Enhanced conductivity detection of common inorganic anions in electrostatic ion chromatography using water eluent

Daisuke KOZAKI1* Chao-Hong SHI1 Kazuhiko TANAKA12 Nobutake NAKATANI3

1. International Development and Cooperation[] Hiroshima University[[] Higashi-Hiroshima 739-8529[] Japan[]
2. Department of Chemistry[] Tsinghua University[] Beijing 100084[] China[]
3. Faculty of Environmental Systems[] Rakuno Gakuen University[] Ebetsu[] Hokkaido 069-8501[] Japan[]

Abstract[] To enhance the conductivity detection sensitivity of common anions[] Na-anions[] in electrostatic ion chromatography[] EIC[] by elution with water[] a conductivity enhancement column packed with strong acid cation exchange resin in the H-form was inserted between an octadecyl silane[] ODS]-silica separation column modified with zwitterionic surfactant[] CHAPS[] 3 3-cholamidopropyl]-dimethylammonio]-propanesulfonate[] and a conductivity detector. Specifically[] the Na-anion pairing is converted to H-anion pairing after the EIC separation and then detected sensitively by the conductivity detector. The effects of conductivity enhancement and suppression in the EIC by the enhanced conductivity detection were characterized for the common strong acid anions such as SO4 2- [] Cl - [] NO3 - [] I- and ClO4 - and weak acid anions such as F- [] NO2 - [] HCOO- [] CH3COO- and HCO3- . For the conductivity enhancement effect in the EIC[] it is found that the conductivity of measured for all strong acid anions[] Na-anions[] was enhanced according to the theoretical conductivity predicted for H-anions and that of the measured for weak acid anions was suppressed depending on their pK_a of H-anions. For the calibration linearity in the EIC[] the strong acid anions were linear[] r^2 = 0.99 - 1.00[] because the degree of dissociation is almost 1.0 over all the concentration range and that of the weak acid anions was non-linear because the degree of dissociation decreased by increasing the concentration of the weak acid anions. In conclusion[] the EIC by enhanced conductivity detection was recognized to be useful only for the strong acid anions in terms of conductivity detection and calibration linearity.

Key words[] electrostatic ion chromatography[] EIC[] common anions[] conductivity enhancement[] water eluent

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Ion chromatography[] IC[] has been commonly applied world-wide as a useful and powerful official analytical method to the water quality monitoring and the management of various environmental and industrial waters[] 1[].

When applying the conventional IC equipments to the water quality monitoring[] a lot of separation columns[] chemical reagents[] and prepared eluents are needed. Generally[] these items are costly.

In modern IC system equipped with an electrochemical eluent generator and an electrochemical eluent suppressor[] only water is used as eluent for the anion exchange separation of common anions. The water eluent is converted to LiOH eluent and this eluent is finally converted to pure water by the electrochemical suppressor after the anion exchange separation process. Therefore[] the ideal future IC is " water-eluent IC" without an electrochemical generator and a suppressor" like the modern Dionex IC.

In our previous work[] it is recognized that the electrostatic ion chromatography[] EIC[] by elution with water is a very simple and convenient tool for the determination of the common anions[] 2 - 10[]. Additionally[] the EIC using an ODS-sili-
ca gel column modified with zwitterionic surfactant has been demonstrated to be useful for monitoring environmental water like river water samples in our previous study\[10\]. The retentions of the common anions are depending on their ion-pairing form when using ODS-silica separation column modified with zwitterionic surfactant CHAPS[3] 3-cholamidopropyl\-dimethylammonio\-propanesulfonate. Generally the monovalent cations such as H\(^+\) Li\(^+\) Na\(^+\) K\(^+\) NH\(_4^+\) are employed as counter cations for the EIC separation of the common anions because the retention of H-anion is extremely strong due to the CHAPS column. On the other hand\[\] when conductivity detection is used in the EIC of H-anion pairing\[\] much higher conductivity detection sensitivity is expected because H\(^+\) is the highest equivalent conductance in monovalent cations group.

In this study\[\] to enhance the conductivity detection sensitivity of the common anions\[\] Na-anions\[\] in the EIC by elution with water\[\] a conductivity enhancement column packed with strong acid cation exchange resin in the H\(^-\)-form was inserted between the ODS-silica-CHAPS separation column and the conductivity detector. Namely the tested anions such as SO\(_4^{2-}\) Cl\(^-\) NO\(_3^-\) I\(^-\) ClO\(_4^-\) F\(^-\) NO\(_2^-\) HCOO\(^-\) CH\(_3\)COO\(^-\) and HCO\(_3^-\) were separated in the Na\(^+\)-form. These separated anions were converted H\(^+\)-form by using conductivity enhancement column and then detected by conductivity detector.

