-River waters taking at different sampling sites in Chongqing metropolitan area was carried out using the advanced IC system. As a result, the effectiveness of this novel water quality monitoring methodology using the IC system was demonstrated on the several practical applications to a typical biological sewage treatment plant on Jialing-River of Chongqing.

Key words advanced ion chromatography, water quality monitoring/evaluation, Jialing-River

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Recently, there are serious aquatic environmental pollution problems not only in developed countries but also in developing countries. Especially, the great-river stream in the developing country like China is facing by the serious water pollution problems due mainly to the remarkably increased human-activity including industrialization and urbanization. Therefore, the water quality monitoring operation using the advanced water quality monitoring system is an extremely important task for the effective river-water quality management/control. In such context, ion chromatography (IC) technologies which have been authorized internationally as the official analytical methods such as the standard methods United States Environmental Protection Agency US-EPA Japanese Industrial Standards JIS and International Organization for Standardization ISO have been world-wide applied to the water quality monitoring of various environmental waters including river-water. Ideally, the innovation of several advanced IC methodology enabling simple, convenient, highly sensitive, simultaneous and low-cost water quality monitoring is required for enhancing the capacity of river-water quality management/control.

For the water quality evaluation of common river-water it has been shown that the ionic balance between these anionic and cationic components is almost unity \(\sim 1.0\) suggesting that other ionic components make an insignificant contribution. Therefore, this ionic balance theory is an extremely important concept in terms of water quality evaluation in aquatic environment chemistry as shown in the following equation using the equivalent concentration based on the principle of...
electro-neutrality.

Ion balance \( \sum \text{anions} = \sum \text{cations} - \text{Unity} \div 1 - 4 \div \)

In this study, the novel simple convenient simultaneous water quality monitoring system was applied to Jialing-River in Chongqing by using the advanced IC system consisting of ion-exclusion chromatography/cation-exchange chromatography (IEC/CEC) with conductivity detection for determining simultaneously the common anions such as \( \text{SO}_4^{2-} \), \( \text{Cl}^- \), and \( \text{NO}_3^- \) and the cations such as \( \text{Na}^+ \), \( \text{NH}_4^+ \), \( \text{K}^+ \), \( \text{Mg}^{2+} \), and \( \text{Ca}^{2+} \) 1 - 4 the IEC with visible detection for determining simultaneously phosphate and silicate ions as the nutrient components 5 6 and the IEC with enhanced conductivity for determining \( \text{HCO}_3^- \) alkalinity as an inorganic-carbon source 7 10 based on the “Ionic Balance Theory” for the common environmental waters.

In this paper, the effectiveness of water quality monitoring system of common anions cations nutrient components and \( \text{HCO}_3^- \) alkalinity using the advanced IC methodology introducing the novel separation and detection technologies to the several practical applications regarding the water quality monitoring of urban Jialing-River waters in Chongqing China is described.

1 Experimental

1.1 Instrumentation

A Tosoh IC-2001 non-suppressed ion chromatographic system with conductivity detection on a weakly acidic cation-exchange resin column in the H’-form TSKgel Super IC-A/C at 40 °C invented by us Japanese Patent No. 20557522 was used by elution with dilute tartaric acid-crown ether aqueous solution at 1.0 mL/min for the simultaneous determination of common anions and cations 4.

A Tosoh IC-2001 with spectrophotometric detection at 700 nm on the TSKgel Super IC-A/C column at 40 °C was used by elution with water at 0.4 mL/min for the simultaneous determination of phosphate and silicate ions 5.

A Tosoh IC-2001 with enhanced conductivity detection on the TSKgel Super IC-A/C column at 40 °C was used by elution water at 0.4 mL/min for the determination of \( \text{HCO}_3^- \) alkalinity. In this system to enhance the conductivity of carbonic acid eluted from the separation column a conductivity enhancement column packed with TSKgel SCX in the K’-form is placed between the separation column and the conductimetric detector for the determination of \( \text{HCO}_3^- \) alkalinity 8.

The results were acquired and analyzed by a Tosoh IC work station.

1.2 Chemicals

Commercially available chemicals were used for preparing standard solutions eluents and color-forming reactant using de-ionized water > 18 MΩ cm.

