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Chemical quality of bottled mineral waters from markets of Curitiba-PR-Brazil

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ABSTRACT

Twenty-seven bottled mineral waters from local markets in Curitiba, State of Paraná, Brazil were analyzed for a number of constituents, including: pH, conductivity, *total dissolved solids*, *hardness*, HCO_3^- and CO_3^{2-} , as well as Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , F^- , Cl^- , NO_3^- , NO_2^- and SO_4^{2-} by ion chromatography (IC); Al, Ba, Cd, Cr, Cu, Fe, Li, Mn, Ni, Sr, V and Zn by inductively coupled plasma optical emission spectrometry (ICP OES); Hg by cold vapor generation-ICP OES and As, Pb, Sb and Se by ICP-mass spectrometry (ICP-MS). The obtained limits of quantitation (LOQ) were adequate for the determination of all analytes using the various analytical techniques. Results for the analysis of AccuStandard certified reference materials QCS-01-5, QCS-02-R1-5 and TCLP-02-1 as well as spike recoveries to samples show acceptable values, within 90-111 % of expected concentrations with relative standard deviations below 10 %, demonstrating the accuracy of the determinations. Both NO_2^- and NO_3^- were above the maximum limits set by Brazilian legislation in two samples, indicating a microbiological contamination. One imported sample presented As ($6.1 \pm 0.2 \mu\text{g L}^{-1}$) near the maximum limit ($10 \mu\text{g L}^{-1}$) while all other elements of interest were below the values specified by Brazilian legislation. Principal component analysis revealed that four imported samples and one from the Minas Gerais State have the highest mineral concentrations.

Key words: bottled mineral waters, elemental composition, chemical quality, principal component analysis.

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INTRODUCTION

Increased consumption of bottled mineral waters in recent decades implies a greater need for quality monitoring. Knowledge of the chemical composition is necessary to assure the quality of such products (Ikem et al., 2002). Their consumption is increasing in large cities, in part because of doubts over the quality of water supplies. Water provides essential elements such as calcium, magnesium, iron, and others which have proven therapeutic properties. However, mineral water may also naturally contain contaminants such as metals or non-metals toxic to human health. The origin of bottled waters can be quite diverse and includes aquifers, springs, reservoirs or even tap water. In many cases, the source of the water is not clearly specified on the label and so investigation of the quality is necessary (Astel et al., 2014). In Brazil, in accordance with RDC Resolution No. 274/2005 of the Ministry of Health, mineral water is “water obtained directly from natural or groundwater extraction sources”. Concern over the quality of mineral water on the market is highlighted in several articles devoted to this subject. Ikem et al. investigated the chemical quality of twenty-five bottled waters from cities in the state of Alabama, USA, through a one-way parametric analysis of variance (ANOVA) and showed that several samples available on the market had physical-chemical parameters (pH and conductivity) as well as essential and non-essential elements exceeding the EU and US EPA drinking water standards (Ikem et al., 2002). Saleh et al. evaluated five major brands of commercial bottled water from Egypt. Inorganic constituents and trihalomethanes in all samples were within the acceptable levels of the World Health Organization (WHO) guidelines (Saleh et al., 2001). Dinelli et al. investigated a large number of chemical parameters when comparing the quality of 178 mineral and 158 tap waters bottled in Italy (Dinelli et al., 2012). Recently, Astel et al. presented a study of forty-seven different brands of bottled sparkling and mineral waters from Poland using hierarchical cluster analysis (Astel et al., 2014) and Felipe-Sotelo et al. published a comparison of thirty seven different bottled waters from British and continental Europe using multivariate analysis (Felipe-Sotelo et al., 2015). In these studies, the concentrations of inorganic ions as well as parameters such as pH,