Using this novel EIC system by elution with water on ODS-silica-CHAPS\[\] the effects of conductivity enhancement and suppression are characterized for the common strong acid anions and weak acid anions. Additionally the linearity of calibration graphs was also characterized for the common strong acid anions and weak acid anions.

1 Experimental

1.1 Instrumentation
A Tosoh IC-2001 non-suppressed IC equipped with a non-metallic eluent delivery pump\[\] a conductivity detector\[\] an auto-sample injector\[\] 30 \(\mu\)L\[\] and a work station for data processing was used. A home-made Tosoh TSKgel ODS-100S column\[\] 150 mm \(\times\) 6 mm i. d. \[\] coated dynamically with CHAPS was used for the separation based on the EIC mechanism on elution with water at 0.2 mL/min to separate the Na-anion pairings.

A Tosoh TSKsupress IC-A column\[\] 50 mm \(\times\) 1 mm i. d. \[\] packed with a strong acid cation exchange resin in the H\(^+\)-form was used as the conductivity enhancement column to convert Na-anions to H-anions and the conductivity enhancement column was inserted between the separation column and the conductivity detector.

1.2 Modification of the column
A Tosoh TSKgel ODS-100S column\[\] 150 mm \(\times\) 6 mm i. d. \[\] was coated dynamically with 30 mmol/L CHAPS in water for about 60 min at a flow rate of 0.6 mL/min at 40 \(^\circ\)C. This column was chromatographically stable at least for 3 months without re-modification procedure.

The chemical structure of CHAPS is illustrated in Fig. 1\[\] from which it can be seen that it contains an anionic functional group\[\] a cationic functional group\[\] and a hydrophobic region which enables it to be retained strongly on the ODS-silica stationary phase\[\] 4\[\].

![Fig. 1 Chemical structure of CHAPS used for modifying surface of an ODS-silica gel column in EIC by elution with water](image)

CHAPS\[3\] 3-cholamidopropyl\-dimethylammonio\-propanesulfonate.

1.3 Reagents
All reagents were of analytical reagent-grade\[\] purchased from Wako Chemical Co. \[\] Osaka\[\] Japan\[\]. Some 0.1 mol/L stock solutions of the strong acid anions such as I\(^-\) ClO\(_4^-\) Cl\(^-\) SO\(_4^{2-}\) NO\(_3^-\) and weak acid anions such as F\(^-\) NO\(_2^-\) HCOO\(^-\) CH\(_3\)COO\(^-\) and HCO\(_3^-\) were prepared by dissolving their Na-form pairings in de-ionized water.
2 Results and discussion

2.1 Effect of conductivity enhancement column

To evaluate the effect of the conductivity enhancement column, the EIC with and without the enhancement column was studied.

Fig. 2 shows typical ion chromatograms of the strong acid anions with a and without b the enhanced conductivity detections. As can be expected from the conductivity enhancement mechanism, the conductivity responses for all of the strong acid anions were enhanced. Whereas those of the weak acid anions were remarkably decreased by the enhancement process due to the decrease in the degree of dissociation of their corresponding acids.

As shown in Table 1 when the Na-strong acid anions were injected into the separation column, the conductivity detected as H-anions was enhanced 3.25 times for $\text{SO}_4^{2-}$ and the enhancement ratio measured enhancement ratio/predicted enhancement ratio MER/PER was ca. 1.0 and the values of MER/PER of other strong acid anions were also between ca. 0.96 – 1.06 complete dissociation. Whereas the values of MER/PER of weak acid anions were between ca. 0.88 – 0.06 depending on their $pK_a$ incomplete dissociation.

![Enhanced EIC chromatograms of strong acid anions](image)

Sample concentration 1.0 mmol/L for each.

