Determination of Chemical Species in Drinking Water by Ion Chromatography

Maria Aparecida F. Pires*, Elizabeth S. K. Dantas and Casimiro S. Munita**

Chemistry Characterization Division

**Radiochemistry Division

Instituto de Pesquisas Energéticas e Nucleares. Comissão Nacional de Energia Nuclear, C.P.11049, CEP 05422-970, São Paulo, Brazil

Abstract. The ion chromatography technique was used to determine the concentrations of F^-, Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+} from the drinking water supply systems in 19 districts from the five geographical zones - North, South, East, West and Center - of São Paulo city. The linearity, detection limit and the accuracy of the method was studied by means of calibration curves for each specie, in the range of 0.03 to 20.0 mg/l. For all the ions, the precision values obtained were less than 2%. The results were compared with that of American cities and European drinking water standards.

Key words: drinking water, ion chromatograpy, anions, cations, environmental analysis.

The determination of chemical species in water is an extremely difficult task due to the very low concentration of these species. Although physical analysis methods providing low limits of

*To whom correspondence should be addressed

detection are widely used in several kinds of matrices, the direct determination of trace elements in water is only possible for a limited number of elements [1]. Methods such us flameless atomic absorption spectroscopy, anodic stripping voltametry, neutron activation analysis and spark mass spectroscopy in most cases of multielemental analysis, are not sufficiently sensitive to detect ultra-trace level elements. Generally, it is necessary to preconcentrate the elements prior to their determination.

Several preconcentration techniques are available for the determination of metal samples, among them solvent extraction [2,3], ion exchange resin [4,5], cellulose [6], co-precipitation and crystallization [7]. Although some of these techniques are quite effective, their methods of preparation are lengthy and involve rigid conditions to avoid contamination from a multitude of sources and at the same time, serious losses of metal. The main sources of contamination are chemicals, vessels and tools used for sample handling. Therefore, sampling equipment and storage containers should be made of materials which are relatively free from metallic impurities and anions. The traditional chemical methods to directly determine trace anions are not sufficiently rapid and selective. In many cases, sample pretreatment is required. Different oxidation states of some elements have different levels of toxicities (i.e. N: NH_4^+, NO_3^-, NO_2^-) thus the separation and determination of these species are very important. Hence, other methods must be sought.

A new era in analytical research of elemental composition of aqueous solutions began in the late 1970's with the development of ion chromatography,IC. The reasons for this are numerous. The most significant reasons include changeability, selectivity, sensitivity, rapidness and the capacity of identifying and quantifying a variety of anions and cations at trace and ultra-trace levels with a minimum sample volume.

Today, the IC technique has reached a mature state and has been applied to hundreds of problems in various fields, such as the environment [8-10], petrochemical industry [11], semi-conductors [12], metallurgy [13] and biomedicine [14,15].

The composition of water is of great importance, since it is the prime source of the trace elements essencial for the growth of living organisms. The quality of water strongly depends on the location of the source. Drinking water is usually obtained from subsoil sources or from rivers or lakes. In this context, IC appeared to be an attractive technique to evaluate anions and cations in drinking water from the city of São Paulo. The metropolitan area has about 15 million people and 50,000 industries of all kinds and sizes, including the heavy industries: iron and steel works, cement plants, sulfuric acid plants, fertilizer plants, petrochemical plants, chemical manufacturing plants, etc.

The city of São Paulo is located on a plateau of approximately 750m in elevation. There are no adequate natural water resources available to meet the ever-increasing water demands caused by a population explosion that has been continuous since the turn of the century.

The city has six major water supply systems: Cantareira, Guarapiranga, Rio Grande, Rio Claro, Alto Cotia and Baixo Cotia utilizing all the surface water resources available in the area, reaching a total capacity of 46,85 m^3/s. Each system is fully independent of the others, but all are connected to large-diameter feed lines that encircle the perimeter of the greater São Paulo metropolitan area.

