ION CHROMATOGRAPHIC DETERMINATION OF SOME ANIONS IN FRESH AND SALINE WATER SAMPLES

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ABSTRACT

Water samples were collected from the different stages of potable water treatment plant at Suez region as well as from inlet and outlet of Suez Oil Processing Company. The water samples were filtered using 0.2μm membrane filter paper to avoid the column plugging of the ion chromatograph. The monitoring of chloride, fluoride, bromide, nitrite and nitrate in the water samples was carried out by using Ion Chromatography(IC) where the buffer Na_2CO_3 was used as eluent and conductance as a detector. The separation of the previous anions is identified using the retention time (min) of each anion, which was compared to those of standard solutions. The results obtained from the Ion Chromatography(IC) instrument indicated that, the range of anions are 67-187mg L^{-1}, 0.11-0.481mg L^{-1}, 0.042-0.193 mg L^{-1}, nil-0.47mg L^{-1} and 0.11-0.481 mg L^{-1} for chloride, fluoride, bromide, nitrite and nitrate respectively recorded in the different stages of potable water treatment plant in Suez. The average range of anion contents measured in the inlet and outlet of Suez Oil Processing Company are: 24656.9-26944.1 mg L^{-1}, 0.019-0.079 mg L^{-1}, 0.954-1.15 mg L^{-1}, 0.045-0.835 mg L^{-1} and 6.685-8.518 mg L^{-1} for chloride, fluoride, bromide, nitrite and nitrate respectively. Finally, the Ion Chromatography has become a new line in the field of analytical chemistry and an important technique for the monitoring of water quality and for quantifying anions at low concentration in different types of water.

1. INTRODUCTION

The introduction of ion chromatography into analytical practice caused revolutionary changes in inorganic analysis [**Krokhin et al., (2002)**].This is particularly true for the determination of the common anions such as chloride, fluoride, bromide, nitrite, nitrate, phosphate and sulphate which is often desirable to characterize a water and assess the need for specific treatment. Although conventional colorimetric, gravimetric and titrimetric methods are available for the determination of individual anions, only ion chromatography provides a single instrumental technique that may be used for their rapid and sequential measurement. Furthermore, ion chromatographic methods offer several advantages over conventional methods:

1- speed or short time needed for the analysis
2- sensitivity (anions can be detected at a 10µg/lconcentration in 50 µl sample)
3- selectivity, which is ensured by selecting a combination of suitable analytic separation and detection
4- simultaneous detection of multiple ions [**Weiss (1995)**]

Originally the term 'ion chromatography' referred to the column technique basedon the separation of ions on ion exchanger and subsequent conductmetric detection [**Krokhin et al., (2002)**]. In ion optimized ion chromatography the employed working eluent is usually made up of carbonate- hydrogen carbonate buffers. This eluent can be converted into species of low conductance such as H_2CO_3, after the ion exchange of their cations with hydrogen ions is done by suitable devices such as packed- bed chemical suppressor or membrane suppressors.

Nitrates are widely used as inorganic fertilizers and in explosive and oxidizing agents in the chemical industry. They are also used as food preservatives, especially in cured meats [**Agriculture Canada (1991)**]. The other sources of nitrate in water include decaying plant or animal material. domestic sewage and geological formations containing soluble nitrogen compounds [**Egboka (1984)**].

The study of health effects of nitrate showed that ingested nitrate is absorbed in the upper small intestine and distributed rapidly through the body. Roughly 25 % is recirculated into the saliva. where approximately 20 % is reduced to nitrite by the oral micro flora.

If the pH of the stomach is elevated the growth of nitrite-reducing bacteria is allowed and nitrates are converted to nitrites. Nitrite may react in the stomach with secondary or tertiary amines and amides present in foods such as cheese or meat to form a toxic nitroso compounds. Several studies on rats fed sodium nitrite in the diet or via drinking water have found an increased incidence of tumors **[Mirvish et al., (1980)]**. However, dental fluorsis would be expected to be associated with fluoride intake (0.05 mg/kg/day) **[Zohouri et al., (2002)]**. This work is an attempt to quantify chloride, fluoride, bromide, nitrite and nitrate in the water samples collected from potable water treatment station (fresh water) and wastewater of Suez Oil Processing Company (saline water) using ion chromatography procedure.