1.3 Sampling sites and pretreatment

River-water samples were collected at ca. 10AM on summer season of 2011 for both upstream and downstream river-waters at typical urban sewage treatment plant with activated sludge process for biochemical oxygen demand and chemical oxygen demand BOD/COD removal under the aerobic conditions placed on Jialing-River of Chongqing metropolitan area and then the river-water samples were air-transported to our laboratory. This biological treatment plant constructed in 1997 is currently facing the over-loading situation by several pollutants due mainly to the increased urbanization and industrialization in Chongqing. The water quality of river-water samples after onsite filtration with 0.2-μm membrane filters were determined for the common anions cations phosphate silicate and \( \text{HCO}_3^- \) alkalinity by applying the advanced IC system.

2 Results and discussion

2.1 Simultaneous determination of common anions and cations by IEC/CEC

As described in the previous papers the IEC/CEC is recognized to be effective water quality monitoring method to various environmental water samples 1 4. As shown in Fig. 1a a good simultaneous separation of common anions and cations standard solution was obtained in ca. 6 min using the IEC/CEC by elution with 5
mmol/L tartaric acid-4 mmol/L 18-crown-6 at pH ca. 2.6. Under the optimized IEC/CEC conditions, the calibration linearity, $r^2$, ranged from 0.998 to 0.999 for both the anions and cations. The detection limits at signal-to-noise ratio $S/N = 3$ ranged from 0.14 to 0.30 $\mu$mol/L for the anions and 0.18 to 0.61 $\mu$mol/L for the cations. In the repeated IEC/CEC runs, $n = 15$, the reproducibilities, relative standard deviation, RSD, for the anions and cations were 0.1% - 0.3% for retention times and 1.1% - 2.6% for peak areas. The satisfactory analytical performance results were the same as those in the previous papers obtained using this advanced IC 1-4.

Similarly, as shown in Figs. 1b and 1c, a good IEC/CEC separation was also obtained for the water quality monitoring of urban river-waters of Jialing-River in Chongqing. Interestingly, the water quality was significantly different between the upstream and downstream river-waters before and after the biological sewage treatment plant. Especially, the concentration of NH$_4^+$ in the downstream river-water after the biological sewage treatment plant was remarkably higher than that in the upstream river-water. This increase meant that the NH$_4^+$ formed from the nitrogen-containing BOD/COD components in urban sewage largely discharged directly into the Jialing-River. Whereas, the concentrations of NO$_3^-$ were almost unchanged between the upstream and downstream river-waters. This result meant that at least the biological nitrification reaction to form NO$_3^-$ from NH$_4^+$ was extremely poor in the sewage treatment process containing various BOD/COD components.

2.2 Simultaneous determination of phosphate and silicate ions by IEC

As described in the previous papers, the IEC is recognized to be effective water quality monitoring method to nutrients such as phosphate and silicate ions in various environmental water samples, 1-3. As shown in Fig. 2a, the good simultaneous separation for both phosphate and silicate ions was obtained in ca. 15 min using the IEC eluted with water. The satisfactory separation and highly sensitive visible detection at 700 nm were obtained for both the phosphate and silicate ions. Under this optimized chromatographic conditions, the calibration linearity, $r^2$, were 0.999 in the range of 50 – 2000 $\mu$g/L for phosphate-P and 0.999 for silicate-Si in the range of 250 – 10 000 $\mu$g/L. The detection limits at $S/N = 3$ ranged from 1.5 $\mu$g/L for phosphate-P and 8.7 $\mu$g/L for silicate-Si. In the repeated IEC runs, $n = 15$, the reproducibilities, RSD, for phosphate and silicate ions was 0.41% – 0.30% for retention times and 1.05% – 1.15% for peak areas, 5.
The satisfactory analytical performance results were the same as those in the previous papers obtained using this advanced IEC

![Graph a](image)

![Graph b](image)

![Graph c](image)

Fig. 2 Simultaneous separation of phosphate and silicate ions by IEC eluted with water.

- a. standard solution 0.8 mg/L phosphate-P and silicate-Si for each b. upstream river-water before biological sewage treatment plant on Jialing-River c. downstream river-water after biological sewage treatment plant on Jialing-River.