In this work we will present a research of the applicability of the IC technique to determine F^-, Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, Ca^{2+} and pH in drinking water collected in the city of São Paulo.

The analysis of the chemical species are of special interest when considering the lack of information of drinking water composition in the city, as well as other cities in the world.

Experimental

Apparatus

The chromatographic apparatus used was a Dionex model 10 equipped

with 110A pump 1000 psi and 100 µl injection loop. The wetted parts of the pump are non-metallic, so as not to contaminate the concentrator and/or analytical columns with metals. Chromatographic separations for anions were carried out using an anion separator column (250 mm x 3 mm I.D., Dionex AS1), and suppressor column (100 mm x 6 mm ID, R-H form). For monovalent and divalent cations, a cation separator column (200 mm x 3 mm I.D., Dionex CS1) and suppressor column (100 mm X 6 mm, R-OH form) were used. The mobile phase was pumped at a flow rate of 2.3 ml/min. at room temperature. Data acquisition and reduction were performed on a strip chart recorder.

Reagents

All chemicals were of analytical grade and were prepared with distilled-demineralized water (Milli-Q-water-system). The eluent solution for anions analysis was 0,0030M in sodium hydrogen carbonate and 0,0024 M in sodium carbonate. Sulfuric acid solution was used as a regenerant for the suppressor column. The standard eluent solution for monovalent cation was used: 0,0050M nitric acid and, for divalent cations: 0,0025M m-phenylenediamine dihydrochlroride/0,0025 M nitric acid. Sodium hydroxide was used as a regenerant for the suppressor column.

Sampling

Samples were collected in polyethylene bottles which were filled to overflow level, then capped, so as to exclude air. Samples were

stored at -4°C and analyzed within 48 hours of sampling.

Procedure

To reach equilibrium, eluent was pumped through all columns until a stable baseline was obtained. This occured in aproximately 20 to 60 minutes. This equilibrium can normally be accomplished while the samples and standards are being prepared.

After equilibrium was reached, water samples were injected into the desired sample loop (100 µl) and the chromatogram of each sample was recorded.

The retention time for each anion or cation was determined by analyzing a standard solution, containing only the anion or cation of interest, and noting the time required for a peak to appear on the chromatogram. Calibration curves were constructed using peak height.

Linearity, Accuracy and Sensitivity of the Method

The linearity of the method was studied in the concentration range of 0.03 to 20.0 mg/l by adding increasing masses of each specie. The results were analyzed and evaluated by linear least-square regression, $y = bx + a$, where x is the amount added and y is the value found. The studied parameters were intercepts "a", slopes "b", and determination coefficients "r^2". The results are given in Table 1. In order to verify the accuracy of the method, the t-test

[16] was applied to the parameters, "a" and "b", showing that at 0.05 significance level, the value a = 0 and b = 1 may be assumed for all species. In all the results the r^2 is greater than 0.99 indicating that 99% of the variation of x overlaps with the variation of y, demonstrating good linearity. The coefficient of the variation of the peak area ratio at each calibration point was less than 2% for all the ions indicating good precision.

In order to calculate the determinations limit, data from calibration curves were used at a relative standard deviation of ±20%. The value was assumed acceptable and applied in the following equation [16].

$$S_{x'} = \pm 0.20 \left(\frac{y' - a}{b} \right) = \pm \frac{S_o}{b} \left[1 + \frac{1}{n} + \frac{(y' - \bar{y})^2}{b^2 (\sum x_i^2 - n\bar{x}^2)} \right]^{1/2}$$

where

y' - result when the mass of the specie in the sample is the determination limit

x' - determination limit

$S_{x'}$ - standard deviation of the determination limit

S_o - regression standard deviation

$\bar{x}, \bar{y}$ - average of the n values x_i and y_i, respectively

n - number of results

The detection limit x" was calculated by assuming as positive any result above twice the standard deviation, i.e, $x'' > 2|S_{x'}|$. The

value x" was obtained after solving the equation:

$$X'' = \left(\frac{y'' - a}{b}\right) \pm 2 \left[\frac{S_o}{b}\left(1 + \frac{1}{n} + \frac{(y'' - \bar{y})^2}{b^2\left(\sum x_i^2 - n_i \bar{x}^2\right)}\right)\right]^{1/2}$$

The results obtained are given in Table 1.

