Recent Environmental Problems in Indonesia and the Application of Advanced Ion Chromatography to Water Quality Monitoring

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Abstract

The development of separation systems for the simultaneous determination of anions and cations in ion chromatography (IC) has been presented. The determination of these ionic species in various water samples is now an important matter to evaluate the water quality, due to the rapidly growing complexity of environmental problems such as increasing various type of pollutants, acid rain, hazardous waste and others, and it is an urge to find out a convenient and simple separation method that can be used for the routine purpose in their determination. The environmental problems in Indonesia have reached a very serious level and some ways should be found to overcome the problems. The simultaneous determination of anions and cations in a single run has been increasing at accelerating rate, because it is one of the most attractive topics in IC due to the saving of reagents and analysis time. This paper elucidated a separation system that consists of one pump, one injection valve, an anion-exchange column, a cation-exchange column, two 6-port switching valves or a single 10-port switching valve, and a conductivity detector.

Keywords: Detection Methods Developing, Ion Chromatography, Column Switching, Common Inorganic Ions, Peak Parking, Tunable Separation.
1. Introduction

The recent environmental problems have been presented at the 40th Seminar Program of The 21st Century Center of Excellence (COE) on the recent environmental problems in Indonesia and the application of advanced ion chromatography (IC) to water quality monitoring, held at the Hiroshima University. Since the scope of Indonesian environmental problems is too large, water pollution will be focused for the evaluation in this discussion paper. Air pollution may also be an important factor to be evaluated due to the continuously occurring acid rain. Therefore, these environmental water samples should be analyzed from time-to-time to ensure the real quality of the waters.

An analytical method known as IC is suitable for the analysis of a variety of inorganic and organic anions and cations. It is characterized by high selectivity and sensitivity. Even though IC is well-reported in various fields of applications, the present discussion will only focus on environmental analysis (e.g., water analysis) as one of the most important fields of application of IC.

The main focus of applications in environmental analytical chemistry is the qualitative and quantitative analysis of anions and cations in all kind of waters [1]. For example, the anions of interest involve fluoride, phosphate, nitrite, nitrate, chloride, bromide, sulfate, and others, whereas the cations of interest involve sodium, ammonium, potassium, magnesium, calcium, and others, from of which water quality depends, may be simultaneously determined and separated.

According to the Jakarta Post “water pollution has reached an alarming level due to the industrial, household and farmland wastes. Many factories, notably in some big cities in Indonesia like Riau and East Java, are still dumping their liquid waste to rivers, so are thousands of households in Jakarta, Surabaya, Medan and Makassar, while residues of fertilizers and pesticides have also damaged water resources in farmlands”. In the report of Indonesian State Ministry for the Environment is also reported to acknowledge that many factories continue to dump their liquid waste into rivers without treatment. A lack of regulations on agricultural chemicals has led to damage of water resources in Indonesian farmland.

2. Brief introduction of Indonesia

Indonesia is the largest archipelago in the world. It has an area of 1.91 million km² scattered over 17,508 islands. The main islands are Sulawesi (formerly Clebes), Java, Sumatra, Kalimantan (formerly Borneo), and Irian Jaya. Indonesia is the fourth most populous country in the world, with a population of more than 234 (2007 est.) million people with the population growth of 1.213% (2007 est.), and consisted of 309 ethnic groups and more than 200 local languages.

Administratively, Indonesia is divided into 30 provinces (propinsi-propinsi, singular-propinsi), two special regions (daerah-daerah istimewa, singular-daerah istimewa), and 1 special capital city district (daerah khusus ibukota).

Indonesian climate is definitely tropical. There is no autumn or winter and distinctive "dry" and "wet" seasons share the year. In April the "dry" season sets in, the temperature is ranging from 21 to 30 degrees Celsius.
Throughout Indonesia, there are ten major cities classified as metropolitan cities which have a population of more than a million people. The ten largest cities in Indonesia are Jakarta, Surabaya, Bandung, Medan, Bekasi, Tangerang, Semarang, Depok, Palembang, and Makassar.

3. Water quality and pollution
The terms water quality and pollution are important terms that should firstly be defined. Various definitions have been offered for water quality and pollution by many scientists.

Water quality reflects the composition of water as affected by natural causes and man’s cultural activities, expressed in terms of measurable quantities and related to intended water use. Water quality is perceived differently by different people, for example, a public health official is concerned with the bacterial and viral safety of water used for water drinking and bathing; aquatic scientists are concerned with the health of aquatic habitats.

The term pollution is a change in the physical, chemical, radiological, or biological quality of the resource (air, water, or land) caused by man or due to man’s activities that is injurious for existing, intended, or potential uses of the resource [2, 3].

4. Water pollution
4.1. Water quality classification
Before discussing the method for analyzing the natural water, it is necessary to define the parameters which need to be monitored. The common parameters should be taken may be split into some aspects: physical, biological, chemical, and radiological, and others. However, this discussion paper will focus on physical, chemical, and biological parameters [2].

4.1.1. Biological parameter
Natural and human activities contribute to the organic contaminant of environmental waters. The presence of organic matter is usually ascertained by measuring the oxygen demand of the pollutant.

$BOD$ (biochemical oxygen demand); this test is the most frequently used for the determination of the biological load of water. The test determines the amount of oxygen absorbed by a sample of water.

$COD$ (chemical oxygen demand); this is an important rapidly measured parameter to determine the degree of pollution in a watercourse.

$CCE$ (carbon chloroform extract); active carbon is used to absorb the organic material from a known quantity of water. This method does not, however, determine the total organic content of water, but the technique can provide a relative measure of pollution load.