electrolytic conductivity and inorganic and total organic carbon were determined. For this purpose, the main analytical techniques employed were ion chromatography (IC), inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS). In Brazil, studies have also highlighted concern over the quality and composition of bottled mineral waters available on the market. Godoy et al. investigated the natural radionuclides ^{228}Ra , ^{226}Ra and ^{210}Pb in Brazilian bottled mineral waters (Godoy et al., 2001). A physical-chemical evaluation of bottled mineral waters marketed in Campinas, SP, Brazil was made by Morgano et al. (Morgano et al., 2002), Dias et al. evaluated the quality of thirty-two samples of commercially available bottled mineral waters from South and Southeast Brazil (Dias et al., 2012) and Zan et al. investigated the quality of bottled mineral waters available in cities from the Jamari valley, western Amazon, Brazil-Rondonia (Zan et al., 2013). The objective of this complementary study was to evaluate the quality of twenty-seven samples of bottled mineral waters from markets in Curitiba – PR – Brazil, taking into account acceptable levels of components stipulated in Brazilian legislation (RDC N° 274, 2005), mineral classification according to Portaria DNPM 540 and Decreto-Lei 7841, as well as information declared on the sample labels. A multivariate statistical analysis of the data was conducted to assess the variability of the composition (Portaria DNPM 540, 2014 and Decreto-Lei 7841, 1945). To the best of our knowledge, such a complete study as this, involving characterization of a variety of sources of bottled waters available for consumption in Brazil for their chemical and physical parameters, mineral constituents and toxic elements, has not been earlier conducted.

MATERIALS AND METHODS

Instrumentation: Aluminum, Ba, Cd, Cr, Cu, Fe, Li, Mn, Ni, Sr, V and Zn were determined using a VISTA PRO simultaneous axial view ICP OES spectrometer (Varian, Mulgrave, Australia). Mercury was determined by cold vapor generation (CVG) coupled to ICP OES. Arsenic, Sb, Pb and Se were determined using a Varian model 820-MS (ICP-MS). Argon and H_2 of 99.99995 % purity were supplied by White Martins (São Paulo, Brazil) for plasma operation. Optimized

experimental conditions are summarized in Table 1.

Table 1. ICP OES, CVG-ICP OES and ICP-MS instrumental parameters.

	ICP OES	CVG-ICP OES	ICP-MS
Radiofrequency	40 MHz	40 MHz	27.12 MHz
Forward power	1.25 kW	1.2 kW	1.4 kW
Plasma gas flow rate	15.0 L min ⁻¹	15.0 L min ⁻¹	18.0 L min ⁻¹
Auxiliary gas flow rate	1.5 L min ⁻¹	1.5 L min ⁻¹	1.8 L min ⁻¹
Sheath gas flow	-----	-----	0.21 L min ⁻¹
Carrier gas flow rate	-----	120 mL min ⁻¹	-----
Nebulizer pressure	180 kPa	-----	-----
Nebulizer type	Concentric glass K	-----	-----
Spray chamber	Standard Axial Varian	Standard Axial Varian	-----
Replicate read time	15 s with 4 replicates	15 s with 4 replicates	20 s with 8 replicates
Torch type	1.8 mm I.D. alumina injector tube	Quartz for axial view	Quartz
NaBH ₄ concentration	-----	0.3 % (m/v) in 0.4%, m/v, NaOH	-----
HCl concentration	-----	5 mol L ⁻¹	-----
Analytical lines / isotopes (ICP-MS)	Al: 396.152 nm, Ba: 455.403 nm, Cd: 214.439 nm, Cr: 267.716 nm, Cu: 327.395 nm; Fe: 238.204 nm, Li: 610.365 nm, Mn: 257.610 nm, Ni: 231.604 nm, Sr: 421.552 nm, V: 292.401 nm, Zn: 213.857 nm	Hg: 252.652 nm	⁷⁵ As, ¹²¹ Sb, ^{206,207,208} Pb and ⁷⁸ Se
Collisional gas CRI	-----	-----	H ₂ (⁷⁸ Se)
Internal standard	-----	-----	⁸⁹ Y, ¹¹⁵ In

Fluoride, Cl⁻, NO₃⁻, NO₂⁻, SO₄²⁻, Na⁺, K⁺, Ca²⁺, Mg²⁺ and NH₄⁺ were determined using a model Dionex ICS-5000+ IC from Thermo Fischer Scientific (Sunnyvale, CA, USA). Experimental conditions are summarized in Table 2. A Thermo

Orion model 710A potentiometer was used for pH measurements. Conductivity and Total Dissolved Solids (TDS) were acquired with a Mettler Toledo (Schwerzenbach, Switzerland) model SevenCompact pH meter.

Table 2. IC operating parameters.

