Anions Analysis in Ground and Tap Waters by Sequential Chemical and CO_2-Suppressed Ion Chromatography

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ABSTRACT

An ion chromatographic method using conductivity detection with sequential chemical and CO_2 suppression was optimized for the simultaneous determination of fluoride, chloride, bromide, nitrate, phosphate and sulfate in ground and tap water. The separation was done using an anion exchange column with an eluent of 3.2 mM Na_2CO_3 and 3.2 mM $NaHCO_3$ mixture. The method was linear in the concentration range of 5 to 300 µg/L with correlation coefficients greater than 0.99 for the six inorganic anions. The method was also shown to be applicable in trace anions analysis as given by the low method detection limits (MDL). The MDL was 1µg/L for both fluoride and chloride. Bromide, nitrate, phosphate and sulfate had MDLs of 7 µg/L, 10 µg/L, 9 µg/L and 2 µg/L, respectively. Good precision was obtained as shown in the relative standard deviation of 0.1 to 12% for peak area and 0.1 to 0.3% for retention time. The sensitivity of the method improved with the addition of CO_2 suppressor to chemical suppression as shown in the lower background conductivity and detection limits. The recoveries of the anions spiked in water at 300 µg/L level ranged from 100 to 104%. The method was demonstrated to be sensitive, accurate and precise for trace analysis of the six anions and was applied in the anions analysis in ground and tap waters in Malolos, Bulacan. The water samples were found to contain high concentrations of chloride of up to 476 mg/L followed by sulfate (38 mg/L), bromide (1 mg/L), phosphate (0.4 mg/L), fluoride (0.2 mg/L) and nitrate (0.1 mg/L).

Keywords: Ion chromatography, chemical suppression, CO_2 suppression, anions

INTRODUCTION

Ion chromatography (IC) provides the advantage of being a simple, fast, small sample volume demanding, and fit for purpose technique for the routine analysis of anions in water samples (Miskaki et al., 2007). Much importance is given to monitoring water quality to ensure safe and potable water for public consumption. Along with microorganisms, heavy metals and organic pollutants, inorganic anion contaminants are monitored. Fluoride and nitrate anions are considered contaminants in drinking water by the US EPA National Primary Drinking Water Regulations. High concentrations of fluoride when ingested can result to bone disease while nitrate can cause birth defects (US EPA, 2011). Although not considered harmful, chloride and sulfate should not exceed 250 mg/L for water to become potable according to the EPA's National Secondary Drinking Water Regulations (US EPA, 2011). In addition, based on the Philippine National Standards for Drinking Water (PNSDW), fluoride and nitrate concentrations in water should not exceed 1 mg/L and 50 mg/L, respectively. Chloride and sulfate levels have limits of 250 mg/L in accordance with the standards used by the US EPA (DOH, 2007).

Elevated levels of bromide in water were shown to increase the formation of disinfection by-products (DBPs) such as trihalomethanes and haloacetic acids during chlorination (Sun et al., 2009); while with ozonation, the formation of bromate was observed (Richardson et al., 2007). These DBPs were reported to cause increased risk of cancer (US EPA, 2011). Phosphate concentrations in groundwater are also monitored because they were found to be contributing to eutrophication in surface waters (Holman et al., 2008).

To comply with strict regulations in water standards, analytical methods need to constantly provide accurate and reliable results on the levels of contaminants in water such as inorganic anions. Ion chromatography has been used extensively for this purpose employing different approaches and detection techniques.

Ion chromatography, in the early years, has been used for anions analysis with spectrophotometric UV detection. In those methods, prior formation of organic derivatives and ion-pairs were necessary before the samples are analyzed using UV detection (Stefanovic et al., 2001). Other detection techniques are amperometry, potentiometry and post-column reaction (Buchberger, 2001). Currently, the method used for anions analysis is by conductimetric detection because of its better sensitivity for ions. New techniques are also explored such as hyphenation of IC systems using atomic absorption, fluorescence or emission detection as well as mass spectrometric detection (Haddad et al., 2008).

The analytical performance of IC with conductimetric detection can be improved with suppression techniques although non-suppressed IC as reported by Stefanovic et al. (2001) can achieve good separation using computer programs for optimization. In chemically suppressed IC, a cation exchanger is used to replace the metal cations accompanying the anions of interest with more conductive hydronium ions. This process also transforms highly conductive eluents like Na_2CO_3/$NaHCO_3$ to weakly conductive substances. This significantly improves the conductivity signal of the analyte (Kleimann et al., 2007).