IC conditions injected volume 200 μL the other IC conditions are the same as in Fig. 1.

Peaks 1. phosphate ion 2. silicate ion.

As can be seen from Figs. 2b and 2c a good water quality monitoring was also obtained for phosphate and silicate ions in the urban rivers.

interaction for metal species in the river-water containing soil/clay materials to phosphate ion in Jialing-River watershed.

2.3 Determination of bicarbonate-alkalinity by IEC

It is known that HCO$_3^-$-alkalinity is the inorganic carbon source absolutely needed for biomass synthesis in biological nitrification of NH$_4^+$. As shown in Fig. 3a a good IEC separation and highly sensitive enhanced conductimetric determination for HCO$_3^-$-alkalinity was obtained in ca. 13 min when using only water as the eluent at 0.4 mL/min.

![Graph a](image)

![Graph b](image)

![Graph c](image)

Fig. 3 Separation of bicarbonate-alkalinity obtained by IEC eluted with water.

- a. standard solution 0.5 mmol/L HCO$_3^-$-alkalinity b. upstream river-water before biological sewage treatment plant on Jialing-River c. downstream river-water after biological sewage treatment plant on Jialing-River.

IC conditions injected volume 30 μL eluent flow rate 0.4 mL/min.

Peaks 1. strong acid anions such as SO$_4^{2-}$, Cl$^-$, and NO$_3^-$ 2. bicarbonate-alkalinity.
Under the optimized IEC conditions, the calibration linearity \( r^2 \) was 0.999 in the range of 0.005 – 10.0 mmol/L for bicarbonate-alkalinity which could expand rather than in the previous study 0.05 – 8.20 mmol/L [8]. The detection limits at S/N = 3 were 1.5 μmol/L for bicarbonate-alkalinity. In the repeated IEC runs \( n = 6 \) by injecting 5 μmol/L bicarbonate-alkalinity the reproducibility RSD was 0.92% for retention times and 0.15% for peak areas [8]. The satisfactory analytical performance results were the same as those in the previous papers obtained using this advanced IC [6][7].

Similarly as can be seen from Figs. 3b and 3c, a good IEC separation and highly sensitive enhanced conductivity detection were also practically obtained for HCO\(_3^-\)-alkalinity in the Jialing-River-water samples.

The concentrations of HCO\(_3^-\)-alkalinity were unchanged between the upstream and downstream river-waters before and after the biological sewage treatment plant. This no-change in the concentrations meant that the HCO\(_3^-\)-alkalinity as the inorganic carbon-source was not needed in the poor biological nitrification reaction to form NO\(_3^-\) from NH\(_4^+\) in the biological sewage treatment plant.

### 2.4 Water quality evaluation of Jialing-River before and after the sewage treatment plant

The water quality such as common anions, cations, phosphate ion, silicate ion, bicarbonate-alkalinity was evaluated using the analytical results obtained by the three advanced IC systems developed here as shown in Table 1.

The concentrations of common anions and cations were almost the same as those between the upstream and downstream river waters. Whereas the concentration of NH\(_4^+\)-N was 0.007 mmol/L for the upstream river water before biological sewage treatment plant and 0.029 mmol/L for the downstream river water after the biological sewage treatment plant. This concentration difference meant that the treated water discharged from the biological sewage treatment plant was the significant pollution source for NH\(_4^+\)-N due to the incomplete biological nitrification.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Upstream river water(^{[1]})</th>
<th>Downstream river water(^{[2]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO(_4^{2-})</td>
<td>0.379</td>
<td>0.381</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>0.182</td>
<td>0.187</td>
</tr>
<tr>
<td>NO(_3^-)</td>
<td>0.122</td>
<td>0.124</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>0.286</td>
<td>0.292</td>
</tr>
<tr>
<td>NH(_4^+)</td>
<td>0.007</td>
<td>0.029</td>
</tr>
<tr>
<td>K(^+)</td>
<td>1.089</td>
<td>1.092</td>
</tr>
<tr>
<td>Mg(^2+)</td>
<td>0.329</td>
<td>0.332</td>
</tr>
<tr>
<td>Ca(^2+)</td>
<td>0.051</td>
<td>0.051</td>
</tr>
<tr>
<td>Phosphate, H(_2)P(_2\O_7)(^{2-})</td>
<td>0.013</td>
<td>0.024</td>
</tr>
<tr>
<td>Silicate, HSIO(_4)(^2-)</td>
<td>0.255</td>
<td>0.275</td>
</tr>
<tr>
<td>Bicarbonate-alkalinity</td>
<td>1.566</td>
<td>1.573</td>
</tr>
</tbody>
</table>