	Anions	Cations
Column	IonPac® AS19 2x250mm	IonPac® AS12A 2x250mm
Guard Column	IonPac® AG19 2x50mm	IonPac® AG12A 2x50mm
Eluent	20 mmol L ⁻¹ KOH	10 mmol L ⁻¹ H ₂ SO ₄
Flow	0.25 mL min ⁻¹	0.25 mL min ⁻¹
Temperature	30°C	30°C
Suppressor	13 mA	15 mA
Detector	Conductivity	Conductivity
Injection loop	10 µL	10 µL
Run time	20 min	20 min

Reagents and samples: All chemicals were of analytical grade, unless otherwise specified. High-purity water (18.2 MΩ cm resistivity) was de-ionized in a Milli-Q system (Bedford, MA, USA). The following Merck reagents (Darmstadt, Germany) were used: NaBH₄ to prepare a 0.3 % m/v solution in NaOH; 65% v/v HNO₃ suprapur®; 37% v/v HCl from which a 5 mol L⁻¹ solution was prepared. Buffer solutions for pH 4.00 and pH 7.00 were supplied by Êxodo (Hortolândia, Brasil). Monoelemental standard solutions containing 1000 µg mL⁻¹ of Al, As, Hg, In, K⁺, Mn, Na⁺, Pb, Se, Sb, Sr, V, Y, Zn, Cl⁻, NO₂⁻ and NH₄⁺ were obtained from AccuStandard (New Haven, USA); those for Ba, Cd, Cr, Ca²⁺, Cu, Fe,

Li, Mg²⁺ and Ni from UltraScientific (North Kingstown, USA), while solutions of F⁻, NO₃⁻ and SO₄²⁻ were supplied by Fluka Analytical (St. Louis, USA). A conductivity standard of 84 µS cm⁻¹ was obtained from Mettler Toledo. Quality control Certified Reference Materials comprising acidified aqueous solutions containing 100 µg mL⁻¹ As, Sb, Ca, Cd, Cr, Cu, Fe, Li, Mg, Mn, Ni, Pb, Se, Sr, V and Zn (QCS-01-5), 100 µg mL⁻¹ of Al, Ba, K and Na (QCS-02-R1-5) and 20 µg mL⁻¹ of Hg (TCLP-02-1) were obtained from AccuStandard. These served as quality control standards. Twenty-seven samples of bottled mineral waters were purchased from local markets in Curitiba city, State of Paraná (PR)-Brazil and included twenty samples from

Paraná State, one from São Paulo State, one from Minas Gerais State, one imported from Portugal, two imported from France and two imported from Italy. Information regarding the mineral composition available on the labels of these samples is presented in Table 3.

Analytical procedures and standard calibration: All samples were simply acidified to 1% v/v HNO₃ for determination of elements by ICP OES, ICP-MS and Hg by CVG-ICP OES. For the determination of analytes by IC, aliquots of the samples were injected directly, or diluted appropriately when the analyte concentration present in the samples presented a concentration greater than the working range, without any preliminary treatment.

Hydrogen carbonate (HCO₃⁻), carbonate (CO₃²⁻) and Hardness were determined by titrimetry. All determinations were made following the recommendations in Standard Methods for the Examination of Water and Wastewater, 2012.

Multielement standard calibration solutions spanning the concentration range 100 – 2000 µg L⁻¹ for Al, Ba, Cd, Cr, Cu, Fe, Li, Mn, Ni, Sr, V and Zn were prepared in 1% v/v HNO₃ for their determination by ICP OES; for Hg the calibration standards were prepared in 1% v/v HNO₃ spanning the range 0.2 - 1.0 µg L⁻¹, and for determination of As, Pb, Sb and Se by ICP-MS, multielement calibration curves were prepared in 1% v/v HNO₃ spanning the range 1.0 – 20 µg L⁻¹. Operating conditions summarized in Table 1 were used. For determination of analytes by IC, multielement standard solutions containing Ca²⁺, Mg²⁺, K⁺, Na⁺ in the range 0.1 – 2.0 mg L⁻¹ and NH₄⁺ in the range 0.03- 0.5 mg L⁻¹ were prepared in de-ionized water and a multielement calibration standard solution for F⁻, Cl⁻, NO₃⁻, SO₄²⁻ and NO₂⁻ was prepared in de-ionized water spanning the ranges 0.01-10 mg L⁻¹. Analytical conditions summarized in Table 2 were used.

Statistical evaluation: The statistical program Statgraphics Plus 5.0 (Statgraphics Graphics Corp., ST. SC., USA) was used for principal component analysis (PCA).