Peaks 1. $\text{SO}_4^{2-}$ 2. $\text{Cl}^-$ 3. $\text{NO}_3^-$ 4. $\text{I}^-$ 5. $\text{ClO}_4^-$.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Injected</th>
<th>Detected</th>
<th>PER $\text{H-anion/Na-anion}$</th>
<th>MER $\text{H-anion/Na-anion}$</th>
<th>Relative enhancement ratio</th>
<th>MER/PER</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{I}^-$</td>
<td>$\text{Na}$</td>
<td>$\text{HI}$</td>
<td>3.36</td>
<td>3.55</td>
<td>1.06</td>
<td>–10</td>
<td></td>
</tr>
<tr>
<td>$\text{ClO}_4^-$</td>
<td>$\text{NaClO}_4$</td>
<td>$\text{HClO}_4$</td>
<td>3.55</td>
<td>3.71</td>
<td>1.04</td>
<td>–8.6</td>
<td></td>
</tr>
<tr>
<td>$\text{Cl}^-$</td>
<td>$\text{NaCl}$</td>
<td>$\text{HCl}$</td>
<td>3.37</td>
<td>3.45</td>
<td>1.02</td>
<td>–8</td>
<td></td>
</tr>
<tr>
<td>$\text{SO}_4^{2-}$</td>
<td>$\text{Na}_2\text{SO}_4$</td>
<td>$\text{H}_2\text{SO}_4$</td>
<td>3.30</td>
<td>3.25</td>
<td>0.99</td>
<td>–3</td>
<td></td>
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<tr>
<td>$\text{NO}_3^-$</td>
<td>$\text{NaNO}_3$</td>
<td>$\text{HNO}_3$</td>
<td>3.46</td>
<td>3.60</td>
<td>1.04</td>
<td>–1.4</td>
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<td>$\text{F}^-$</td>
<td>$\text{NaF}$</td>
<td>$\text{HF}$</td>
<td>3.84</td>
<td>3.39</td>
<td>0.88</td>
<td>2.67</td>
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<tr>
<td>$\text{NO}_2^-$</td>
<td>$\text{NaNO}_2$</td>
<td>$\text{HNO}_2$</td>
<td>3.46</td>
<td>2.28</td>
<td>0.66</td>
<td>3.4</td>
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<tr>
<td>$\text{HCOO}^-$</td>
<td>$\text{NaHCOO}$</td>
<td>$\text{HCOOH}$</td>
<td>3.86</td>
<td>2.21</td>
<td>0.57</td>
<td>3.77</td>
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<tr>
<td>$\text{CH}_3\text{COO}^-$</td>
<td>$\text{NaCH}_3\text{COO}$</td>
<td>$\text{CH}_3\text{COOH}$</td>
<td>4.29</td>
<td>1.02</td>
<td>0.24</td>
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<tr>
<td>$\text{HCO}_3^-$</td>
<td>$\text{NaHCO}_3$</td>
<td>$\text{H}_2\text{CO}_3$</td>
<td>4.17</td>
<td>0.24</td>
<td>0.06</td>
<td>6.35</td>
<td></td>
</tr>
</tbody>
</table>

* Conductance value of predicted H-anion/Na-anion $\mu$S/cm. ** Peak area measurement of H-anion/Na-anion $\mu$S·s.

From the above results, the conductivity enhancement process in the EIC on elution with water was judged to be useful only for the strong acid anions.

2.2 Calibration graphs of strong and weak acid anions in EIC by enhanced conductivity detection

Generally, it is known that the calibration graph is linear for the strong acid anions and convexly non-linear depending on their $pK_a$ for the weak acid anions when the conductivity detector is used in suppressed IC like that from Dionex. This is because the strong acid anions are complete dissociation and the weak acid anions are incomplete
dissociation in neutral water.

The calibration graphs in the concentration range of 0—7.5 mmol/L in the EIC using the conductivity enhancement column on elution with water are constructed for both the strong and weak acid anions. As shown in Fig. 3 the calibration graphs of the strong acid anions were linear \( r^2 = 0.99 – 1.00 \) because the degree of dissociation is almost 1.0 all over the concentration range. Whereas the calibration graphs of the weak acid anions were non-linear and low conductivity. These are because the degree of dissociation is decreased by increasing the concentration of the weak acid anions.

![Calibration graphs of strong and weak acid anions in EIC by enhanced conductivity detection on elution with water](image)

**Fig. 3** Calibration graphs of strong and weak acid anions in EIC by enhanced conductivity detection on elution with water

From the above results we know that the conductivity enhancement process in the EIC on elution with water was judged to be useful only for the strong acid anions in terms of the calibration linearity.

3 Conclusions

As mentioned above the EIC on elution with water by the enhanced conductivity detection using the conductivity enhancement column packed with strong acid cation exchange resin in the H⁺-form was useful only for the strong acid anions in terms of both of the conductivity enhancement effect and the calibration linearity.

In the future this simple convenient and low-cost IC consisting of novel separation mechanism and detection system will be applied practically to real samples including environmental waters in developed and developing countries 11.

References

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