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The Water Quality as Anions of the Han River Around Water Reservation Area by Noble Ion Exchange Chromatography

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Surface water of the Han River is used to be a supplying drinking water for tap water in Seoul. The investigation on quality of the Han River water plays a very important role on the conservation of that valuable natural resource. Ion exchange chromatography with a Dionex DX-80, Ionpac AS14A, AMMS® system is used for the analysis of nitrogenous and phosphorus compounds causing water contamination such as nutrient sources for green algae during summer destroying ecosystem. The method is based on an anion exchange chromatographic separation followed by a sequential analysis through conductivity detector. Samples were collected over several months in different locations around the Han River. In all the samples, the separations among peaks have been shown satisfactory resolution including peak symmetry. The results indicated the average level of chloride and sulfate. Unexpectedly, nitrate has been detected to be a frequently considering contaminant around 10 mg/L. However, other species have been monitored as average level of main or side stream. This data could be importantly used to protect city water supply and to decide the policy blocking the containment of water in Han River. And this study has an important role in the respect to present the method of measuring and monitoring water quality.

Key words: ion exchange chromatography, water quality, Han river.

1. Introduction

Drinking water is indispensable for our life. Water is exploited from various sources such as surface, rain or ground water basing on geographical characteristics and natural resources of each specific location. Surface waters that originate in basins where the major rocks are granite contain very small amounts of dissolved minerals. The second general type of surface water derives from basins other than the granite. This water is typified by intermediate hardness, alkalinity and total mineral content. This type of water is widely used for public supply in many countries in the world.

The nitrogen cycle involves several important biological processes that are related to the production of nutrients essential for the growth of microorganism. Nitrate, nitrite and ammonium ions take part in several important environmental transformations involving nitrogen. Their levels in natural water are also important indicators of water quality. Nitrite can be formed during the biodegradation of nitrate in ground and surface water. Nitrate and ammonium are sources of nitrogen for the synthesis of proteins by microorganism. In addition, nitrite is readily oxidized to nitrate by dissolved oxygen, thus decreasing oxygen levels in water. However, large amounts of these species may be toxic and cause eutrophication of aquatic system.[1) When nitrate contaminated in water supplies are used as a source for drinking water adverse human health effects are also great concern. Relative to nitrites, nitrates are compounds of lower toxicity, representing a danger only when ingested in excessive doses or when converted to nitrite. Nitrites, however, can have some several adverse effects upon human health. For instance, the in vivo reaction between nitrite and secondary or tertiary amines produces N-nitrosamines, which are potential carcinogens, mutagens and teratogens.[2) Furthermore, nitrite interacts with blood pigment to cause meta-haemoglobinemia, especially infants (blue baby syndrome). This condition limits the bloods ability to carry oxygen from the lungs to the rest of the body. Nitrite ions are toxic even in low concentrations and may cause death by asphyxia. To protect against the above effects, the US EPA have set the maximum contaminant level for nitrate in drinking water at 10 mg/L. Therefore, the determination of nitrate, nitrite, ammonium and other related ions in water is often required to make decisions concerning water quality control.

There are a large number of analytical methods applicable to above anions quantification based on both spectrophotometric and chromatographic techniques. Chromatographic method relies upon the distribution of solutes between a mobile and a stationary phase. In this category, ion exchange system is conducted for the routine determination of concerned anions. The essential principle of this technique is an ion exchange process between the mobile phase and the exchange groups covalently bound to the stationary phase. For the hydrophobic ions, in particular, adsorption processes are also involved. Ion exchange chromatography can be used for separating both inorganic and organic anions and cations. The ion exchange chromatographic method results in both improved reproducibility and sensitivity if the sample contains common anions. Furthermore, analytical procedure is fairly simple without sample pretreatment. Hence, it is used for routine determination of anions in Han River sample. Besides, a fast colorimetric method, Ecotest, is also carried out for cross checking in order to gain precise results. Analysis by IC is not a new method, but we presented the method of measurement data of water quality in Han River. Therefore this data could be used to predict the water quality change and to decide a future plan blocking the containment of city water supply.