Further improvement in anions detection may be done using a CO_2 suppressor after chemical suppression. The carbonic acid formed during chemical suppression is in equilibrium with CO_2 and water. Installing a CO_2 suppressor removes CO_2 from the eluent and shifts the equilibrium forward towards the formation of water (Kleimann et al., 2007). As a result, the background conductivity is reduced to that of water which leads to lower detection limits.

We report here a study that used an ion chromatographic-conductivity detection system with sequential chemical and CO_2 suppression to analyze fluoride, chloride, bromide, nitrate, phosphate and sulfate in local ground and tap waters. The optimized method was applied to actual samples taken from groundwater and water from the distribution lines in Malolos, Bulacan. The results of this study not only established the levels of the anions in the water samples but also provided an accessible method for routine anions analysis in potable water that can be used by water providers and government monitoring agencies in the Philippines.

MATERIALS AND METHODS

Instrumentation

The chromatographic system used was a Metrohm 881 Compact IC pro (Metrohm, Switzerland) consisting of a sample and eluent degasser, IC high-pressure pump, six-port injection valve, column heater, separation column and conductivity detector. The separation column used was a Metrohm Anion Column Metrosep A Supp 5-150, 150 mm x 4.0 mm, packed with polyvinyl alcohol with quaternary ammonium groups and was used with a 5 mm x 4 mm Metrosep A Sup 4/5 guard column. The chromatograph was equipped with a Metrohm suppressor module for chemical suppression and a Metrohm CO_2 suppressor. Samples and standards were injected into a 20 µL sample loop. The eluent flow was 0.80 mL/min with a total run time of 14 min. Data acquisition was performed using a MagIC Net 2.2 chromatography software.

Reagents

Standard solutions for calibration were prepared by dilution of the stock 10.0 mg/kg certified multianion standard solution (Sigma-Aldrich, Switzerland) containing fluoride, chloride, bromide, nitrate, phosphate and sulfate. The concentrations of the calibration solutions ranged from 5 to 300 µg/L. All solutions were prepared with 16 to 18 megaohm-cm ultrapure water (Barnstead, Dubuque, Iowa).

The eluent composition was a mixture of 3.2 mM Na_2CO_3 and 3.2 mM $NaHCO_3$ prepared by dissolving appropriate amounts of $NaHCO_3$ and Na_2CO_3 (Hi-Media, Mumbai, India) in ultrapure water. The 100 mM H_2SO_4 regenerant solution used for the anion conductivity suppressor device was prepared from 18.0 M H_2SO_4 (Mallinckrodt Baker, Inc., Paris, KY, USA).

Optimization and Validation of Instrument Parameters

Preliminary studies on suppression effects and eluent composition were performed using a 300 µg/L standard solution. Chromatograms of the standard solution were obtained from the IC setup that used chemical suppression only, and from the modified system which employed sequential chemical and CO_2 suppression. The same solution was also subjected to eluent compositions of 5.0 mM $Na_2CO_3/NaHCO_3$ and 3.2 mM $Na_2CO_3/NaHCO_3$ to determine the optimum mobile phase based on sensitivity, resolution and analysis time. Studies on linearity, method detection limit, repeatability and accuracy of the method were performed using the optimum eluent composition and sequential suppression technique.

Anions Analysis of Ground and Tap Water Samples

Ground and tap water samples were obtained from household deepwells and distribution lines in Baranggay Panasahan and Baranggay Tikay in Malolos, Bulacan. The sampling sites are shown in Figure 1. The water samples were collected in pre-cleaned 330 mL mineral water bottles. During sampling, water was allowed to flow for 1 min before pouring into the water-rinsed bottles. Turbid water samples were vacuum filtered through 0.45 µm nylon membrane filters (Whatman, Maidstone, England).

Using the optimized chromatographic parameters, the anions in ground and tap water samples were identified based on individual retention times which were evaluated using standard anions solutions. Serial dilution of water samples was performed to quantify anions that were initially out of the established linear range. All analyses were done at room temperature. The concentrations of the anions in the water samples were calculated using linear regression and external standard calibration method.

RESULTS AND DISCUSSION

Optimization of Ion Chromatographic System

Common ion chromatographic systems using $Na_2CO_3/NaHCO_3$ eluent produce weakly conductive H_2CO_3 which exists in equilibrium with CO_2 and H_2O. The instrument's sensitivity for the anions may be enhanced by reducing the concentration of CO_2 generated through the use of a CO_2 suppressor. In this way, the conductivity of water will be approached to serve as the chromatogram's baseline.