Table 3. Mineral composition presented on sample labels of tested bottled mineral waters.

sample	pH	Cond. ($\mu\text{S cm}^{-1}$)	HCO_3^- (mg L^{-1})	F^- (mg L^{-1})	Cl^- (mg L^{-1})	NO_3^- (mg L^{-1})	SO_4^{2-} (mg L^{-1})	Na^+ (mg L^{-1})	K^+ (mg L^{-1})	Mg^{2+} (mg L^{-1})	Ca^{2+} (mg L^{-1})	Ba (mg L^{-1})	Sr (mg L^{-1})	Li (mg L^{-1})
01	5.22	153	2.09	0.01	----	----	----	0.2	0.1	0.12	0.27	0.007	0.003	----
02	5.10	10	3.2	0.02	0.15	----	0.3	0.38	1.47	0.07	0.12	----	----	----
03	6.88	111.5	75.35	0.07	0.6	2.8	0.2	6.2	0.2	1.82	17.65	----	0.015	----
04	6.88	111.5	75.35	0.07	0.6	2.8	0.2	6.2	0.2	1.82	17.65	----	0.015	----
05	5.98	83	37.2	0.09	1.94	7.27	0.36	6.592	3.595	1.832	5.346	0.09	0.151	----
06	8.66	108.4	62.49	0.05	<0.09	----	0.18	16.09	1.485	0.34	7.792	----	0.343	----
07	7.60	254	146.62	0.02	0.64	----	----	1.079	0.542	14.29	24.88	----	0.019	----
08	5.45	48	16.8	0.03	0.85	7	0.7	0.98	1.89	1.82	3.73	0.064	0.042	----
09	5.68	31.2	15.59	----	0.34	2	1.4	1.17	1.63	1.54	2.15	0.057	0.022	0.022
10	5.48	130.7	26.28	0.02	6.72	3.47	----	4.01	0.3	6.46	13.05	0.087	0.073	----
11	6.96	157.5	92.7	0.05	2.47	6.4	0.4	8	2.03	5.62	16.94	0.006	0.107	----
12	6.79	211	118.79	0.3	3.38	----	2.34	10.8	2.103	6.359	21.39	0.01	0.154	0.005
13	7.92	233	131.19	0.82	2.54	----	3.45	6.844	2.086	11.16	23.22	----	----	----
14	7.36	303	187.38	0.03	----	----	0.65	1.52	0.87	22.08	36.76	0.024	----	----
15	7.09	264	144.54	0.36	3.82	0.07	12.17	33.68	1.237	0.741	23.82	0.007	0.348	0.013
16	6.83	215	116.21	0.06	3.04	20.14	0.84	7.009	0.958	8.753	25.8	0.005	0.127	----
17	9.17	195.8	92.09	0.19	0.83	10	0.68	33.67	0.598	3.141	9.507	----	0.054	----
18	6.73	267	128.91	0.07	3.31	12.56	2.15	8.042	0.572	10.39	30.83	----	0.075	----
19	7.13	317	205.57	0.02	1.43	2.93	0.2	2.429	0.874	17.72	37.6	0.028	0.019	----
20	7.13	421	296.27	----	1.39	1.82	1.14	1.466	1.156	28.94	49.53	0.044	0.052	----
21	7.47	335	199.63	0.02	----	5.08	0.23	0.919	0.368	21.07	32.5	0.007	----	----
22	5.37	464	282.8	0.12	1.53	1.83	1.79	33.49	32.93	12.38	28.41	0.464	0.049	0.028
23	5.5	780	430	----	22	7.8	33	9.5	<1	4.2	160	----	----	----
24	6	----	1300	1.2	44	----	38	165	10	85	190	----	----	----
25	6.10	2670	2044	1.3	29.4	0.19	----	599	30.6	24.6	101	----	----	----
26	7.6	1125	245	----	52	2.6	430	33.3	2.2	51.4	174	----	2.8	----
27	8	216	103	----	8.5	2.9	22	6.4	0.8	6.2	32	----	----	----

RESULTS AND DISCUSSION

Figures of merit and precision

Analytical figures of merit derived from the results of replicate analysis of seven solutions prepared from acidified standards for determination by ICP OES, CVG-ICP OES and ICP-MS, as well as that for analysis of seven solutions prepared in unacidified de-ionized water for determination by IC are summarized in Table 4. The linear correlation coefficients range from 0.9980 to 0.9999, demonstrating adequate linearity. Limits of detection (LOD) were calculated from 3 times the standard deviation of 7 measurements of the

blank divided by the slope of the calibration curve. The practical quantification limits (LOQ) provided estimates of the lowest values of concentration could be determined with acceptable precision and accuracy. The LOQ are fit-for-purpose for determination of all analytes of interest. Analyses of the prepared solutions are in agreement (values within 90 – 111 %) with expected concentrations with relative standard deviations (RSD) below 10 %, indicating that fit-for-purpose recovery and precision can be achieved following prescribed sample preparation procedures and instrumental calibration (Miller, J.N. and Miller, J.C., 2000).