2. Experimental

2.1. Reagents

All chemicals used were of analytical grade quality. The double distillated water was filtered through an ultra pure apparatus, Mili- Q plus with conductivity at 18.2 MΩ

Series of anion standard solution was prepared by dilution stock solution 1000 mg/L provided by Dionex.

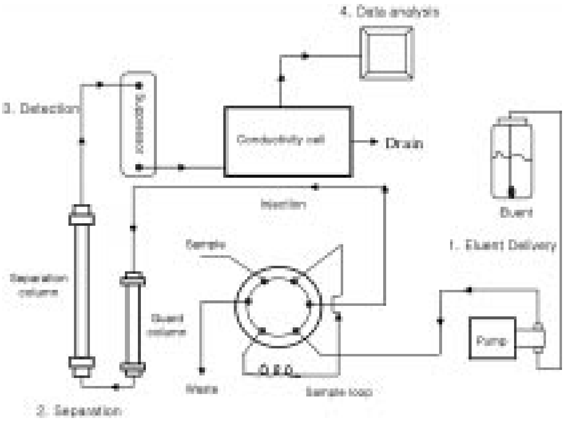

Fig. 1. Schematic representation of the ion chromatography system.

Table 1. Ion exchange chromatographic conditions

Separation	
Column	Ion pack AS14A (Dionex)
Eluent	1.6958g Na_2CO_3 & 0.168g $NaHCO_3$/ 2 l (under nitrogen)
Injection volume	10 µL (loop)
Detection	
Conductivity	DS5 Detection Stabilizer (Dionex)
Suppressor	AMMS® III (Dionex)
Regenerant	2.8 mL sulfuric acid 98%/2 l pure water

Eluant was prepared by dissolving 1.6958g Na_2CO_3 and 0.168g $NaHCO_3$ in 2000 L of ultra pure water. Regenerant was prepared by dropping 2, 8 mL sulfuric acid 98% into 1000 mL ultra pure water, then fill to mark of 2000 mL vessel.

2.2. Apparatus

Fig. 1 shows a schematic representation of the instrumental operation. Details of the operating conditions are given in Table 1. The measurements were carried out by a Dionex DX-80 system. The sulfuric acid for the chemical suppression and eluent were delivered from two transparently plastic vessels.

2.3. Procedure

All samples were stored in refrigerator at 4°C and filtered via Whatman 0.45 mm microfilters before injecting to IC. The sample was loaded through a 10 mL plastic syringe to the loop. After injection, the separation occurred on an anion exchange chromatography column (AS14A). On this high capacity column, carbonate/ bicarbonate eluent separates fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate within 12 minutes.

3. Results and Discussion

3.1. Identification and quantification

Anion peaks identification was based on retention times and standard injection. Two sets of calibration graphs for mixed standards with different concentration ranges (0.1-10 ppm and 1-100 ppm for chloride, nitrite, bromide, nitrate, sulfate) with good linear regressions were used. The chromatography calibration was obtained using four concentration levels of each anion. One of these was near, but above the minimum detectable concentration, and others covered the expected range of values found in real samples. The working calibration curve was verified weekly by injection of standard number 3 (2, 10, 10, 10, 10, 20 and 10 ppm of F^-, Cl^-, NO_2^-, Br^-, NO_3^-, HPO_4^- and SO_4^{-2}, respectively). The minimum detectable concentration of an anion is the function of the sample injection size and the conductivity scale used. In this investigation, with the scale of 300 μS and 10 μL loop and current conditions of instrument, the minimum detectable concentrations of Cl^-, NO_2^-, Br^-, NO_3^- and SO_4^{-2} are 0.05 ppm and 0.02 ppm for F^-, HPO_4^-. F^-, Cl^-, Br and SO_4^{-2} are not used as an index of eutroph-

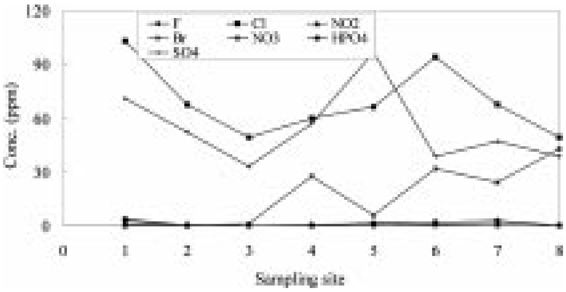

Fig. 4. Han River samples in the third sampling. The sample were collected with water sampler and stored at 4 in the refrigerator until IC test.