Figure 1. Sampling Sites: Baranggays Panasahan and Tikay in Malolos, Bulacan (Maps adapted from CPDO, 2008 and Gonzales, 2005).

The anions included in this study were fluoride, chloride, bromide, nitrate, phosphate and sulfate, six of the commonly analyzed inorganic anions in environmental monitoring. Optimization of the ion chromatographic method that uses Na_2CO_3/$NaHCO_3$ was performed by first evaluating the effects on the sensitivity of measurement using chemical suppression alone, and using chemical and CO_2 suppression in sequence. The effects of CO_2 suppression illustrated in Figure 2 show that the incorporation of CO_2 suppressor after chemical suppression significantly improves detection of the six anions. CO_2 suppression decreased the baseline conductivity to less than 1.6 µS/cm. In effect, the sensitivity increased as evident from sharper and enhanced anion peaks. Additionally, the CO_2 suppressor dramatically reduced the water dip in the beginning of the plot that may interfere with the first eluting anions. With the lowered background conductivity, anions separation and analysis time were optimized. Good resolution with shorter analysis time was achieved by using the right eluent composition. An initial run with chemical suppression alone was done with an eluent of 3.2 mM Na_2CO_3/ 1.0 mM $NaHCO_3$. Although complete separation was achieved, the analysis required 28 min to elute all the anions. With chemical plus CO_2 suppression, the eluent composition was modified to 5 mM Na_2CO_3/ 5 mM $NaHCO_3$ resulting in separation of the anions in 9 min (Figure 3). However, bromide and nitrate peaks overlapped to form a broad peak at about 7 min. Peak separation of these two anions was achieved when the eluent was changed to 3.2 mM Na_2CO_3/ 3.2 mM $NaHCO_3$. All the anions were completely separated in a total analysis time of 14 min. A chromatogram presenting the ion chromatographic

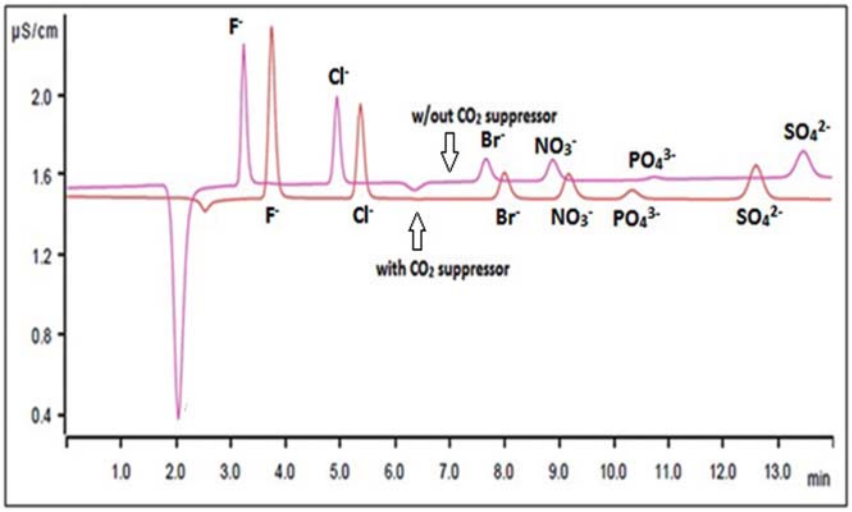
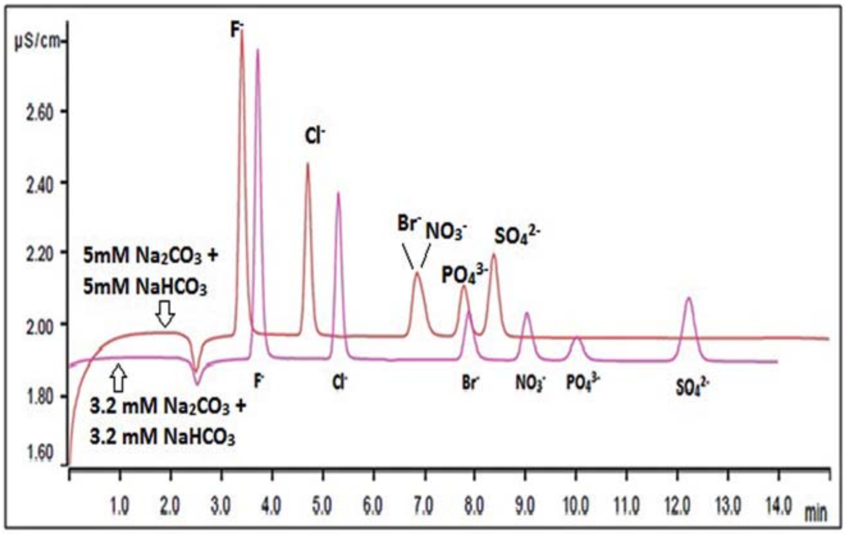