Application

The method was applied to determine the concentration of chemical species in the drinking water used in São Paulo's public supply system. The collection samples were made in five geographical zones: North, South, East, West and the Center of the city. In each zone, samples from several districts were analyzed, reaching a total of 19 districts. In Table 2 the zones and the districts are presented.

Results and Discussion

The concentration of F^-, Cl^-, SO_4^{2-}, Na^+, K^+, $Mg^{2+}$and Ca^{2+} and pH in the city's public supplied drinking water are shown in Table 3. The values reported represent the mean of the districts within each zone, where 5 analyses were made within each district. The ions NH_4^+, Li^+, Sr^{2+}, Ba^{2+}, NO_2^-, NO_3^- and PO_4^{3-} in all the samples are lower than the detection limit. In Table 3, it can be seen that the variation range of the chemical species concentrations analyzed in the five geographical zones are relatively small.

The concentration of all species are within the reported concentration ranges of the 100 largest cities in the United States [17], the recommended standards by the World Health Organization [18], as well as the standards applied to the member states of the European Community [19].

The pH range in the supplied drinking water of the districts were 6.0 to 8.7 with a mean of 6.7±0.5. Only two districts had pH levels higher than 8.0, Alto de Pinheiros with 8.4 and São Lucas with 8.7. The guide level recommended by the European Community is 6.5 to 8.5 with a maximum admissible value of 9.5. In the American cities, 90% of the supplies had a pH of 9.0 or less and 10% had a pH value of less than 7.0 [17]. The pH of non-treated water compared to that of treated water indicates that chemical treatment greatly influences the pH. The pH determines the amount of hypochlorous acid (HClO) and hypochlorite ion (ClO^-) in solution [20]. Hypochlorous acid is the predominant form at pH 6.0 to 7.5 and hypochlorite ion is the predominant form at pH of 8.0 to 10.0. It is important to know the dissociated forms of chlorine present at various pH values, because HClO is the form that possesses the destructive power as a microbiocide. Research has shown that HClO is 80 times more effective than ClO^- for the inactivation of *Escherichia coli* and about 150 times more effective for cysts of *Entamoeba histolytia*.

The maximum permissible level of fluoride in the Brazilian

Federal Drinking Water Quality Standard is 1.4 mg/l [21]. The range found in São Paulo was 0.09 to 0.58 mg/l with a mean of 0.4±0.2 mg/l. The value recommended by the European Community States at 8 to 12°C is 1.5 mg/l and at 25 to 30°C is 0.7 mg/l. Durfor and Bequer [17] found that in American supplied drinking water 92% of the supplies of the cities had 1 mg/l or less. According to Carney [19], the maximum admissible concentration varies according to the average temperature in the geographical area concerned.

Sixty-nine cities in the United States [17] had a sodium content level between 21 to 40 mg/l. The guide level by the European Community is 20 mg/l. In São Paulo, the amount of Na^+ found in all the districts was in the range of 1.5 to 5.0 mg/l with a mean of 2.4±0.9 mg/l for the five zones. Sodium in drinking water supplies is of current interest, especially for people with sodium restricted diets. For example, a daily consumption of 2 liters of water, would provide 8 mg of sodium. Consequently, before effective sodium restricted diets can be designed, the sodium content of water must be known.