Bacteriological parameters; total of fecal coliform (F-C) and total-coliform (T-C).
4.1.2. Physical parameter

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taste and odor</td>
<td>May give an indication of changes in the water no units of measurement exits</td>
</tr>
<tr>
<td>Color</td>
<td>Aesthetically affects the potability</td>
</tr>
<tr>
<td>Turbidity</td>
<td>Suspended insoluble materials mainly occurring in surface waters</td>
</tr>
<tr>
<td>Colloids</td>
<td>Suspended material in the water that behaves like a true solution</td>
</tr>
</tbody>
</table>

4.1.3. Chemical and other parameters

According to the Standard value of National Water Quality Standard for Water Quality Management (Indonesian Government Regulation No.82/2001), many of the more environmental important parameters should be use for monitoring the environmental conditions. The standard values of water quality, as shown in Table 2.

The evaluated parameters such as temperature, turbidity, electrolytic conductivity, total dissolved solids (TDS), total suspended solid (TSS), hydrogen ion concentration (pH), phosphates (PO₄), total nitrogen (T-N) (NO₂⁻, N₂, NH₄⁺, NO₃⁻, and organic nitrogen, etc), ammonia-nitrogen (NH₃-N), nitrite-nitrogen (NO₂⁻-N), nitrate-nitrogen (NO₃⁻-N), lead (Pb), iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), silica (SiO₂), chloride (Cl), fluoride (F), cadmium (Cd), mercury (Hg), chromium (Cr), cyanide (CN), arsenic (As), phenolic compounds, detergents, human acids. These parameters are most important to be evaluated for ensuring the water quality.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class I</td>
<td>Water usable for raw water for drinking water supply</td>
</tr>
<tr>
<td>Class II</td>
<td>Water usable for recreational activity and other uses mentioned for classes III and IV</td>
</tr>
<tr>
<td>Class III</td>
<td>Water usable for fisheries and other uses mentioned for class IV</td>
</tr>
<tr>
<td>Class IV</td>
<td>Water usable for agricultural and livestock farming</td>
</tr>
</tbody>
</table>

4.2. Acid rain

Acid rain is now a new phenomenon; it is become an important aspect to be evaluated for ensuring the real conditions of one area. Acid rain occurs when sulfur dioxide and nitrogen dioxide are emitted from combustion processes in industry and power stations or from volcanic eruptions into the atmosphere.
Acid rain contains nitrate and sulfate ions which form sulfuric and nitric acid in rainwater. The sources of the nitrate and sulfate are air pollutant emissions. Nitrate (NO₃) and sulfate (SO₄) concentrations in rainwater are high in many cities in Indonesia.

As known well, pure water has a pH of 7 (neutral), while normal rain has a pH of about 5.6. A change in the pH scale of one unit reflects a tenfold change in the concentration of acidity. Normally, rain with a pH value lower than 5.6 is defined as acid rain.

Some of the possible ways in which sulfur dioxide may react in the atmosphere are (1) photochemical reaction; (2) photochemical and chemical reaction in the presence of nitrogen oxides and/or hydrocarbons, particularly alkenes; (3) chemical processes in water droplets; (4) reactions on solid particles in the atmosphere. However, it should be kept in mind that the atmosphere is a highly dynamic system with great variations in temperature, composition, humidity, and intensity of sunlight; therefore, different processes may predominate under various atmospheric conditions [4].

The sources of acid rain are summarized below;
1. Industrial activities, which emit a variety of atmospheric pollutants including SO₂, particulate matter, photochemically reactive hydrocarbons, chlorofluorocarbons, and inorganic substances such as toxic heavy metals.
2. Burning of large quantities of fossil fuel, which can introduce CO₂, CO, SO₂, and NOₓ, hydrocarbons (including CH₄), and particulate soot, polycyclic aromatic hydrocarbons, and fly into the atmosphere.
3. Transportation practice, which emit CO₂, CO, NOₓ, photocemically reactive (smog forming) hydrocarbons (including CH₄).
4. Burning of biomass and vegetation, including tropical and subtropical forests and savanna grasses, which produce CO₂, CO, NOₓ, and particulate soot and polycyclic aromatic hydrocarbons.
5. Agricultural practices, which produce methane and NO₂ from bacterial denitrification of nitrate-fertilized soils.

5. Detection methods for the monitoring of ionic species in ion chromatography

5.1. Historical aspects of ion chromatography

“Chromatography” is a physicochemical method for separating mixtures of substances. The separation effect is based on repeated distribution between two phases; one phase is stationary while the second, mobile phase moves in a particular direction.

Chromatography was originally used in the late 1890s by the Russian botanist, Mikhail Tswett [5, 6] to separate and isolate various plant pigments. The colored band he produced on the adsorbents bed and evoked the term chromatography (color writing) for this type of separation. Initially, the work of Tswett was not generally accepted, partly due to the original paper being in Russian and thus, at that time, was not readily available to the majority of western chemists and partly due to condemnation of the method by Willstatter and Stoll in 1913.

In the late 1930s, Martin and Synge proposed the concept of theoretical plates, which was adapted from the theory of distillation processes, as a formal measurement of the efficiency of
chromatographic process [1]. In the 1969, Kirkland suggested the use of small particles and high pressures in liquid chromatography (LC) to improve the separation which proved to the critical factors that initiated the development of high performance liquid chromatography (HPLC) [5].

The history of IC goes back to the development of ion exchangers, as shown in Table 3 [7]. Ion exchange is one the oldest separation process. The major differences between both IC and HPLC processes are the method of sample introduction and the type of detection systems being used.