Table 4. Figures of merit and results for analysis of quality control materials and standards (n=7).

Analyte	Linear correlation coefficients	Limit of detection ($\mu\text{g L}^{-1}$)	Limit of quantification ($\mu\text{g L}^{-1}$)	expected concentration ($\mu\text{g L}^{-1}$)	recovery	RSD, %
Al	0.9998	2	10	10.0	10.0 ± 0.2	2.0
As	0.9997	0.1	1.0	10.0	10.3 ± 0.2	1.9
Ba	0.9999	1	5	10.0	11.0 ± 0.1	0.9
Ca ²⁺	0.9999	10	100	100	106 ± 4	4
Cd	0.9999	0.2	1.0	10.0	9.6 ± 0.1	1.0
Cu	0.9996	1	10	10.0	10.1 ± 0.2	2.0
Cr	0.9999	0.2	1.0	10.0	9.8 ± 0.1	1.0
Cl ⁻	0.9999	30	100	100	101 ± 10	10
F ⁻	0.9993	1	20	10.0	9.1 ± 0.3	3.3
Fe	0.9999	2	10	10.0	10.5 ± 0.1	1.0
Hg	0.9980	0.04	0.2	1.0	0.9 ± 0.03	3.3
K ⁺	0.9999	10	100	100	102 ± 3	3
Li	0.9996	2	10	10.0	11.2 ± 0.2	1.8
Mn	0.9999	0.2	1.0	10.0	10.2 ± 0.2	1.8
Mg ²⁺	0.9999	5	100	100	98 ± 2	2
NO ₃ ⁻	0.9999	5	100	100	89 ± 1	1
NO ₂ ⁻	0.9999	1	10	10.0	10.2 ± 0.3	2.9
NH ₄ ⁺	0.9999	10	30	30.0	33.0 ± 2.1	6.4
Na ⁺	0.9999	10	100	100	100 ± 4	4
Ni	0.9999	2	10	10.0	9.5 ± 0.3	3.2
Pb	0.9995	0.1	1.0	10.0	10.2 ± 0.2	2.0
Sb	0.9996	0.2	1.0	10.0	11.1 ± 0.3	2.7
Sr	0.9997	1	5	10.0	10.0 ± 0.3	1.0

Se	0.9987	0.1	1.0	10.0	0.1 10.1 ±	1.0
SO ₄ ²⁻	0.9999	10	100	100	0.1 98 ± 2	2.0
V	0.9999	2	10	10.0	9.0 ± 0.1	1.1
Zn	0.9999	2	10	10.0	9.6 ± 0.3	3.1

Trace elements and contaminants

Tables 5 and 6 summarize results obtained characterizing the twenty-seven commercial samples purchased for this study. The presence of NH₄⁺ and NO₂⁻ are indicative of microbiological contamination. The concentration of NH₄⁺ was below the limit of quantification but for NO₂⁻ samples 14, 19 and 21 (0.01 mg L⁻¹) concentrations near the maximum limit set by Brazilian legislation were evident whereas that for sample 16 (0.04 mg L⁻¹) exceeded the maximum limit set by RDC N° 274, 2005, i.e., 0.02 mg/L. In such cases, microbiological testing is required. Toxic elements such as Cd, Hg, Ni, Pb and Cu were all present below their LOQ and hence below the maximum values specified by Brazilian legislation (RDC N° 274, 2005). Arsenic, Cr, Mn, Sb and Zn were detected in some samples: As in five samples was present from 1.1 to 6.1 µg L⁻¹; Cr in six samples occurred in the range 1.3 - 4.9 µg L⁻¹; Mn in eight samples was in the range 1.1 - 155.6 µg L⁻¹; Sb was present in two samples at 1.0 µg L⁻¹ and 2.3 µg L⁻¹, and Zn in three samples was quantified at 14 µg L⁻¹, 22 µg L⁻¹ and 37 µg L⁻¹. All were below the maximum specified by Brazilian legislation, i.e., As 10 µg L⁻¹, Cr 50 µg L⁻¹, Mn 500 µg L⁻¹, Sb 5 µg L⁻¹ (RDC N° 274, 2005) and Zn 500 µg L⁻¹ (Portaria 2914/2011). Further investigation would be required to determine the origin of these elements, whether natural or anthropogenic. Detectable aluminium is detected in only one sample from Brazil (sample 22 from Minas Gerais State) whereas all imported samples lie in the range 10 - 30 µg L⁻¹. As Al has no known biochemical function (Silva Pereira and Dos Reis, 2012), Brazilian legislation specifies a tolerable limit of 200 µg L⁻¹ in drinking water (Portaria 2914/2011). Iron is only detected in two imported samples from Italy: 10 µg L⁻¹ (sample 26) and 21 µg L⁻¹ (sample 27), but its concentration is not declared on the sample labels. Selenium is present in the range 1.2 - 6.4 µg L⁻¹ (four samples) and V in the range 10 - 150 µg L⁻¹ (ten samples). Sample 24, imported from France, and sample 17, from Paraná State, are identified as containing the highest concentrations of Se: 6.4 ± 0.3 µg L⁻¹ and V: 150 ± 5 µg L⁻¹,

