An Attempt to Identify Commercial Drinking Water Through Means of Some Ionic Species

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SUMMARY. Ion chromatography technique was used to determine the concentrations of F^-, Cl^-, NO_3^-, SO_4^{2-}, Mg^{2+}, Ca^{2+} and pH in five different brands of bottled drinking water sold in São Paulo supermarkets. To choose from the samples, the consumption criteria was used. Results were compared to the recommended standards of the World Health Organization (WHO) and the standards applied to the member states of the European Community (EC). A statistical method was used to determine which of the ionic species differentiated from the different brands.

Key words: drinking water, ion chromatography, ionic species, anions, cations.

INTRODUCTION

There is increased interest in the amounts of ions present in foodstuffs such as drinking water[1]. Because food is the main source of intake of ionic species, it is necessary to assess the adequacy and safety of diet by monitoring the concentration of ions in various foods consumed daily. Excessive concentration of ionic species in food or drinking water may induce toxicity manifestation. The aim of this study was to compare five different brands of commercial drinking water, and to determine which chemical components differentiate within various brands. A similar strategy has been applied to Brazilian cigarette tobacco[2].

Of the choice of the five different brands, consumption criteria was used. The A through E brands were those of the highest and lowest consumer value, respectively. The five analyzed brands were those of higher consumption.

MATERIALS AND METHODS

The chromatographic equipment used was a Dionex 10 equipped with 110A pump psi and 100 µL 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 ID, 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 ID, 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.

All chemicals were of analytical grade and were prepared with distilled-demineralized water (Milli-Q-water system). The eluent solution for anions analysis was 0.003M in sodium hydrogen carbonate and 0.0024M in sodium carbonate. Sulfuric acid solution was used as a regenerant for the suppressor column. The standard eluent solution for monovalent cation was used; 0.005M nitric acid and, for divalent cations 0.0025M m-phenylenediamine dihydrochloride 0.0025M nitric acid. Sodium hydroxide was used as a regenerant for the suppressor column.

Samples were collected from commercial bottled drinking water sold in supermarkets, and analyzed within 48h of sampling.

RESULTS AND DISCUSSION

Obtaining reliable data for the determination of elements in drinking water samples requires the use of analytical method that has been validated as to their accuracy, and these analytical methods must be continuously monitored to verify that they remain in control.

One method for validating analytical procedures is the use of reference materials that has been well characterized with respect to the analyte of interest.

In this paper the precision and accuracy of the method was tested by analyzing Simulated Rainwater, NIST-SRM-2694aII. The precision of the technique was demonstrated by the relative standard deviation evaluated through three determinations. The accuracy was verified by the relative error. As shown in Table 1, RSD is less than 6% and the relative error is <5% indicating high precision and accuracy of method.

Table 1. Results for simulated rainwater, NIST-SRM-2694aII (mean for n=3)

Element	Certified Value (μg/mL)	Found (μg/mL)	RSD (%)	Relative Error (%)
F^-	0.108±0,004	0.103±0.006	5.8	-4.6
Cl^-	(0,94)	0.96±0.03	3.1	2.1
NO_3^-	7.19±0.16	7.12±0.16	2.2	-1.0
SO_4^{2-}	10.6±0.1	10.5±0.06	5.7	-0.9
Mg^{2+}	0.048±0.001	0.0484±0.002	4.1	0
Ca^{2+}	0.0364±0.0006	0.0357±0.002	5.6	-1.9

The results of F^-, Cl^-, NO_3^-, SO_4^{2-}, Mg^{2+}, Ca^{2+} and pH in five different commercial brands of São Paulo bottled drinking water (originating from five different companies) are shown in Table 2. The values are within the recommended standards of WHO[3], as well as the standard applied to the member states of the European Community (EC)[4].