Table 3: The history of IC, the analytical technique based on ion exchange

<table>
<thead>
<tr>
<th>Year</th>
<th>Description</th>
<th>Author(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ca. 1850</td>
<td>Soil as an ion exchanger for Mg$^{2+}$, Ca$^{2+}$ and NH$_4^+$</td>
<td>Thomson &amp; Way</td>
</tr>
<tr>
<td>1935</td>
<td>Sulfonated and aminated condensation polymers (phenol/formaldehyde)</td>
<td>Adams, Holmes</td>
</tr>
<tr>
<td>1942</td>
<td>Sulfonated PS/DVB resin as cation exchanger (Manhattan Project)</td>
<td>d'Alelio</td>
</tr>
<tr>
<td>1947</td>
<td>Aminated PS/DVB resin as anion exchanger</td>
<td>McBurney</td>
</tr>
<tr>
<td>1953</td>
<td>Ion exclusion chromatography</td>
<td>Wheaton, Baumann</td>
</tr>
<tr>
<td>1957</td>
<td>Macroporous ion exchangers</td>
<td>Corte, Meyer, Kunin et al.</td>
</tr>
<tr>
<td>1959</td>
<td>Basic theoretical principles</td>
<td>Helfferich</td>
</tr>
<tr>
<td>1967-70</td>
<td>Pellicular ion exchangers</td>
<td>Horvath, Kirkland</td>
</tr>
<tr>
<td>1975</td>
<td>Ion exchange chromatography with conductivity detection using a &quot;suppressor&quot;</td>
<td>Small, Stevens, Baumann</td>
</tr>
<tr>
<td>1979</td>
<td>Conductivity detection without a &quot;suppressor&quot;</td>
<td>Gjerde, Fritz, Schmuckler</td>
</tr>
<tr>
<td>1976-80</td>
<td>Ion pair chromatography</td>
<td>Waters, Bidlingmeier, Horvath et al.</td>
</tr>
</tbody>
</table>

IC was developed and introduced as a variable commercial technique in the early 70’s. At that time, major advances were made in the capabilities for the separation and detection of a number of inorganic anions or inorganic cations. Due to a number of its advantages, IC has become an indispensable tool for analytical chemists in the area of ionic species analysis. In many cases, this method has superseded conventional wet chemical methods such as titration, photometry, gravimetry, turbidimetry, and colorimetry, all of which are labor-intensive, time-consuming, and occasionally susceptible to interferences [8].

IC is a mode of HPLC in which ionic analyte species are separated on cationic or anionic sites of the stationary phase. The separation mechanism can be broadly compared to ion-exchange, using fixed-site resins of various composition and ion-interaction methods, using a variety of columns as substrates to support dynamically exchanged or permanently bonded ionic groups.

Modern IC is built on the solid foundation created by many years of work in classical ion-exchange chromatography. The relationship between the older ion-exchange chromatography and modern IC is similar so that between the original LC and the later HPLC in
which automatic detectors are used and efficiency of the separations has been drastically improved. IC as currently practiced is certainly “high performance” even though these words are not yet part of its name. Sometimes in the future an even better form of IC may be dubbed HPIC.

5.2. System and type of IC

Fig. 1: Basic components of a non-suppressor IC

The basic components of a non-suppressor IC are described in Fig. 1. The hardware comprises pump, injector, detector and data processor, whereas the software consists of the variable components of the system (principally the nature of the stationary phase, the composition of the eluent and the flow rate). The pump delivers the mobile phase through the chromatographic system. The sample is injected to the system via an injector. The separator column is the most important part of the chromatographic system because the choice of a suitable stationary phase and the chromatographic conditions determine the quality of the analysis. The analytes are detected and quantified by a detection system.

5.3. Advantages of IC

Inorganic chromatography as practiced today has deep roots in the pioneering work of the forties and fifties period. It has gained increasingly wide acceptance as the method of choice for many inorganic ion analysis problems.

Speed, sensitivity, selectivity, simultaneous determination both negative and positive charge of ions and stability of the separator column are the advantages of IC [1].

5.4. Principle of IC

The separation method of IC is based on exchange process occurring between the mobile phase and ion-exchange groups bonded to the support packing material. An ion-exchanger in aqueous solution consists of anions, cations and water, where either cations or anions are chemically bonded to insoluble matrix.

The ion-exchanger is classified as a cation-exchange material when the fixed ion carries a negative charge and as anion-exchange material when the fixed ion carries a positive charge.
6. Development of detection methods

This section of the discussion paper focused on the development of simple detection methods for the simultaneous determination of common inorganic anions and/or cations.

Since IC was firstly introduced by Small et al. [1] as a good analytical technique used to separate, identify, and quantify ions, it has then used in many laboratories for determination of inorganic and organic ionic species. The determination of ionic species in many types of natural water samples is one of its most typical applications.

Basically, anions and cations were independently separated by using suppressed IC methods. Contrarily, IC methods have been expanded for the simultaneous determination of inorganic anions and cations in a single chromatographic run, owing to its capability to provide accurate and rapid determination [12-32].

There are two approaches currently known for the simultaneous determination of anions and cations in a single chromatographic run. The first approach uses a single column for this purpose based on chelation of cations to form anions [9-11], use of zwitterionic ion-exchangers [12-15] or mixed-bed ion-exchange columns [16], etc. However, these methods allow partially simultaneous separation of anions and cations. An alternative method involves mixed-mode separation such as ion-exclusion chromatography and cation-exchange chromatography [17-21]. This system provides a simple, rapid determination means for inorganic common ions. However, it is ineffective for a wide variety of anions contained in samples and an appropriate eluent should also be carefully selected.

The second approach uses two columns connected in series or parallel with or without column switching (CS). For the approach without CS [22-25], a suitable eluent should be chosen for the simultaneous separation of both anions and cations, but these peaks sometimes overlap and the method is not applicable widely. The determination of these common ions can be also achieved on short permanently coated silica monolithic anion-exchange and cation-exchange columns [25]. The both columns are connected in parallel arrangement. However, common monovalent cations such as Na⁺, NH₄⁺ and K⁺ could not be separated when these ions contained in real samples.

6.1. “Peak parking” technique

In this section, the system called as “peak parking” technique for separating the anions and cations [26]. The name of peak parking is a unique name in the analytical method, so it is important to understand the work mechanism of this technique.

CS is a powerful technique for the separation and cleanup of complex multi-component samples. In this approach a portion of the effluent from an upstream column is transferred selectively to the inlet of a downstream column by switching the valve during a chromatographic run, where the separation of analytes is simultaneously carried out on both upstream and downstream columns.