Figure 2. Chromatograms showing water dip reduction upon addition of CO_2 suppressor to chemical suppressor. [Conditions: Metrosep A Supp 5 150/4.0 column, 3.2 mM $NaHCO_3$/3.2 mM Na_2CO_3 eluent, 0.8 mL/min flow rate, 20 µL injection volume, 300 µg/L standard solution]

Figure 3. Effects of eluent composition in anions separation and analysis time. [Conditions: Metrosep A Supp 5 150/4.0 column, $NaHCO_3$/Na_2CO_3 eluent, 0.8 mL/min flow rate, 20 µL injection volume, 300 µg/L standard solution, sequential chemical and CO_2 suppressor]



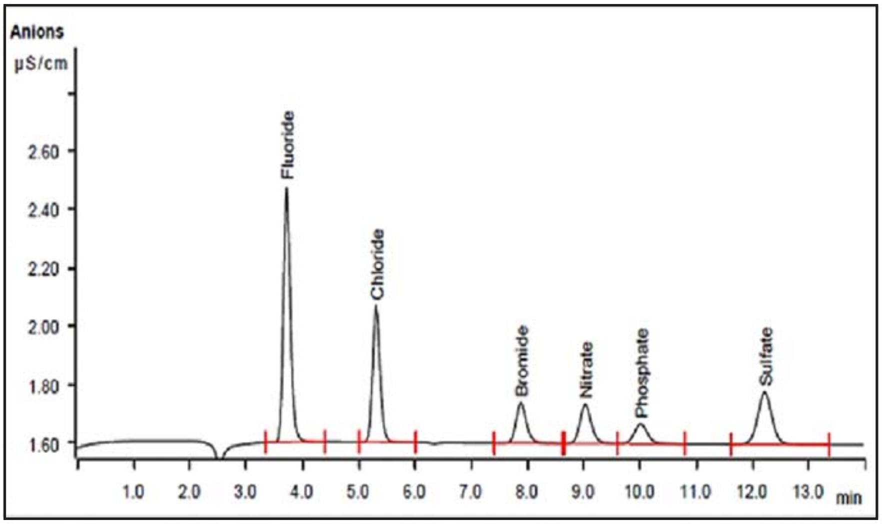


Figure 4. Chromatogram showing separation of the six anions using the optimized method. [Conditions: Metrosep A Supp 5 150/4.0 column, 3.2 mM $NaHCO_3$/ 3.2 mM Na_2CO_3 eluent, 0.8 mL/min flow rate, 20 µL injection volume, 300 µg/L standard solution, sequential chemical and CO_2 suppressor]

analysis of the six anions under the optimized conditions is shown in Figure 4.

Performance of the Optimized Ion Chromatographic Method

With the optimized method, calibration plots (n=3) covering the concentration range of 5 to 300 µg/L were constructed and are shown in Figure 5. The linear relationship of peak area with concentration was assessed using linear regression. The results from the calibration data show that in this range, the response for all anions with increasing concentration was linear with near unity correlation coefficients of 0.9903 to 0.9998.

Moreover, the 10 µg/L standard solution that was within the calibration range was analyzed to confirm if the anion peaks for this concentration would have signal to noise ratio of greater than 3. All anions came out in the chromatogram with acceptable signal to noise ratios and were clearly detectable with good resolution. The standard solution of 10 µg/L anions concentration was analyzed eight consecutive times to determine the method's detection limit for each ion. The detection limit, in accordance to EPA Method 300.1, was estimated from the standard deviation multiplied by the student's t-value at 99% confidence level. The detection limit was calculated using the equation