The mean of calcium found was 8.3±2.1 mg/l. The maximum calcium content in American cities was 145 mg/l, however 93% of the supplies contained 50 mg/l or less. The guide level recommended by the European Community is 100 mg/l. Calcium is known to affect the absorption of a variety of elements in the

intestinal tract. The absorption of Cd, Pb and Zn is significantly reduced when the dietary intake of calcium is high, whereas absorption of these elements is increased when dietary intake of calcium is low. The absorption of Pb and Ca from hard water is significantly lower than that of soft water. Experimental data with Cd and Pb have shown that these elements induced hypertension and aortic atherosclerosis [22].

The magnesium concentration found was 0.9±0.2 mg/l. The guide level of the European Community is 30 mg/l with a maximum admissible level of 50 mg/l. Magnesium is a required element for normal heart function. Several studies [23,24] have shown a positive correlation between soft water and cardiovascular disease. The Mg content of soft water is extremely low compared with that of hard water. The level of this element in the diet is often borderline. Several investigators believe that because of the low level of Mg in drinking water, a Mg deficiency develops, which leads to increased cardiovascular mortality. Hard water with increased Mg may be sufficient to prevent this deficiency.

Conclusion

The aim of this work was to verify the linearity, accuracy, precision and sensitivity of the IC technique. In the range of 0.03 to 20 mg/l, the method proved to be accurate and precise, confirmed by the statistical tests applied. If the working range exceeds the linear range, a sufficient number of standards must be

analyzed to allow an accurate calibration curve to be established. Many parameters influence the optimization of the anion or cation separation: eluent, concentration of mobile phase, column, etc. To obtain accurate results, calibration curve cheks must be completed on a daily basis or after every 10^{th} analysis of the samples.

This method was applied to determine F^-, Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+} in the drinking water of São Paulo city. The values obtained are within the international guide level recommended. The procedure can be adapted in different samples, such as surface water, rain water and mixed domestic and industrial wastewater. In some cases, little sample pretreatment is required.

References

[1] M.J. Fishman, D.E. Ehrman, T.R. Steinheimer, Anal.Chem. 1981, 53, 182R.

[2] J. N. King, J. S. Fritz, Anal.Chem. 1985, 57, 1016.

[3] K. W. Bruland, R. P. Franks, G. A. Knauer, J. M. Martin, Anal. Chim. Acta 1979, 105, 233.

[4] A. van Geen, E. Boyle, Anal. Chem. 1990, 62, 1705.

[5] S. Osaki, T. Osaki, Y. Takashima, Talanta 1983, 30, 683.

[6] P. Burha, P. G. Wilma, Talanta 1983, 30, 381.

[7] V. Hudnik, S. Gomiscek, B. Gorenc, Anal. Chim. Acta 1978, 98, 39.

[8] D. Brocco, R. Trappa, J. Chromatogr. 1986, 367, 240.

[9] J. P. Ivey, D. M. Davies, Anal. Chim. Acta 1987, 194, 281.

[10] N. Chauret, J. Kubert, J. Chromatogr. 1989, 469, 339.

[11] R. D. Rocklin, E. L. Johnson, Anal. Chem. 1983, 55, 4.

[12] W. F. Koch, J. W. Stolz, Anal. Chem. 1982, 54, 340.

[13] R. M. Cassidy, S. Elchuck, J. Liq. Chromatogr. 1981, 4, 379.

[14] R. L. Wimalasena, G. S. Wilson, J. Chromatogr. 1991, 572, 85.

[15] G. K. Poon, R. McCague, L. J. Griggs, M. Jarman, J. Chromatogr. 1991, 572, 143.

[16] V. V. Nalimov. The Application of Mathematical Statistcs to Chemical Analysis, Addison-Wesley Publ. Co., Reading Mass, 1963.

[17] Ch. N. Durfor, E. Becker, J. Am. Water Works Assoc. 1962, 56, 237.

[18] Guidelines for Drinking Water Quality, vols. 1 and 2. World Health Organization, Geneva, Switzerland, 1984

[19] M. Carney, J. Am. Water Works Assoc. 1991, 83, 48.