2. MATERIAL AND METHODS

2.1. Collection of water samples

Water samples were collected form Suez potable water treatment station, which includes inflow water (fresh water), outlet of clarifier unit, outlet of sand filter unit, outlet of the station, as well as Suez Oil Processing Company. The samples were collected from inflow water (Sues bay water) and outflow effluent (wastewater) during a period 2003-2004. The water samples used for chemical analysis were refrigerated until the time of analysis. Water samples were filtered using 0.2μm membrane filter paper to avoid the column plugging of the ion chromatograph.

2.2. Preparation of mobile phase (eluent).

It should be freshly prepared daily by dissolving 0.1848 g of sodium bicarbonate (BDH) and 0.2968 g of sodium carbonate (BDH) in deionized water and diluted to one liter; the eluent was degased by sparing with nitrogen.

2.3. Preparation and injection of standard solutions

1000 ppm of each standard anion solutions (sodium chloride, sodium fluoride, sodium bromide, sodium nitrite and sodium nitrate)was prepared. The chemicals used were of analytical grade (BDH).

2.4. Determination

The anions were determined by using ion chromatograph (DX-120, Dionex Ion Pac, USA) and AS14 (250mm×4mm I.D) column .The buffer solution of $Na_2CO_3/NaHCO_3$ was used as eluent and conductance as detector .The separated anions were identified via retention time as compared to standard anions solutions. The ion chromatograph was turned on and the eluent rate (1ml/min) was adjusted to obtain stable phase line. The standard anion solutions were injected to plot calibration curve (peak height against conductivity of each anion), then the filtered water samples were injected into the ion chromatograph. The chromatogram obtained from the instrument is the relation between conductivity (μs) and retention time of each anion (min).However, The determination of chloride and sulphate in water samples was carried out after making suitable dilution with deionized water.

2.5. Data analysis

Statistical analysis of the results was carried out with the statistical SPSS 11.0 package.

2.6. Calibration and reproducibility

Standard curves were prepared by plotting the concentration of a known standard versus the peak conductivity. The standard curve for each of the elements was made by the IC instrument using one standard and one blank and then stored in the instrument's memory. The standard anion calibration values and. reproducibility tests based on five injections of anion standards solutions of Chloride, Fluoride, Bromide, Nitrite and Nitrate were performed.

2.7. Accuracy and precision of measurements

Using the calibration standards listed above precision values of low sample volume anion analysis were between 1.2 and 2.8 % relative standard deviation(RSD) as shown in Table 1, that is comparable to precision using standard IC method. Recent advances in suppression technology made lowering the sensitivity of the detector possible. By improving the suppression technology and adjusting method parameters such as eluent concentration, sample volume, eluent flow rate, sample buffer, and detector range the detection limits were lowered without

lengthening the analysis time or increasing the volume of sample required for analysis. The precision and accuracy decreased slightly but still remained within acceptable limits.

Table (1): standard calibration values and detection limit of different anions in fresh and saline water.

Anions	Calibration value mgl^{-1}	Detection limit value mgl^{-1}	%RSD N= 5
Fluoride	2	0.2	1.4
Chloride	2	0.2	1.2
Bromide	2	0.2	1.2
Nitrite	10	1.0	2.5
Nitrate	15	1.5	2.8

N = number of samples

3. RESULTS AND DISCUSSION

3.1. Chloride

The concentrations of chloride for the different stages of potable water treatment station are given in Table (2).These concentrations are varied from a minimum value of 76 mg L^{-1} in spring 2003 to a maximum value of 187 mg L^{-1} in autumn 2003.While, for outlet of potable water station, the chloride contents are changed from the low value of 65 mg/l to the high one of 85.57 mg L^{-1}in summer 2003 as shown in Table (2). The higher chloride content in the inlet of potable water station may be due to the decrease for depth water in the main channel of raw water, which feeds the station with fresh water. Therefore, excessive chloride concentration in the water could increase the rate of corrosion of metals in the distribution system, which in turn leads to raise the concentration of metals in the drinking water [Wand et al., (1994)].