$$\mathrm{MDL} = 2.998 \times SD \qquad (for\ n=8) \qquad (1)$$

where MDL is the method detection limit; 2.998 is the student's t-value for n=8; and SD is the standard deviation of all the measurements. The calculated MDLs were comparable to the MDLs reported in US EPA Method 300.1. Nitrate had the highest MDL of 10 µg/L followed by phosphate (9 µg/L), bromide (7 µg/L), sulfate (2 µg/L), and lastly, chloride and fluoride with the same MDL of 1 µg/L. The results signify that trace anions level can be quantified using the optimized method given that the anions concentrations are above the reported detection limits. The MDL for each anion from the optimized method and from the EPA Method 300.1 (Hautman et al., 1997) are shown in Table 1. Except for nitrate, the MDLs for all the anions obtained using the optimized method are lower than the values reported by the US EPA Method 300.1. The difference can be attributed to the different IC systems used for both methods. More importantly, a Dionex AG9-HC / AS9-HC column and a 10 µL sample loop were used in the US EPA Method 300.1.

In order to verify precision, replicate measurements of 10 µg/L and 300 µg/L standard solutions were carried out using the optimized method. Precision was assessed in terms of repeatability of the retention time of each anion, peak area, and concentration expressed as percent relative standard deviation (%RSD). Except for phosphate in 10 µg/L solution, the anions' retention times, calculated concentrations and areas remained stable as shown from the %RSD that are less than

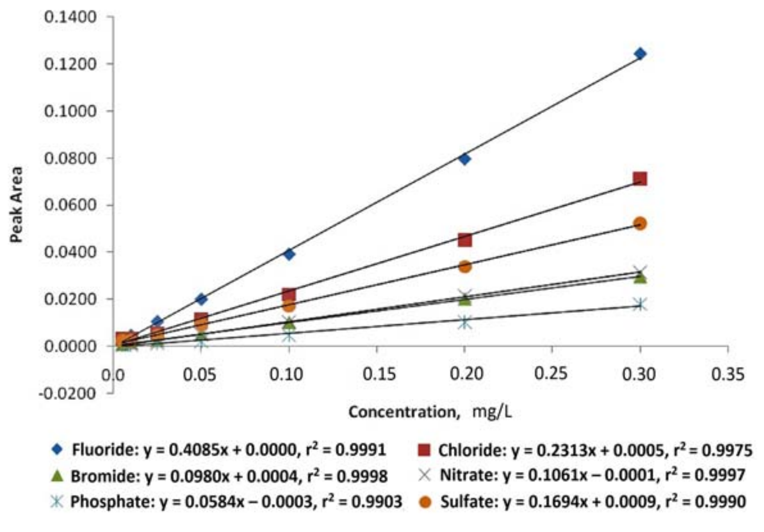


Figure 5. Calibration plots in the linear range of 5 to 300 µg/L for the quantification of the six anions (n=3 for each concentration). [Conditions: Metrosep A Supp 5 150/4.0 column, 3.2 mM $NaHCO_3$/ 3.2 mM Na_2CO_3 eluent, 0.8 mL/min flow rate, 20 µL injection volume, sequential chemical and CO_2 suppressor.]

Table 1. Comparison of detection limits for US EPA Method 300.1 and the optimized method

Anion	MDL of optimized Method in this study, in µg/L [a]	MDL of US EPA Method 300.1, in µg/L [b]
Fluoride	1	9
Chloride	1	4
Bromide	7	14
Nitrate	10	8
Phosphate	9	19
Sulfate	2	19

[a] Conditions: Metrosep A Supp 5 150/4.0 column (150 x 4 mm); 3.2 mM Na_2CO_3/3.2 mM $NaHCO_3$; conductivity detector after chemical and CO_2 suppression; 0.80 mL/min; 10 µg/L standard solution in ultrapure water;20 µL injection volume; 14 min analysis time; n=8.

[b] Reference: USEPA, ORD, NERL, 1997; Conditions: Dionex AG9-HC/AS9-H (250 x 2 mm); 9.0 mM Na_2CO_3; suppressed conductivity detector, DIONEX CD20 with an ASRS-I external source electrolytic mode at 100 mA; 0.40 mL/min; 20 µg/L fluoride, 20 µg/L chloride, 40 µg/L bromide, 10 µg/L nitrate, 40 µg/L phosphate, 40 µg/L sulfate standard in reagent water, 10 µL injection volume; 25 min analysis time; n=7.

10%. These data are shown in Table 2 while the reproducibility of the measurements is graphically illustrated in Figure 6.