**Ionic balance** = \( \Sigma \text{anions}/\Sigma \text{cations}\)^\(^{[3]}\)

- **1** The upstream river water samples were taken before urban biological sewage treatment plant on Jialing-River of Chongqing.
- **2** The downstream river water samples were taken after urban biological sewage treatment plant on Jialing-River of Chongqing.
- **3** The ionic balance was calculated from values of equivalent concentration for each ion.

According to official information by this biological sewage treatment plant at summer season of 2011, since the water quality of biologically treated water discharged into Jialing-River were 5.6/28.0 mg/L for BOD/COD and 7.7 for pH, the biological treatment process management/control was judged to be reasonable for BOD removal and pH. However, it is estimated that the much higher COD 28.0 mg/L compared to BOD 5.6 mg/L as well as the increased concentration of NH\(_4^+\)-N were caused by both of the almost complete biological oxidation reaction for the BOD/COD as well as the incomplete biological nitrification reaction to NO\(_3^-\)-N of NH\(_4^+\)-N appeared from the nitrogen containing BOD/COD substances in the biological treatment process under the aerobic conditions.

Therefore, the additional biological nitrification process to convert completely ammonium ion to nitrate ion after the BOD/COD treatment process should be introduced and the optimization of process control parameters like DO, dissolved oxygen and ORP oxidation reduction potential should be carried out to enhance the capacity of water quality management to the Jialing-River watershed.
For the concentration of phosphate ions there was significant difference between the upstream water 0.013 mmol/L and the downstream water 0.024 mmol/L. This large concentration difference meant that the biological digestion reaction to utilize phosphate ion in the biomass synthesis reaction under the aerobic conditions was very poor. Therefore a coagulation process for phosphorus removal/recovery should be introduced to enhance the capacity of water quality management to the urban Jialing-River watershed.

The concentrations of silicate ion were 0.255 mmol/L for the upstream river water and 0.275 mmol/L for the downstream river water respectively. This small difference between the upstream and downstream waters might be caused by the difference in water source.

The concentrations of bicarbonate-alkalinity were almost unchanged between the upstream 1.566 mmol/L and the downstream 1.573 mmol/L river waters. This will be caused by the poor biological nitrification at the BOD/COD-based biological sewage treatment process.

When calculating the ionic balance between the total equivalent concentrations of anions and cations including nutrients and bicarbonate-alkalinity on the upstream and downstream river waters obtained using the three advanced IC the values obtained were 1.352 for both river-waters. Although this result is satisfactory for the ionic balance theory as mentioned above the values of ionic balance were more than 1.0. This result means that there will be due mainly to the luck of IEC/CEC determination of heavy metal cations like Fe³⁺ in Jialing-River waters.

3 Conclusion

In this study to enhance the aquatic environmental management/control capacity on Chongqing area the advanced environmental monitoring technologies using the novel three IC systems were developed for water quality monitoring and several practical applications to Jialing-River with urban biological sewage treatment plant is carried out for the water quality evaluation.

As the results the water quality monitoring system using the novel and advanced IC technologies on Tosoh TSKgel Super IC-A/C column consisting of the IEC/CEC of common anions and cations using the tartaric acid-crown ether eluent at pH 2, 6 the IEC of phosphate and silicate ions using water eluent and the IEC of bicarbonate-alkalinity using water eluent was recognized to be useful and powerful tools on the several practical applications for evaluating the effect of treated water discharged from typical urban biological treatment plant in megacity like Chongqing.

In future work the feasibility study on a long-term water quality monitoring operation using the advanced IC system will be carried out continuously at different sampling places times seasons for enhancing the capacity of water quality management/control of Jialing-River watershed.

Acknowledgement

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References