Table (2): Concentration of (Cl⁻, F⁻, Br⁻, NO_2^- and NO_3^-) mg L⁻¹ at the different stages of potable water treatment station at various seasons.

Location	Season ＼ Anion	C l⁻	F⁻	Br⁻	NO_2^-	NO_3^-
1	spring 2003	76.00	0.390	0.130	Nil	0.68
	summer 2003	97.21	0.300	0.193	0.37	1.12
	autumn 2003	187.60	0.481	0.200	0.47	7.80
	winter 2004	87.80	0.265	0.100	0.15	1.95
	Average	**112.00**	**0.359**	**0.156**	**0.33**	**2.89**
2	spring 2003	73.00	0.330	0.050	Nil	0.60
	summer 2003	92.36	0.220	0.061	0.12	1.01
	autumn 2003	96.00	0.340	0.066	0.18	5.15
	winter 2004	81.62	0.235	0.042	0.10	1.86
	Average	**85.75**	**0.281**	**0.055**	**0.13**	**2.16**
3	spring 2003	71.44	0.220	0.050	Nil	0.42
	summer 2003	89.18	0.170	0.060	0.12	0.79
	autumn 2003	80.00	0.230	0.063	0.11	2.70
	winter 2004	77.04	0.155	0.040	nil	1.66
	Average	**79.31**	**0.193**	**0.053**	**0.115**	**1.39**
4	spring 2003	65.00	0.110	0.043	Nil	0.11
	summer 2003	85.57	0.120	0.051	Nil	0.40
	autumn 2003	67.00	0110	0.052	Nil	1.74
	winter 2004	74.70	0.135	0.031	Nil	1.40
	Average	**73.22**	**0.119**	**0.037**	**Nil**	**0.94**

1- infiow water (fresh water).   2- outlet of clarifier unit.
3- outlet of sand filter unit.   4- outlet of the station.

On the other hand, the data of chloride in the inlet water and outlet effluent of Suez Oil Processing Company are summarized in Table (3). Looking at Table (3), the values of chloride in the outflow effluents are greater than those recorded in the inflow water. This may be related to the mixing of salty water with oil during the process of withdrawing petroleum considered as a source of salts petroleum wastewater.

Table (3): Concentration of (Cl^-, F^-, Br^-, NO_2^- and NO_3^-)mg $L^{-1}$of the inflow water and the outflow effluent of the Suez oil Processing company at various seasons during 2003-2004.

Location	Anion Season	Cl^-	F^-	Br^-	NO_2^-	NO_3^-
Inflow water (5)	spring 2003	24511.4	Nil	0.517	Nil	1.100
	summer 2003	26035.0	Nil	1.900	Nil	7.400
	autumn 2003	24847.0	0.011	1.200	Nil	18.00
	winter 2004	23234.0	0.065	0.200	1.80	0.240
	Average	**24656.9**	**0.331**	**0.954**	**1.80**	**6.685**
Outflow effluent (6)	spring 2003	26600.0	Nil	0.551	Nil	1.31
	summer 2003	28155.3	Nil	2.080	1.360	12.50
	autumn 2003	27521.0	0.014	1.740	0.167	20.00
	winter 2004	25500.0	0.300	0.230	1.813	0.26
	Average	**26944.1**	**0.157**	**1.150**	**1.113**	**8.51**

3.2. Fluorine

Fluorine accounts for about 0.3g/kg of the earth's crust. Inorganic fluorine compounds are used in the production of aluminum and fluoride is released during manufacture and use of phosphate fertilizers which contain up to 4% fluorine [Chou et al., (1994)]. In addition, hydrofluoric acid is used extensively in semiconductor manufacturing, for wafer etching and quartz cleaning operations. Fluoride concentration of 1000-3500mg/l is found in typical wastewater of local semiconductor industry

[Cao et al., (2000)]. Fluoride is sometimes added to drinking water to prevent dental cavities while excessive fluoride in drinking water causes dental fluorsis or mantling of teeth [Elewa (1991)]. As shown in Fig.1, the reported fluoride concentration drop from the inlet water to outlet of the potable water station is mainly due to the precipitation of calcium fluoride which was adsorbed on magnesium hydroxide or suspended solids [Shahine (2005)] and its precipitation to the bottom of the clarification ponds in the potable water treatment . This interpretation was supported by a significant negative correlation (r =-0.64, p≤0.05) between calcium and fluoride contents in water.