The recoveries of the anions spiked in ultrapure water at 10 µg/L and 300 µg/L concentrations were determined and reported in Table 2. The actual concentrations were calculated from the established calibration curves and compared to the expected concentrations. The calculated recoveries for all the anions in both low and high concentrations were above the 90% minimum for the US EPA Method 300.1 (Hautman et al., 1997). Acceptable recoveries of 94 to 154% for the 10 µg/L spiked anions and 100 to 104% for the 300 µg/L spiked anions were obtained.

In recent years, priority anions in water systems are determined using ion chromatography evolving from non-suppressed IC to new technologies of suppression which include the method that was used in this study. Studies on non-suppressed IC were done by Stefanovic et al. (2001) using a phthalic acid based eluent. For all the six anions, the method detection limits ranged from 3 to 4 µg/L, the % recoveries were 98 to 103%, and the linear range was 500 to 50000 µg/L. Miskaki et al. (2007) also proposed a method for the six anions in

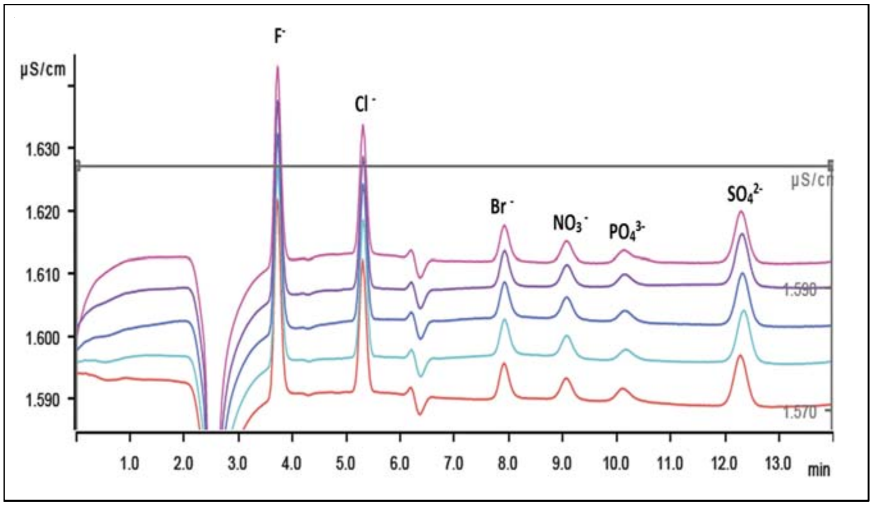


Figure 6. Stacked chromatograms showing reproducibility of anions measurement at 10 µg/L spike level using the optimized method. [Conditions: Metrosep A Supp 5 150/4.0 column, 3.2 mM $NaHCO_3$/ 3.2 mM Na_2CO_3 eluent, 0.8 mL/min flow rate, 20 µL injection volume, sequential chemical and CO_2 suppressor]

Table 2. Repeatability and accuracy of the optimized method in low (10 µg/L) and high (300 µg/L) spike levels

Anion	Ret. Time (min)[a]	Ret. time %RSD[a]	10 µg/L (n=5) spike level			300 µg/L (n=3) spike level		
			Peak area %RSD	Conc. %RSD	%Rec.	Peak area %RSD	Conc. %RSD	%Rec.
Fluoride	3.73±0.00	0.08	1.16	1.16	116	0.12	0.12	102
Chloride	5.31±0.01	0.10	1.35	1.59	122	0.21	0.22	102
Bromide	7.92±0.01	0.09	3.39	4.86	94	0.19	0.20	100
Nitrate	9.07±0.01	0.08	4.86	4.38	96	0.55	0.55	100
Phosphate	10.16±0.03	0.34	11.79	7.86	154	5.03	4.95	104
Sulfate	12.33±0.04	0.29	1.71	2.60	102	0.11	0.11	101

Conditions: Metrosep A Supp 5 150/4.0 column, 3.2 mM $NaHCO_3$/ 3.2 mM Na_2CO_3 eluent, 0.8 mL/min flow rate, 20 µL injection volume, sequential chemical and CO_2 suppressor, [a] n=8 at 10 µg/L anions concentration

surface, ground and potable waters. Their method utilized chemical suppression alone with 0.10 N H_2SO_4 and 1.3 mM Na_2CO_3/ 2.0 mM $NaHCO_3$ eluent. The detection limits ranged from 2.0 to 27.0 µg/L and the %RSD for concentration were from 0.80 to 4.60%. Douglas et al. (2002) demonstrated the use of CO_2 suppression technology with the Na_2CO_3/$NaHCO_3$ eluent with detection limits of 0.3 to 2.8 µg/L. A similar suppression technique using a Metrosep A Supp 5 – 100 column but a different eluent composition of 1 mM $NaHCO_3$/3.2 mM Na_2CO_3 was employed by Kleimann et al. (2007). The method had a good performance as evident in the low detection limits of 0.7 – 1.9 µg/L.