[20] E. C. Lippy, J. Am. Water Works Assoc. 1986, 78, 49.

[21] Brazil. Min. do Des. Urb. e Meio Amb. Cons. Nac. do Meio Amb. Resol. 20, 18 junho 1986. Diario Of. União, 30 jul. 1986, Sec. 1, p. 11356.

[22] N. W. Rewis, R. L. Schmoyer, R. Bull, J. Am. Water Works Assoc. 1982, 74, 656.

[23] T. Crawford, M. D. Crawford, Lancet 1967, 1, 229.

[24] T. W. Anderson, Lancet 1976, 1, 644.

Table 1. Statistical analysis of calibration curves and sensitivity. Concentration range: 0.03 to 20 mg/l, n = 6 (conditions: F.S. 10, loop 100ul)

Specie	Regression			Detection Limit (mg/l)
	slope	intercept	r^2	
F^-	0.99(0.01)[a]	0.28(0.20)[a]	0.998	0.05
Cl^-	1.43(0.48)	0.25(0.29)	0.984	0.14
NO_2^-	1.84(0.93)	-0.22(0.26)	0.991	0.28
Br^-	1.23(0.18)	-0.48(0.32)	0.994	0.32
PO_4^{3-}	1.04(0.01)	-0.48(0.52)	0.994	1.20
NO_3^-	1.25(0.09)	0.14(0.18)	0.997	0.50
SO_4^{2-}	1.07(0.04)	0.21(0.22)	0.998	0.40
Li^+	1.41(0.20)	0.35(0.18)	0.990	0.03
Na^+	1.02(0.01)	0.34(0.20)	0.997	0.009
NH_4^+	0.89(0.06)	0.24(0.12)	0.999	0.04
K^+	0.89(0.17)	0.30(0.21)	0.999	0.02
Mg^{2+}	1.20(0.13)	-0.50(0.39)	0.997	0.30
Ca^{2+}	1.22(0.09)	-0.60(0.35)	0.995	0.72
Sr^{2+}	0.98(0.01)	0.29(0.17)	0.995	0.84
Ba^{2+}	1.07(0.05)	-0.32(0.22)	0.997	1.80

a : standard deviation value

Table 2. Districts where the samples were collected and analyzed

Zone	District
North	Tucuruvi
	Casa Verde
	Santana
South	Itaim Bibi
	Jardim Paulistano
	Moema
	Saúde
	Jabaquara
East	Vila Formosa
	São Lucas
	Vila Matilde
	Moóca
West	Butantã
	Jaguaré
	Pinheiros
	Alto de Pinheiros
Center	Consolação
	Liberdade
	Sé

Table 3. Means of the concentration data (in mg/l) and pH of the zones

Zone	pH	F^-	Cl^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
North	6.4±0.5	0.09±0.01	3.7±0.3	5.3±0.2	1.6±0.01	1.7±0.1	0.65±0.08	5.3±0.1
South	6.7±0.6	0.4±0.2	12.2±5.0	7.4±1.1	3.6±0.9	2.2±0.2	1.0±0.2	10.0±1.7
East	7.3±1.1	0.4±0.2	4.6±1.4	8.7±6.2	1.7±0.2	1.5±0.3	0.6±0.1	8.5±4.5
West	7.1±0.9	0.6±0.1	12.9±4.3	7.4±1.3	3.1±1.4	2.0±0.5	1.0±0.3	10.5±4.1
Center	6.0±0.1	0.5±0.3	4.5±1.7	5.4±0.4	1.9±0.4	1.6±0.1	1.1±0.8	7.2±0.7
Mean	6.7±0.5	0.4±0.2	7.6±4.6	6.8±1.5	2.4±0.9	1.8±0.3	0.9±0.2	8.3±2.1
Range	6.0-7.3	0.09-0.6	3.7-12.9	5.3-8.7	1.6-3.6	1.5-2.2	0.6-1.1	5.3-10.5