6.1.1. Performance of column switching

The technique of CS can increase the versatility of IC significantly. Moreover, CS is simplest and easiest to apply when the same eluent flows through each column. An example of a 6-port switching valve arranged for CS is given in Fig. 2. The arrangement utilizes the same valve as that used for the external loop sampling system. It is seen that in the position A; column (1) is
connected between ports (5) and (6) and column (2) is connected between ports (2) and (3).

![Diagram of switching valves and detector](image)

**Fig. 2:** Valve arrangements for column switching with 6-port switching valve

The detector is connected to port (4) and the eluent from the 6-port switching valve enters to port (1) and passes through column (1) and goes out to the detector. And the separation will take place in the separator column (1). When the valve is rotated, the position is depicted on the right hand side of Fig. 2.

A great advantage using two 6-port switching valves and two ion-exchange columns lies in the fact that peak overlapping between the analyte anions and analyte cations can be avoided in case anion-exchange and cation-exchange separations are separately carried out.

### 6.1.2. Analysis conditions

The experimental apparatus was assembled from a PU-2080i plus HPLC pump (Jasco, Tokyo, Japan), a model 5095 loop injector (Rheodyne, Cotati, CA, USA) with an injection-loop volume of 20 µl, a CM-8020 conductivity detector (Tosoh), TSKgel Super-IC-Cation (150×4.6 mm I.D.), TSKgel IC-Anion-SW (50×4.6 mm I.D.), two Model-7000 six-port switching valves (Rheodyne) and a Computer Aided Chromatography data processor (Nippon Filcon, Tokyo, Japan). The two separation columns were connected in series via the two 6-port switching valves and each column was connected to each switching valve. The present flow system allows us to select the position of each switching valve for peak separation or peak parking. The separations were carried out under isocratic mode in this work.

Two ion-exchange columns based on different packing materials were used for the determination of the common anions and the common cations, where an anion-exchange column was used for separating the inorganic anions whereas a cation-exchange column was used for separating the inorganic cations.

Fig. 3 shows the schematic diagrams of the apparatus and the positions of the switching valves. The single run involves three steps as follows:
Both valves A and B were switched for the peak separation and the eluent passes through both anion-exchange and cation-exchange columns, until a straight baseline is obtained. A 20 μl volume of sample solution is then injected to the system. The cations are retarded on the cation-exchange column while the anions pass through the cation-exchange column without retardation and get to the anion-exchange column.

In 2.15 min after the injection of the sample, the downstream valve was switched to the peak parking position in order to separate the cations alone.

After completing the separation of cations, the downstream valve was switched for the peak separation while the upstream valve was switched for the peak parking position. The anions parked in the anion-exchange column were then separated.

### 6.1.3. Selection of optimal eluent concentration

In initial technique, tartaric acid was used as the eluent for the separation of both anions and cations. Fig. 4 shows the relationship between the concentration of tartaric acid as the eluent on the retention volumes ($V_R$) of anions (Cl$^-$ and NO$_3^-$) and cations (Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, and Ca$^{2+}$) using anion-exchange and cation-exchange columns commercially available.
The above results suggested that we should adjust the concentration of tartaric acid that will give optimal peak resolutions, separation speed, retention times and peak shapes for the analyte cations, whereas the anion exchanger should be selected so that SO$_4^{2-}$ can be eluted with tartaric acid. The optimum concentration of tartaric acid for the simultaneous separation of anions and cations was judged to be 5 mM.

Fig. 5 shows the separation of the anions and cations standard using 5 mM tartaric acid as the eluent. Under the conditions in Fig. 2-4, Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, and Ca$^{2+}$ are appeared as negative peaks while Cl$^-$ and NO$_3^-$ are appeared as positive peaks.

However, from the above chromatogram, the common anion, SO$_4^{2-}$ could not be eluted using tartaric acid eluent. For optimizing the detection technique, the anion-exchange column was then modified with chondroitin sulfate C to enhance the selectivity. Fig. 6 demonstrates the separation of anions and cations with the anion-exchange-column modified with chondroitin sulfate C. The separation is achieved in 30 min by using 5 mM tartaric acid as the eluent.
6.1.4. Validation of the system

The detection limits of anions and cations were calculated at S/N=3 are also given in Table 4. The detection limits obtained by the present method are 25-132 ppb (μg/l) for cations and 0.3-5.3 ppm (mg/l) for anions.

<table>
<thead>
<tr>
<th>Analytes</th>
<th>Detection limits / μM</th>
<th>t_R / min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>1.1 (25 ppb)</td>
<td>3.42</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>2.7 (49 ppb)</td>
<td>3.71</td>
</tr>
<tr>
<td>K⁺</td>
<td>3.4 (132 ppb)</td>
<td>5.40</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>3.2 (77 ppb)</td>
<td>7.70</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>4.5 (180 ppb)</td>
<td>10.18</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>8.1 (0.3 ppm)</td>
<td>13.29</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>20 (1.2 ppm)</td>
<td>14.71</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>55 (5.3 ppm)</td>
<td>27.40</td>
</tr>
</tbody>
</table>

Table 4: Summarized calibration data for inorganic anions and cations.

Chromatographic conditions as in Fig. 6.

6.1.5. Application of peak parking technique to the real water samples

The IC method developed here was applied to the simultaneous determination of common inorganic anions and cations in river water sample, and the results showed that the content of ionic species in these studied samples were all higher than the detection limits as shown in Fig.7.

Each sample was injected after filtration through a 0.45 μm membrane filter. The river water sample was taken from near Gifu University, Gifu city, Japan. All samples were filtered with a 0.45 μm membrane filter and were injected to the chromatographic analysis system without dilution.
6.2. Improvements of peak parking technique

In the work mentioned in section 6.1, tartaric acid was used as the eluent for the separation of both cations and anions. However, we found that anion-exchange column had to be modified with chondroitin sulfate C. Otherwise divalent anion such as $SO_4^{2-}$ could not be eluted from the unmodified column by using a tartaric acid eluent.