Overall, the optimized method in our study is acceptable and comparable to those reported in literature. It was determined to be suitable for the analysis of fluoride, chloride, bromide, nitrate, phosphate and sulfate in water at a concentration range of 5 to 300 µg/L.

Analysis of Anions in Ground and Tap Waters

The optimized method was applied in the simultaneous analysis of the six anions in groundwater and tap water in Malolos, Bulacan. The concentrations of fluoride, chloride, bromide, nitrate, phosphate and sulfate in the water samples were determined simultaneously. The concentrations are summarized in Table 3. The water samples were found to contain high concentrations of chloride of up to 476 mg/L followed by sulfate (38 mg/L), bromide (1.07 mg/L), phosphate (0.42 mg/L), fluoride (0.20 mg/L) and nitrate (0.09 mg/L). The samples were taken from Malolos City in Bulacan whose main water supplies come from either the local water district or from household artificial pumps. One set of samples was taken from Baranggay Panasahan which is in the vicinity of seawater connecting to Manila Bay. Another set was taken from Baranggay Tikay which is the entrance point of Malolos from Metro Manila. Both sampling sites are located in build up areas that consume approximately 220,000 to 320, 000 cu. m. and 4,000 to 13,000 cu. m. of water daily for household and commercial uses, respectively (CPDO, 2008).

During the analysis, serial dilution of water samples was performed to fit the areas of some ions within the linear range of the method. Thus, there is a drawback when the same linear range for all ions is used to simultaneously determine the anion levels in samples having extremely low and extremely high anion concentrations. This is particularly true for chloride and sulfate in the actual water samples. Quantifying sulfate required 1:50 dilution while chloride needed two 1:50 dilutions to fit in the linear range of the quantification method. Diluting sample solutions several times caused some of the anions to be below the detection limits. Hence, for these types of water samples, a further work would be to establish a wider linear range which is realistically up to 10 mg/L only; this is limited by the concentration of the commercially available mixed standard solution. Another approach, albeit time-consuming, would be to work with different sets of calibration solutions after doing preliminary analyses to estimate the anions level in the water samples.

Significantly, the results here show that chloride ions, at the time of sampling, exceeded the maximum contaminant level (MCL) of the PNSDW for chloride which is 250 mg/L (DOH, 2007). Panasahan ground water has higher chloride levels than its tap water treated with chlorine disinfectant. This possibly indicates that saltwater intrusion is prevalent in the area. In Tikay, higher chloride levels were observed for tap water. Chloride levels from this sample may be dictated primarily by the dose of disinfectant added to the water supply. In addition, the presence of chloride and bromide in the water samples implies the possible formation of halogenated DBPs such as trihalomethanes and haloacetic acids in the water systems.

The sampling sites were in areas far from agricultural lands which may be a probable reason why nitrate and phosphate levels in the water samples were found to be low. An interesting further study would be to compare phosphate and nitrate concentrations around Bulacan particularly in areas where synthetic fertilizers are used in farming; this is to determine their effects on water quality. Sulfate in the water samples was below the MCL. Sulfate in groundwater may be caused by the presence of sulfate minerals in the soil. However, sulfate can also be found in water as a result of discharges from agricultural and manufacturing industries present in Malolos. Hence, to completely see an overall picture of anions contamination as a result of the different industrial activities in Bulacan, more samples should be analyzed using the optimized ion chromatographic method.

In Malolos City, drinking water quality is assessed by analyzing the turbidity, color, pH, total dissolved solids, levels of iron, manganese, arsenic, cadmium, lead, and inorganic anions such as nitrate, sulfate and chloride in the water supply (CMWD, 2011). The levels of each water quality parameter are compared to the limits set by the PNSDW and are measured using the standard methods for the examination of water and wastewater (APHA, AWWA, WEF, 2006). None of the tests currently employed in Malolos use ion chromatography in monitoring inorganic anions. Nitrate is measured by colorimetric detection after cadmium reduction; sulfate is by turbidimetry; and chloride is by argentometry (CMWD, 2011). Thus, this study offers an available alternative method in the form of the optimized ion chromatographic method to evaluate levels of nitrate, sulfate and chloride as well as anions not routinely analyzed in water supplies in Malolos such as bromide, fluoride and phosphate. This method requires simple sample preparation, involves fast analysis time and more importantly, offers a procedure for the simultaneous determination of anions.