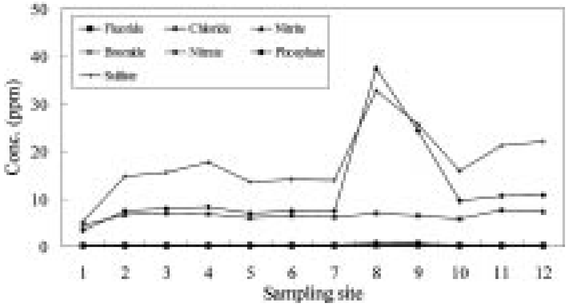

Fig. 2. Han River samples in the first sampling. The sample were collected with water sampler and stored at 4 in the refrigerator until IC test.

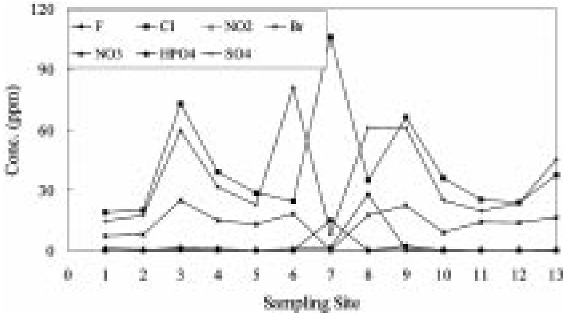

Fig. 5. Han River samples in the forth sampling. The sample were collected with water sampler and stored at 4 in the refrigerator until IC test.

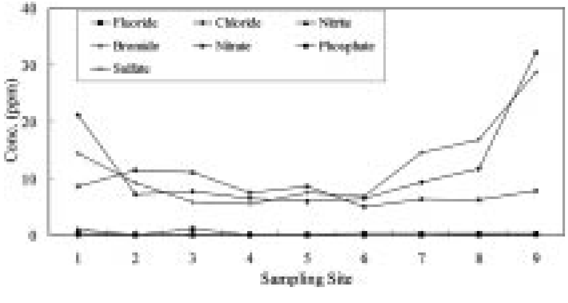

Fig. 3. Han River samples in the second sampling. The sample were collected with water sampler and stored at 4 in the refrigerator until IC test.

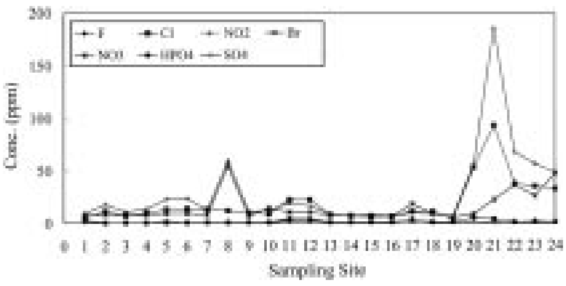

Fig. 6. Han River samples in the fifth sampling. The sample were collected with water sampler and stored at 4 in the refrigerator until IC test.

and help to predict the future water change. Therefore this data would be used as the basic data of anion analysis in the future.

3.2. Analytical data of Han River sample

Samples were periodically taken at various sites along Han River. In most cases, water was collected at 5 m depths from surface with a 1.5 L water sampler. Following analytical results, there are the usual presences of three species with high concentrations, chloride, sulfate and nitrate. This is showed in the following graphs: (names of sampling sites are listed in table below and map is not presented because the area is so broad and some sampling site are a little different in every sampling time.)