Since the modification of anion-exchange column with chondroitin sulfate C is strongly affected by the modification conditions and the packing materials employed, control of the retention time of the anions is difficult. Therefore, in order to use unmodified anion-exchange columns several kinds of organic acids were examined as the eluent for the serial separation of cations ($Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, and $Ca^{2+}$) and anions ($Cl^-$, $SO_4^{2-}$ and $NO_3^-$). In this work, malonic acid, 5-sulfoisophthalic acid, 5-sulfosalicylic acid and 2-sulfobenzoic acid cyclic anhydride were examined. The concentration of these eluents was also optimized in terms of the retention times of $Cl^-$, $NO_3^-$ and $SO_4^{2-}$.

It was found that 5-sulfosalicylic acid eluent alone among the above eluents achieved complete separation of the anions. On the other hand, the above five cations could be separated by using any acidic eluents. In addition, TSKgel Super IC-Cation (150×4.6 mm I.D.) and TSKgel IC-Anion-PWxl (75×4.6 mm I.D.) were selected as the polymer-based cation-exchange and anion-exchange columns, respectively [27].

6.2.1. Analysis conditions

The ion chromatographic system was the same as in the previous method except for the separation columns. The both separation columns were selected as the polymer based columns, and obtained from Tosoh.

6.2.2. Separation of the standard sample

Fig. 8 illustrates a serial separation of authentic mixture of cations and anions by peak parking technique, where 1.75 mM 5-sulfosalicylic acid is used as the eluent. Under the experimental
conditions, Na\(^+\), NH\(_4\)^+, K\(^+\), Mg\(^{2+}\), and Ca\(^{2+}\) appeared as negative peaks while Cl\(^-\), SO\(_4^{2-}\) and NO\(_3^-\) appeared as positive peaks. These results are due to the difference in the conductivity between the analyte ions and the driving eluent ion. It can be seen from Fig. 10 that the serial separations were completed in less than 20 min.

6.2.3. Validation of the system
Several quantification data are summarized in Table 5. Linear relationships between the conductivity response (peak height) and molar concentration were observed up to 1 mM with \(R^2 \geq 0.99\) for all analyte anions and cations. The limits of detection (LODs) for 20 µl injection were calculated at S/N=3. The LODs obtained by the present method were 16-68 ppb (μg/l) for cations and 15-28 ppb for anions.

**Table 5:** Summarized data for the detection limits (LODs), correlation coefficients \(R^2\) of the calibration curves and retention times \(t_R\) of inorganic anions and cations under the chromatographic conditions in Fig. 8.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>LOD (S/N=3)</th>
<th>(R^2)</th>
<th>(t_R) / min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+)</td>
<td>0.77 ppb</td>
<td>0.9956</td>
<td>5.09</td>
</tr>
<tr>
<td>NH(_4)^+</td>
<td>0.90 ppb</td>
<td>0.9981</td>
<td>5.40</td>
</tr>
<tr>
<td>K(^+)</td>
<td>1.05 µM</td>
<td>0.9972</td>
<td>6.11</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>1.20 ppb</td>
<td>0.9969</td>
<td>9.11</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>1.70 µM</td>
<td>0.9939</td>
<td>10.46</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>0.43 µM</td>
<td>0.9928</td>
<td>14.74</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>0.29 ppb</td>
<td>0.9980</td>
<td>16.28</td>
</tr>
<tr>
<td>NO(_3^-)</td>
<td>0.42 ppb</td>
<td>0.9969</td>
<td>17.95</td>
</tr>
</tbody>
</table>

**Fig. 8:** Serial separations of inorganic cations and anions via column switching. Eluent: 1.75 mM 5-sulfosalicylic acid. Columns: TSK\(_{gel}\) Super IC-Cation (150×4.6 mm I.D.) and TSK\(_{gel}\) IC-Anion-PWXL (75×4.6 mm I.D.), connected in series via six-way switching valves. Analyte (concentration, in mM): 1=Na\(^+\) (0.2), 2=NH\(_4\)^+ (0.2), 3=K\(^+\) (0.2), 4=Mg\(^{2+}\) (0.2), 5=Ca\(^{2+}\) (0.2), 6=Cl\(^-\) (0.6), and 7= SO\(_4^{2-}\) (0.2); 8= NO\(_3^-\) (0.4).
6.2.4. Determination of anions and cations in tap water and river water samples

The present IC method was applied to the serial determination of major cations and anions in tap water and river water samples, respectively. The samples were determined according to the experimental conditions in Fig. 8. The chromatograms of these environmental water samples are shown in Fig. 9. All inorganic ions could be detected in tap water and river water samples except for ammonium ion in tap water. It was observed that the contents of sodium and calcium ions were relatively higher in tap water.

![Chromatograms](image.png)

**Fig. 9:** Chromatograms of ions detected in tap water (A) and river water (B). Chromatographic conditions as in Figure 8 except for the samples.

Table 6 summarizes the results and the reproducibility data (n=5) obtained by the improvement of peak parking technique for the cations and anions contained in tap water and river water samples. It suggests that the proposed IC method can be applied for practical use.

**Table 6:** Determination results for inorganic anions and cations in tap water and river water samples (n=5) using the peak parking technique.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Tap water</th>
<th>River water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean value</td>
<td>RSD (%)</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.300 (6.9)</td>
<td>2.11</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>Trace</td>
<td>-</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.029 (1.1)</td>
<td>1.32</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.063 (1.5)</td>
<td>2.29</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.200 (8.1)</td>
<td>1.48</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.129 (4.6)</td>
<td>2.25</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.021 (2.0)</td>
<td>1.37</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.029 (1.8)</td>
<td>1.65</td>
</tr>
</tbody>
</table>
The present flow system continuously allowed either cation-exchange or anion-exchange separation when the switching valve positions were fixed. Each separation was completed in less than 12 min. The determination results obtained by common single-column IC mode without peak parking technique coincided well with the corresponding data in Table 6. This supports that the serial determination of cations and anions is realized by using the peak parking technique.