Other Asian countries evaluate levels of inorganic anions in water to correlate their concentrations with principal contaminant sources which include industrial wastes, municipal landfills, agricultural chemicals, leaks

Table 3. Anion concentration in ground and tap waters [a]

Anion	Concentration, in mg/L				
	Panasahan Tap	Panasahan Ground	Tikay Tap	Tikay Ground	MCL [i]
Fluoride	0.08[c]	0.06[c]	0.20[c]	0.13[c]	1.0
Chloride	190.73[b,f]	337.35[b,f]	476.26[b,f]	184.66[b,g]	250.0
Bromide	0.49[c,h]	0.51[b,e]	1.07[b,e]	0.39[b,d]	-
Nitrate	n.d.	0.08[c]	0.01[c]	0.09[c]	50
Phosphate	0.42 [c,d]	0.14 [c]	0.01[c]	0.20[b,e]	-
Sulfate	4.74[b,e]	4.74 [b,e]	38.04[b,e]	22.51[b,e]	250.0

[a] sampled in February 13, 2011 and analyzed within six days; [b] n=1; [c] n=2; [d] 1:10 dilution; [e] 1:50 dilution; [f] diluted twice using 1:50 dilution; [g] 1:50 to 1:25 dilution; [h] evaluated using 5 to 500 μg/L calibration curve with equation: $y=0.0929x + 0.0008$, $r^2=0.9983$; [i] Reference: The Philippine National Standards for Drinking Water, 2007. Conditions: Metrosep A Supp 5 150/4.0 column, 3.2 mM $NaHCO_3$/ 3.2 mM Na_2CO_3 eluent, 0.8 mL/min flow rate, 20 μL injection volume, sequential chemical and CO_2 suppressor; concentrations were corrected using 300 μg/L spike level recovery measurements; n.d. = not detected

from petroleum pipelines and storage tanks, animal wastes, saltwater intrusion, and irrigation return flow (Park et al., 2002). With the knowledge of the origins of contamination, stricter regulations may be implemented to limit industrial and human waste generating activities. In Korea, inorganic anions were investigated using chemically suppressed single column IC with conductimetric detection and the anions contamination was not severe with respect to their standards (Park et al., 2002). In contrast, problems associated with high fluoride concentrations as evident in the high cases of fluorosis disease occur in China (Wang et al., 2007), India (Gautum, R. et al., 2011) and Sri Lanka (Dissanayake C. B., 1996). In Indonesia, IC was applied to assess their water quality affected directly by environmental problems such as increasing pollutants of various types, acid rain, and hazardous wastes (Amin et al., 2008). Hence, investigations like these in the Philippines are essential to draw attention to the use of good water quality monitoring procedures such as the ion chromatographic method optimized in this study.

The results of our work provide relevant information on the levels of fluoride, chloride, bromide, nitrate, phosphate and sulfate in ground and tap waters in Malolos, Bulacan. Our findings suggest the need to routinely analyze water samples for these anions, particularly chloride that was found in relatively high levels in order to ensure public safety. More importantly, the optimized method described here can be used as an available method for assessing anions contamination in potable water not only in Malolos City but also in water supply systems in other parts of the country. A planned research application of this method is on spatial and temporal variations of the six anions in environmental waters. Another is its application, specifically for bromide and chloride analysis, in tandem determination of halogenated DBPs in tap waters. Finally, a future work on this sequential chemical and CO_2 suppressed ion chromatographic method would be its application in other priority anion contaminants including bromate, chlorite, chlorate, perchlorate, nitrite and chromate.

CONCLUSIONS

An ion chromatographic method with sequential chemical and CO_2 suppression was optimized and validated in this study. The optimized method used to analyze fluoride, chloride, bromide, nitrate, phosphate and sulfate in ground and tap waters was evaluated to be linear in the concentration range of the analysis, sensitive and specific to these anions, highly reproducible, accurate and of comparable detection limits as in the US EPA Method 300.1. In addition, this ion chromatographic method required simple sample preparation. The method was successfully applied in measuring the anions even in the low µg/L levels in ground and tap water.

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