Seasonal average concentration of fluoride is 0.239mg L^{-1}which lies within the maximum permissible limit of fluoride in water (0.8 mg L^{-1}) according to the law of 26/2/1995. Similar results of fluoride concentrations in the 60 water samples in different types of water sources at Tibet-China show that none exceeded 0.18 mg L^{-1} with an average level 0.1 mg L^{-1} [Elewa (1991)]. On the other hand, the concentrations of fluoride in the inflow water and outflow effluents of Suez Oil Processing Company are collected in Table (3). From Table (3) we can see that the concentration of fluoride during autumn 2003 was 0.011 mg $L^{-1}$and 0.014 mg L^{-1} for the inflow and outflow water respectively while it was increased to a value of 0.065 and 0.30 mg L^{-1} in the inflow water and outflow effluent during winter 2004. The presence of fluoride in the inflow water may be due to decay of livings, while for outflow effluent may come from the Earths crust, rocks and ground water containing fluoride during the drilling for petroleum oil [Paulo et al., (2004)].

3.3. Bromide

Bromine is found in seawater and exists as the bromide ion at a level of about 65 mg L^{-1}. Bromine is extremely reactive and corrosive and will produce irritation and burning to exposed tissues. Over than 00.05 mg L^{-1} fresh water indicates the presence of industrial wastes, possibly from the use of pesticides and biocides containing bromine. Bromide is extensively used in the pharmaceutical industry and occurs normally in range of 1.5 to 50 mg L^{-1} [Nessim et al., (1995)]. Concentrations of bromide at different stages of potable water treatment station are given in Table (2). It is clear from Table (2) that the content of bromide decreases during the stages of purification which is mainly related to the using of alum as clarifying reagent.

On the other hand, the concentration of bromide in saline outflow effluent of Suez Oil Processing Company is slightly higher than that reported in the inflow water as indicated in Table (3). Such increase in the bromide content may be attributed to the washing of crude oil with water.

3.4. Nitrite and Nitrate

Nitrate is considered as the most and predominate inorganic nitrogen compound in the water. It is appears to be the most essential and major nutrient for phytoplankton growth [Cecen et al., (1996)]. Experiments suggest that neither nitrite nor nitrate act directly as a carcinogen in animals but there is some concern about increased risk of cancer in humans from the endogenous and exogenous formation of N-nitroso compounds many of which are carcinogenic in animals. Table (2) summarizes the results of nitrate in the fresh water of the potable water treatment station.

The maximum value of nitrate is 7.8 mg L^{-1} recorded during autumn 2003 and the minimum one of 0.68 mg L^{-1} was detected during spring 2003 .The minimum nitrate value may be correlated to the consumption of nitrate by phytoplankton which flourish in spring season .Nevertheless, the maximum content of nitrate may be probably due to the unexpected growth of Phytoplankton during autumn 2003 as a result of the disposal of agricultural wastewater directly to the fresh water canal without any kind of wastewater treatment. The nitrite ion has a similar trend of variation at the potable water treatment station as shown in Table (2) where the nitrite concentration declines from the inlet water to the outlet of the station .This is mainly attributed to the addition of chlorine as a disinfectant which leads to oxidation of nitrite to nitrate .Comparison between the level of nitrate scored in the drinking water at Suez region with that recorded in treated water in municipal supplies in Nova Scotia (Canada) indicated that the nitrate level in treated water in the Suez region was higher than that recorded in Nova Scotia (0.05 mg L^{-1}) [Agriculture Canada (1991)].

The nitrite and nitrate levels detected by IC for the inflow water and outflow water of Suez Oil Processing Company are listed in Table (3). The concentration of nitrate ion tends to decrease when going from the inlet to outlet effluents of Suze Oil Prossing Company. This is mainly due to the reduction of nitrate ion to ammonia by some species of

bacteria [**Nova Scotia Department of health (1981)**]. On the other hand, the relative increase in the concentration of nitrite content in the inlet to outlet effluents of Suez Oil Processing Company in winter 2004 may be related to the decay and redissolution of microorganism and phytoplankton in water.