6.3. “Tunable separation” technique

As a competitive practical method, this work presents a convenient IC method to determine either of anions or cations in a single system [28]. The method comprises one pump, one injection valve, an anion-exchange column, a cation-exchange column, two 6-port switching valves or a single 10-port switching valve, and a conductivity detector. This method is easy and simple to operate compared with the previous method as mentioned in above sections. In previously method, good resolution of cations and anions was achieved when the peak parking technique was performed. However, the CS timing had to be focused to control accurately in order to trap analyte anion on the anion-exchange column, i.e., to avoid peak overlaps.

In the present method, while one ion-exchange column is operated, another ion-exchange column is being conditioned. In other words, since both columns are conditioned with the eluent, they are possible to use at any time. Furthermore, CS is needed only when the required separation will be changed. On that purpose, the two ion-exchange columns are then connected in series via two 6-port switching valves or a single 10-port switching valve while the injection valve is placed between the two columns to allow separating the target ion. The optimized operating system was then applied to the determination of anions and cations in river water samples.

6.3.1. Experimental conditions

The diagrams of the apparatus employed in this study are illustrated in Fig 10. The ion chromatograph consisted of a PU-2080i plus HPLC pump (Jasco, Tokyo, Japan), a Rheodyne 5095 injector equipped with a 20 µl sample loop (Cotati, CA, USA), a CM-8020 conductivity detector (Tosoh, Tokyo, Japan), two Model 7000 6-port switching valves (Rheodyne) or a Model 7610-600 10-port switching valve (Rheodyne), and a Computer Aided Chromatography data processor (Nippon Filcon, Tokyo, Japan). The columns employed were a TSKgel Super-IC-Cation column (150 × 4.6 mm i.d.) and a TSKgel IC-Anion-PWXL column (75 × 4.6 mm i.d.). Both columns were obtained from Tosoh (Tokyo, Japan).

The eluent used for the determination of anions and cations was 2.4 mM 5-sulfosalicylic acid. The conditions were under isocratic mode. The pump was operated at a flow rate of 0.5 ml/min to keep the inlet pressure lower than 7.0 MPa.

6.3.2. Column switching procedures

Two columns were connected in series via two 6-port switching valves. Fig. 10 illustrates of the equipment and the position of both 6-port switching valves for the required separations. The injection valve is placed between the anion-exchange and cation-exchange columns, which
allowed the tuning of either cations separation or anions separation. As in Fig. 10, the separation system works at position as follows:

**Position I**
Both valves A and B are switched for the separation of cations position and the eluent passes through both cation-exchange and anion-exchange column until a straight baseline is obtained. A 20 μl volume of the sample solution is then injected to the chromatographic system. The analytes will pass on the cation-exchange column and then the cations will separate. The separation of cations can be repeated by injecting again a new sample to the chromatographic system. While the separation of cations on the cation-exchange column is operated, the anion-exchange column is being conditioned with the eluent; therefore the anion-exchange column is ready for use at any time.

**Position II**
Both valves A and B are switched for the separation of anions position. A 20 μl volume of the sample solution is then injected to the chromatographic system. The analytes will pass on the anion-exchange column and then the anions will separate. The separation of anions can be repeated by injecting again a new sample to the chromatographic system. While the separation of anions on the anion-exchange column is operated, the cation-exchange column is being conditioned with the eluent; therefore the cation-exchange column is ready for use at any time.

This means that the separation of cations and/or anions in this work is tunable at any time.

It should be noted that the present system does not allow the simultaneous detection of both anions and cations. Either anions or cations can be detected in a single chromatographic run.

Fig. 10: Schematic diagrams of the instruments and the positions of the switching valves for two 6-port switching valves. The injection valve was placed between anion-exchange and cation-exchange columns, which allowed the tuning of either cations separation or anions separation. Separation of cations (position I) and separation of anions (position II).
6.3.3. Cation-exchange separation
The five cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺) were well eluted within 10 min. As described in Fig. 11A, a baseline separation between Na⁺ and NH₄⁺ was not achieved under the eluent concentration. However, both ions could be determined. The results were cross-checked under different eluent conditions. By reducing the molar composition of eluent (e.g., 1.4 mM), the baseline separation could be achieved and the obtained results with those obtained under the conditions in Fig. 11A.

![Fig. 11: Separation of cations and/or anions via column switching. Eluent: 2.4 mM 5-sulfosalicylic acid. Columns: TSKgel Super IC-Cation (150 × 4.6 mm i.d.) and TSKgel IC-Anion-PWXL (75 × 4.6 mm i.d.), connected in series via two 6-port switching valves or a single 10-port switching valve. Analyte (concentration, in mM): (A) 1=Na⁺ (0.2), 2=NH₄⁺ (0.2), 3=K⁺ (0.2), 4=Mg²⁺ (0.2), 5=Ca²⁺ (0.2) and (B) 1=Cl⁻ (0.6), 2=SO₄²⁻ (0.2); 3=NO₃⁻ (0.4), 4=System peak.]

6.3.4. Anion-exchange separation
The resolution and retention time of analyte ions were extremely dependent on the ionic strength of the eluent and its pH. For achieving good resolution, the eluent concentration must be adjusted carefully. Particularly for SO₄²⁻, at lower 5-sulfosalicylic acid eluent concentration, it eluted just after NO₃⁻.

In contrast, at higher concentration (e.g., 2.4 mM), it is eluted before NO₃⁻. As shown in Fig. 11B, complete separation of the three anions (Cl⁻, SO₄²⁻, and NO₃⁻) was also achieved within 10 min.
Table 7: Summarized calibration data for major anions and cations under the optimum chromatographic conditions described in Fig. 11.