In order to evaluate the quality of this water, some

Table 2. Place of sampling sites

Site No.	Place	Site No.	Place
Sampling I		**Sampling II**	
1	Yang-su chulkyo	1	Yangkun Bridge
2	Sinyangsu Brigde	2	SungDuk Stream
3	Jokja Island	3	Sinbok 3ri
4	Jokja Insland (surface)	4	Sanasa
5	Paldang- Dam	5	Bokpo Bridge
6	3 Chuisujang	6	Buyong Stream
7	3 Chuisujang (surface)	7	3 Chuisu Jong
8	Kwangdong Bridge	8	Nam jong
9	Kwangdong Bridge (surface)	9	Kwangdong Bridge
10	Sonae Island		
11	Yongdam Bridge		
12	Water reservation line		
Sampling III		**Sampling IV**	
1	Anyang Stream	1	Bunchun Bridge
2	Dorim Stream	2	Habunchun Bridge
3	Hongje Stream	3	Suha Bridge
4	Bulkwang Stream	4	Kyung-su Bridge
5	Jungrang Stream	5	Pabal Bridge
6	Tan Stream	6	Mokri Stream
7	Sungnam	7	Jikri Stream
8	Sinchon Bridge	8	Sungwon Bridge
		9	Wangsan Bridge
		10	Yangji Bridge
		11	Kumhak Stream
		12	Wunhak Stream
		13	Moesan Stream
Sampling V			
1	Yangsu chulkyo	13	Buyong Stream
2	Jokja Island	14	Mokwang Iri
3	Paldang Dam (north)	15	Muntio Stream
4	Paldang Dam (south)	16	Sehoo Stream
5	Yongdam Bridge	17	Sinbok Stream
6	Water reservation line	18	AsTn Stream
7	Hangli Stream	19	Bobpo Stream
8	Sinae Stream	20	Topyung IC
9	Yungdong Stream	21	Topyung
10	Sungduk Stream	22	Guri-Donong
11	Yangkun Bridge	23	Guri
12	Dukpyung Stream	24	Imsong Bridge

other criteria were also determined such as COD, NH_4^+... but in this investigation, only anionic parameters were analyzed by ion chromatography. The above figures indicate that the high concentration of chloride is frequently come together with that of sulfate, for example, in the forth sampling, at site number 3 and 9, in the fifth sampling at 20, 21, 22, 23, and 24. It is often assumed that chloride in surface water is derived from marine salts, either via salt precipitation; leaching of raining water and streams down from rock mountain located on both sides of Han river. Besides, the intrusion of current seawater should also be considered. Nitrite normally does not appear or does with very low concentrations because in aerobic condition of surface water, it will be easily converted into nitrate. This also explains for the fairly high content of nitrate (around 10 mg/L) in water samples.

3.3. Calibration and Detection limits

Quantification limits of chloride, bromide, nitrate, nitrite and sulfate are 0.1 ppm; that of fluoride and hydrophosphate are 0.02 and 0.2 ppm, respectively. Detection limits of anions in this ion chromatographic investigation strongly depend on sample loop, conductivity scale and the regeneration of suppressor membrane. In a long analysis, the characteristic of this membrane can be slightly changed. An incomplete suppression could increase baseline signal, thus, raises detection limits.

3.4. Interferences

This analysis was suffered from a little interference. However, when a significant amount of organic substances such as organic acids... are present in the water matrix, fluoride in low concentration will soon come out of separation column with above matters. Hence, a wrong identification and quantification of fluoride can be occurred. To solve the problem, an addition of fluoride is assumingly needed.

4. Conclusions

An investigation on Han River water quality in frame of monitoring and reservation was conducted. Ion exchange chromatographic instrument DX-80 Dionex was used to analyze the presences of novel contaminants in surface water samples taken from various sites on Han River. This method is based on anion exchange chromatographic separation sequenced by conductivity detection. The method allowed the simultaneous determination of water matrix anions such as fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate without sample pretreatment. There are frequently high concentrations of chloride and sulfate at nearly most sites. An existence of fairly high content of nitrate as a contaminant (around 10 mg/L) was also found in this investigation.

The instrument appears to be suitable for routine analysis of that samples with acceptable detection limits of anions and simple operation. This data could be importantly used to protect city water supply and to decide the policy blocking the containment of water in Han River. And this study has an important role in the respect to present the method of measuring and monitoring water quality.

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