3.5. Comparison between the IC method and other analytical methods

Anions in mg/ L and µg/ L levels can be analyzed with the direct IC injection technique. For determination of lower levels of anionic impurities (lower than µg/L levels) sample preconcentration is necessary. However, the preconcentration method has several disadvantages if compared with the large volume used in direct injection technique.

On the other hand, the determination of nitrate in water can be achieved by reduction method, where the nitrate is reduced to nitrite ion by Cadmium reduction column and the nitrite ion is then determined by means of the formation of azo dye compound by reaction with sulphanliamide and n-(1-naphthyl ethylene diamine). The absorbance is measured using ultraviolet spectrophotometer at wavelength 220 nm. The disadvantage of this method is the oxidation of the nitrite to nitrate during analysis of the water sample which leads to the error in the results of nitrite. Furthermore, some ions potentially interfere with nitrite determination. These are: Chloride, Bromide, Sulphide and Cyanide. [**SMEWWA (1995)**]

CONCLUSION

A ppm level IC analysis method that can be routinely used in the laboratory has been developed and implemented. This method can be used both for samples containing very low levels of anions and for samples that contain multi anions. The precision and accuracy of this method were between 1.2 and 2.8 % which are comparable to the standard IC method. The detection limits for Bromide Fluoride and Chloride were 0.2 mg L^{-1}; while for Nitrite was 1mg L^{-1} table 1. However, the higher detection limit recorded for Nitrate anion was 1.5-mg L^{-1}. The present method can be taken as an appropriate analytical tool for monitoring the multi anions in drinking water and waste water samples.

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تقدير بالكروماتوغرافيا الايونى لبعض الانيونات فى عينات المياه العذبة والمالحة

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لقد تم جمع عينات الماء من المراحل المختلفة لمحطة معالجة مياة الشرب بمنطقة السويس وكذلك المياة الداخلة والخارجة لشركةالسويس لتصنيع البترول. ولقد تم ترشيح هذة العينات باستخدام ورقة ترشيح قطرة 2. ميكرو متر لتفادى انسداد عمود الكروماتوغرافيا الايونى . وقد تم أجراء مراقبة الكلوريد ،الفلوريد ، البروميد ، النيتريت والنترات فى عينات الماء باستخدام الكروماتوغرافيا الايونى حيث استخدام محلول كربونات الصوديوم المنظم كمحرر واستخدام الموصلية ككشاف.

تم التعرف على الانيونات المفصولة السابقة باستخدام زمن الاستبقاء لكل انيون ، والتى تم مقارنتها مع المحاليل القياسيةمن خلال النتائج المتحصل عليها من جهاز الكروماتوغرافيا الايونى اتضح ان مستوى الانيونات يكون :67 – 187 مليجرام/ لتر، 0.11 – 0.481 مليجرام /لتر ، 0.042 – 0.193 مليجرام /لتر ، صفر – 0.47 مليجرام / لتر ، 0.11 – 0.481 مليجرام /لتر لكل من الكلوريد ، الفلوريد ، البروميد ، النيتريت ، والنترات على التوالى التى سجلت فى المراحل المختلفة لمحطة معالجة مياة الشرب بالسويس. بينما متوسط محتوى الانيونات فى المياة الداخلة والخارجة فى شركة السويس لتصنيع البترول تكون : 24656.9 – 26944 مليجرام /لتر ، 0.019 – 0.079 مايجرام /لتر، 0.954 – 1.15 مايجرام /لتر 0.045 – 0.835 مليجرام /لتر ، 6.685 – 8.519 مليجرام / لتر ، لكل من الكلوريد ، الفلوريد ، البروميد ، النيتريت والنترات على التوالى . واخيرا فان الكروماتوغرافيا الايونى اصبح خط جديد فى مجال الكيمياء التحليلية واسلوب هام فى مراقبة جوده المياه وكذلك التقدير الكمى للانيونات فى التركيز الاقل فى الانواع المختلفة للمياه.