<table>
<thead>
<tr>
<th>Analytes</th>
<th>LOD (S/N=3)</th>
<th>Correlation coefficient ($r^2$)</th>
<th>$t_b$/min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µM</td>
<td>ppb</td>
<td></td>
</tr>
<tr>
<td><strong>Cations</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.91</td>
<td>22</td>
<td>0.9975</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>1.19</td>
<td>21</td>
<td>0.9975</td>
</tr>
<tr>
<td>K$^+$</td>
<td>1.29</td>
<td>50</td>
<td>0.9967</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.81</td>
<td>19</td>
<td>0.9982</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>1.13</td>
<td>45</td>
<td>0.9913</td>
</tr>
<tr>
<td><strong>Anions</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0.27</td>
<td>10</td>
<td>0.9936</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>0.15</td>
<td>14</td>
<td>0.9976</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>0.19</td>
<td>11</td>
<td>0.9959</td>
</tr>
</tbody>
</table>

6.3.5. Validation of the method
In order to evaluate the quantitative applicability of the proposed technique, five different concentration standard sample solutions were determined under the optimized conditions. The peak heights of ions were plotted against the concentration to get the calibration graphs. The correlation coefficients and detection limits are listed in Table 7. From the Table, the correlation coefficients $r^2>0.99$ proved good linearity of the present method. The detection limit at a signal-to-noise ratio (S/N) of 3:1 are also given.

6.3.6. Application to river water samples
The proposed technique was applied to the determination of common anions and cations in river water samples. The samples were determined after filtration with a 0.45 µm membrane filter for IC. Good separations for all common inorganic anions and cations were achieved. The results showed that the contents of ionic species in samples were all higher than the detection limits. The chromatograms of this river water samples are shown in Fig. 12. Fig. 12A demonstrates the separation of cations, whereas Fig. 12B demonstrates the separation of anions.

![Fig. 12](image-url)

Fig. 12: Chromatograms of ions detected in river water sample for (A) cations and (B) anions. Chromatographic conditions as in Fig. 11 except for the samples.
6.4. Improvements of tunable separation technique

The simultaneous determination of the seven common inorganic anions and the five common inorganic cations has not been widely studied. An approach to determine the common inorganic ions is proposed by Q. Xu et al. [21], where they performed a single-column ion-exclusion chromatography/cation-exchange chromatography for the separation of anions and cations, and used DL-malic acid-methanol-water as the eluent. However, this method could successfully separate only four common anions (SO$_4^{2-}$, Cl$^-$, NO$_3^-$, and F$^-$) and five common cations (Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, and Ca$^{2+}$).

As a recommended analytical method, this work presents a better operating condition to determine common inorganic anions or cations with a single eluent in a single run. The method comprises one pump, one injection valve, an anion-exchange column, a cation-exchange column, a single 10-port switching valve, and a conductivity detector. The present operating conditions improves the selectivity of anions compared with the previous mentioned method as in sections 6.3 [29].

In the present method, while the one ion-exchange column is operated, the other ion-exchange column is being conditioned. In other words, since the both columns are conditioned with the eluent, they are possible to use at any time. Furthermore, CS is needed only when the target ion is changed. On that purpose, the two ion-exchange columns are then connected in series via a 10-port switching valve while the injection valve is placed between the two columns to allow separating the target ion. The present system will be applied to the determination of common inorganic anions and/or cations in river water and pond water samples.

6.4.1. Analysis conditions

The IC system was the same as in the previous method as illustrated in above section 6.3, except for the separation columns. The separation columns employed were a TSK$_{gel}$ Super-IC-Cation column (150 $\times$ 4.6 mm i.d.) and a TSK$_{gel}$ IC-Anion-PW$_{XL}$ column (50 $\times$ 4.6 mm i.d.). Both columns were obtained from Tosoh.

6.4.2. Performance of trimellitic acid as the eluent

In the tunable separation technique as described in the previous section, 5-sulfosalicylic acid was used as the eluent for the separation of both anions and cations. However, we found that only three common anions (Cl$^-$, NO$_3^-$, and SO$_4^{2-}$) could be separated on the anion-exchange column. Otherwise the other common anions such as F$^-$, H$_2$PO$_4^-$, NO$_2^-$, and Br$^-$ could not be separated from a commercially available anion-exchange column by using a 5-sulfosalicylic acid eluent. In this work, organic acid such as trimellitic acid was examined as the eluent for the separation of common inorganic anions (F$^-$, H$_2$PO$_4^-$, NO$_2^-$, Cl$^-$, Br$^-$, NO$_3^-$, and SO$_4^{2-}$) and cations (Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, and Ca$^{2+}$).

Fortunately, trimellitic acid as the eluent gave better peak shapes and good selectivity for all inorganic ions.
6.4.3. Cation-exchange separation

The five common inorganic cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺) were well eluted within 35 min. As depicted in Fig. 13A, a baseline separation between Na⁺ and NH₄⁺ was not achieved under the eluent condition, but both ions could be determined. The determination results were cross-checked under different eluent conditions. By reducing the concentration of eluent (e.g., 0.5 mM), the baseline separation of Na⁺ and NH₄⁺ could be achieved and the obtained results coincided with those obtained under the conditions in Fig. 13A.

6.4.4. Anion-exchange separation

In the chromatograms as in Fig. 13B, the system peak appears between nitrate and sulfate. At lower trimellitic acid eluent concentration (e.g., 0.5 mM), the monovalent anions (F⁻, H₂PO₄⁻, NO₂⁻, Cl⁻, Br⁻, NO₃⁻) and divalent anion (SO₄²⁻) could be completely separated from the system peak, but it took longer time. In contrast, at higher concentration (e.g., 1.5 mM), nitrate could not be separated from the system peak. Therefore, it should be carefully chosen to obtain the optimum eluent concentration. As shown in Fig. 13B, complete separation of the seven inorganic anions (F⁻, H₂PO₄⁻, NO₂⁻, Cl⁻, Br⁻, NO₃⁻, and SO₄²⁻) was achieved within 30 min.

