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DETERMINATION OF CHEMICAL SPECIES IN DRINKING WATER BY ION CHROMATOGRAPHY

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ABSTRACT

The ion chromatography technique was used to determine the concentrations of F⁻, Cl⁻, SO₄²⁻, Na⁺, K⁺, Mg²⁺ and Ca²⁺ from the drinking water supply systems in 19 districts from the five geographical zones - North, South, East, West and Center - of Sao Paulo city. The linearity, detection limit and the accuracy of the method was studied by means of calibration curves for each species, in the range 0.03 to 20.0 mg/l. For all the ions, the precision values obtained were less than 2%. The results were compared with those from American cities and European drinking water standards.

RESUMEN

La técnica de cromatografía de iones fue usada para determinar la concentración de F⁻, Cl⁻, SO₄²⁻, Na⁺, K⁺, Mg²⁺ and Ca²⁺ en el agua potable que abastece 19 barrios de la ciudad de Sao Paulo, localizados en 5 zonas geográficas: Norte, Sur, Este, Oeste y Centro. En el intervalo de 0,03 a 20 mg/l se estudió la linealidad, límite de detección y la exactitud del método. Para todas las especies iónicas la precisión fue menor

que 2%. Los resultados se compararon con los de 100 ciudades de EEUU y con los valores patrones recomendados por la Comunidad Económica Europea.

INTRODUCTION

The determination of chemical species in water is a difficult task due to the very low concentration of these species. Although physical analysis methods providing low limits of 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 elements¹. 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}, cellulose⁶, coprecipitation and crystallization⁷. 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 traditional chemical methods to

directly determine trace anions are not sufficiently rapid and selective. In many cases, sample pretreatment is required. In this context, IC appeared to be an attractive technique to evaluate anions and cations in drinking water from the city of Sao 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 Sao Paulo is located on a plateau of approximately 750 m 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 m³ sec⁻¹. Each system is fully independent of the others, but all are connected to large-diameter feed lines that encircle the perimeter of the greater Sao Paulo metropolitan area. The analysis of the chemical species are of special interest

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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 ml injection loop. The wetted parts of the pump are non-metallic. Chromatographic separations for anions were carried out using an anion separator column (250 mm x 3 mm I.D., Dionex ASI), 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-demineralize 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 dihydrochloride/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 occurred in approximately 20 to 60 minutes. After equilibrium was reached, water samples were injected into the desired sample loop

(100 ml) 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 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 "r²". The results are given in Table 1. In order to verify the accuracy of the method, the t-test was applied to the parameters, "a" and "b"⁸, 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 $\pm 20\%$. The value was assumed

acceptable and applied in the following equation⁸.

$$S_x = \pm 0.20 \left(\frac{y'-a}{b} \right) \pm \frac{S_0}{b} \left[1 + \frac{1}{n} \frac{(y'-\bar{y})^2}{b^2(\sum x_i^2 - n\bar{x}^2)} \right]^{1/2}$$

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_0 = 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 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 Sao 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.

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

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
	Saude
East	Jabaquara
	Vila Formosa
	Sao Lucas
	Vila Matilde
	Moóca
West	Butanta
	Jaguaré
	Pinheiros
Center	Alto de Pinheiros
	Consolacao
	Liberdade
	Sé

RESULTS AND DISCUSSION

The concentration of F⁻, Cl⁻, SO₄²⁻, Na⁺, K⁺, Mg²⁺ and Ca²⁺ 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 NH₄⁺, Li⁺, Sr²⁺, Ba²⁺, NO₃⁻, NO₂⁻ and PO₄³⁻ 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.

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	9.7±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

The concentration of all species are within the reported concentration ranges of the 100 largest cities in the United States⁹, the recommended standards by the World Health Organization¹⁰, as well as the standards applied to the member states of the European Community¹¹.

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 Sao 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 7.09. The pH determines the amount of hypochlorous acid (HClO) and hypochlorite ion (ClO⁻) in solution¹². 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. The hypochlorous acid is the form that possesses the destructive power as a microbicide. 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 histolytica.

The maximum permissible level of fluoride in the Brazilian Federal Drinking Water Quality Standard is 1.4 mg/l¹³. The range found in Sao 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 Bequer⁹ found that in American supplied drinking water 92% of the supplies of the cities had 1 mg/l or less. According to Carney¹¹, the maximum admissible concentration varies according to the average temperature in the geographical area concerned.

Sixty-nine cities in the United States⁹ had a sodium content level between 21 to 40 mg/l. The guide level by the European Community is 20 mg/l. In Sao Paulo, the amount of Na⁺ found in all the districts was in the range 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.

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 atherosclerosis¹⁴.

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^{15,16} 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 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. This method was applied to determine F⁻, Cl⁻, SO₄²⁻, Na⁺, K⁺, Mg²⁺ and Ca²⁺ 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, rainwater and mixed domestic and industrial wastewater. In some cases, little sample pretreatment is required.

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