The pH range found was 6.8 to 8.1 with a mean of 7.4. The pH guide level recommended by the EC, WHO, and Canada is 6.5 to 8.5[5]. The pH determines the amounts of HClO (hypochlorous acid) and ClO[-] (hypochlorite ion) in solution. HClO is the predominant form at lower pHs (6-7.5) and possesses the destructive power, and ClO[-] is the predominant form at higher pH values (8-10), and has a relatively poor disinfectant, due to its inability to diffuse through the cell wall of microorganisms by the negative charge[6].

Table 2. Results for ionic species in five different brands of commercial drinking water in mg/L, pH, and experiment F values (mean for n = 5)

Brand	F	Cl⁻	NO₃⁻	SO₄²⁻	Mg²⁺	Ca²⁺	pH
A	0.23	0.17	0.79	0.21	9,49	15.71	8.0
B	0.06	2.46	13.56	1.68	3.21	7.69	7.1
C	0.25	0.83	6.53	2.93	6.74	15.05	7.2
D	0.12	1.08	3.25	0.33	0.41	2.18	6.8
E	0.16	0.05	1.05	0.17	10.92	17.42	8.1
Range	0.05-0.26	0.03-2.49	0.67-13.86	0.17-3.06	0.41-12.69	1.94-17.80	6.8-8.1
$F_{exp.}$	0.87	6234	1207	2107	329	7.6	

$F_{0.05(4.20)} = 2.9$

The Cl⁻ range found in the five brands was 0.03 to 2.49 mg/L with a mean of 0.92 mg/L.

The value recommended by the EC is 25 mg/L[4] ,WHO[3] and the Brazilian Federal Drinking Water Quality Standard is 250 mg/L[7].

The concentration range of Mg found was 0.41 - 12.69 mg/L. The guide level of the EC is 30mg/L with a maximum admissible level of 50mg/L[4]. Magnesium is a required element for normal heart function. Several studies[8] 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. 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[9].

The maximum permissible level of F in the Brazilian Federal Drinking Water Quality Standard is 1.4mg/L[7]. The range found in five brands was 0.05-0.26mg/L. The value recommended by the EC at 8 to 12° C is 1.5mg/L and at 25 to 30° C is 0.7mg/L.

The range of Ca found was 1.94-17.80mg/L. The guide level recommended by the EC is 100mg/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 Ca is high, whereas absorption of these elements is increased when dietary intake of Ca is low[8].

In order to examine the differences observed in the contents of each one of the ions analyzed, the F-test at 0.05 significance level was applied.

The experimental F-values are shown in Table 2. All of the F-values are higher than the tabulated F-value, 2.9, for 4 and 20 degrees of freedom at the 0.05 significance level, unless for F with experimental F-value 0.87. Therefore, the hypothesis of equality of the samples analyzed is valid only for F.

On applying the F-test to the results for contents of each of the ions determined, however, there is not an indication of which pair of the five brands are equally valuable. The purpose last mentioned used the Scheffes test[10], defined as follows:

$$\Delta = \left[MS_r \left(\frac{1}{n_{A_i}} + \frac{1}{n_{M_i}} \right)(n_c - 1) F_{4.20} \right]^{1/2}$$

Where:

MS_r - is the residual mean square

n_c - is the number of columns /brands/

n_{Ai} - is the number of lines /determinations/ for ion i in brand A

n_{Mi} - is the number of lines /determinations/ for ion i in brand M (M=B, C, D or E)

F - is the tabulated value: 2.9

The contents of the ions in the samples of different brands were considered to be the same statistically at a 0.05 significance level, when the differences between the mean values $\overline{X}_{A_i} - \overline{X}_{M_i}$ obtained were equal to or smaller than Δ, where:

$\overline{X}_{A_i}$ is the mean value of element i for brand A .

$\overline{X}_{M_i}$ is the mean value of element i for brand M.

Of the values presented in Table 2, this condition is fulfilled for Mg^{2+} and NO_3^- in brands A and E, for SO_4^{2-} brands A, D and E and for ions Ca^{2+} for brands A and B.

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