![Fig. 13: Separation of inorganic cations and/or inorganic anions via column switching. Eluent: 1.0 mM trimellitic acid. Columns: TSKgel Super IC-Cation (150 × 4.6 mm i.d.) and TSKgel IC-Anion-PWXL (50 × 4.6 mm i.d.). Eluent flow-rate: 0.7 ml/min. Column temperature: room temperature. Analytes (concentration, in mM): (A) 1=Na⁺ (0.3), 2=NH₄⁺ (0.3), 3=K⁺ (0.3), 4=Mg²⁺ (0.3), 5=Ca²⁺ (0.3) and (B) 1=F⁻ (0.3), 2=H₂PO₄⁻ (0.3), 3=NO₂⁻ (0.3), 4=Cl⁻ (0.3), 5=Br⁻ (0.3), 6=NO₃⁻ (0.3), 7=System peak, and 8=SO₄²⁻ (0.3).](image)

6.4.5. Analytical performance parameters

The detection limits of the present method were determined by injecting 20 μL volume of the sample solution and were calculated at S/N=3. The results are shown in Table 8. The detection limits obtained by the method were 0.05-0.58 ppm (mg/l) for the anions and 0.05-0.38 ppm for the cations. Sub-ppm levels of detection will be feasible using this proposed method for the determination of inorganic anions and cations in real water samples.

Linear relationships between the peak heights and the analyte concentrations were found.
experimentally for all the anions and the cations, as shown in Table 8. All the calibration curves of the anions and the cations showed good linear correlations. From the Table, the correlation coefficients $r^2 > 0.999$ proved good linearity of the present method.

**Table 8:** Summarized data for the detection limits (LODs), calibration graphs, and retention times ($t_R$) of cations and anions obtained under the optimum operating condition as in Fig. 13.

<table>
<thead>
<tr>
<th>Analytes</th>
<th>LOD (S/N=3)</th>
<th>Correlation coefficient ($r^2$)</th>
<th>$t_R$/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cations</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$^+$</td>
<td>2.57 µM</td>
<td>0.06 ppm</td>
<td>0.9997</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>2.72 µM</td>
<td>0.05 ppm</td>
<td>0.9998</td>
</tr>
<tr>
<td>K$^+$</td>
<td>3.31 µM</td>
<td>0.13 ppm</td>
<td>0.9997</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>6.24 µM</td>
<td>0.15 ppm</td>
<td>0.9992</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>9.39 µM</td>
<td>0.38 ppm</td>
<td>0.9998</td>
</tr>
<tr>
<td>Anions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F$^-$</td>
<td>4.80 µM</td>
<td>0.09 ppm</td>
<td>0.9998</td>
</tr>
<tr>
<td>H$_2$PO$_4^-$</td>
<td>1.75 µM</td>
<td>0.17 ppm</td>
<td>0.9997</td>
</tr>
<tr>
<td>NO$_2^-$</td>
<td>3.57 µM</td>
<td>0.16 ppm</td>
<td>0.9997</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>1.54 µM</td>
<td>0.05 ppm</td>
<td>0.9998</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>1.81 µM</td>
<td>0.14 ppm</td>
<td>0.9999</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>1.52 µM</td>
<td>0.09 ppm</td>
<td>0.9999</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>6.10 µM</td>
<td>0.58 ppm</td>
<td>0.9995</td>
</tr>
</tbody>
</table>

Concentration range: 0.1-0.5 mM for all ions.

6.4.6. **Application to river water samples**

The method was applied to the determination of anions and cations in river water sample. The water sample was taken from near Gifu University, Gifu, Japan. Good separations for common inorganic anions and cations were achieved. The chromatograms of the water sample are shown in Fig. 14, and Figs. 14A and 14B demonstrate the separation of inorganic cations and anions, respectively.

**Fig. 14:** Separations of inorganic ions in river water sample for (A) cations and (B) anions. Chromatographic conditions as in Fig. 13 except for the samples. Sample: Ijira river water, pH 7.27.
The concentrations of common inorganic anions and cations were determined by using the present CS technique and the results are shown in Table 9. The obtained results showed that the fluoride concentration in the water sample was lower than the detection limit, while the other anions were contained in the water sample at the concentrations higher than their detection limits.

Table 9: Determination results for inorganic anions and cations in river water sample (n=5) using the proposed IC method.

<table>
<thead>
<tr>
<th>Analytes</th>
<th>Ijira river water Mean value (mM (mg/l))</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cations</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.329 (7.9)</td>
<td>2.14</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>0.041 (0.7)</td>
<td>1.98</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.072 (2.9)</td>
<td>1.43</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.126 (3.0)</td>
<td>2.12</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.210 (8.4)</td>
<td>1.94</td>
</tr>
<tr>
<td><strong>Anions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F⁻</td>
<td>ND</td>
<td>-</td>
</tr>
<tr>
<td>H₂PO₄⁻</td>
<td>0.008 (0.8)</td>
<td>2.81</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>0.006 (0.3)</td>
<td>2.45</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.160 (5.7)</td>
<td>1.87</td>
</tr>
<tr>
<td>Br⁻</td>
<td>0.005 (0.4)</td>
<td>2.66</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.094 (5.8)</td>
<td>1.38</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.067 (6.4)</td>
<td>1.65</td>
</tr>
</tbody>
</table>

7. Concluding remarks

1. The environmental problems in Indonesia have reached a very serious level and all developed countries should interfere to solve the problems and save our earth.
2. IC is one of the useful analytical methods that play a curial role to analyze the environmental waters.
3. The application of CS technique in the analysis of fresh water samples has become the best alternative and can be used for routine purposes.
8. References


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