respectively. According to Brazilian legislation, these samples should also be classified as mineral waters “seleniada”, i.e., that contain selenium at minimum 6 µg L⁻¹ and maximum of 10 µg L⁻¹, and “vanadica”, i.e., that contain vanadium at minimum 30 µg L⁻¹ (Portaria DNPM 540, 2014 and RDC N° 274, 2005). However, no statement on the label can be found. With respect to trace element content and potential contaminants, all samples should have more information concerning their concentrations.

Major and constituent elements

Although the physico-chemical parameter pH showed values different from those declared on the labels, as summarized in Table 3, these differences were not significant and in these cases the producers indicate that the values correspond to those characterizing the source of the water. These differences are acceptable since chemical transformations may occur over time that could slightly affect the pH. The pH range varies from mildly acidic (5.53 ± 0.01 , sample 23) to slightly alkaline (8.89 ± 0.10 , sample 24). Alkalinity due to the presence of CO_3^{2-} was detected in four samples wherein the reported pH was 8.49 ± 0.01 (sample 14), 8.79 ± 0.03 (sample 17), 8.44 ± 0.05 (sample 19) and 8.89 ± 0.01 (sample 24). Figure 1 shows the correlation between conductivity and total dissolved solids (TDS) parameters which indicate that the higher the sample conductivity, the greater the amount of TDS present. These two parameters are strongly correlated, especially with imported samples 24 (France), 25 (Portugal) and 26 (Italy). Conductivity is in close agreement with declared values except for sample 01 for which a value of $3.7 \pm 0.1 \mu\text{S cm}^{-1}$ was determined whereas $153 \mu\text{S cm}^{-1}$ declared, and the producer will require notification.

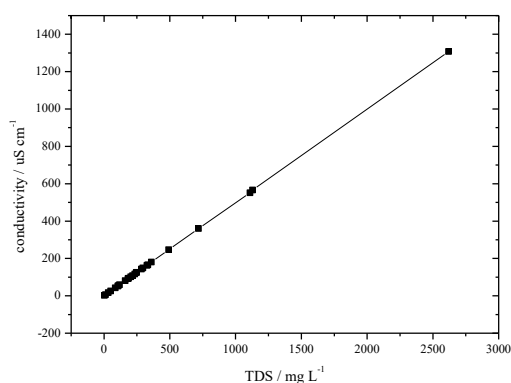


Figure 1. Correlation between conductivity and TDS.

Likewise, the hardness present in the sample can be correlated mainly to the presence of Ca and Mg. Samples 24-26 are again highlighted for their significant values present. The main constituent elements reported on the sample labels include: HCO_3^- , F^- , Cl^- , NO_3^- , SO_4^{2-} , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba, Li and Sr. Principal component analysis (PCA) for the concentrations of these analytes is presented in Figure 2, where PC1 is the first principal component, PC2 is the second and PC3 is the third (Dos Santos et al., 2008, Dos Santos et

al., 2012 and Miller, J. N. and Miller, J. C., 2000). PC1 accounts for 47% of the variance of the data and discriminates samples through the influence of parameters related to HCO_3^- , F^- , Cl^- , Ca^{2+} , and Li. PC2 accounts for 17% of the variance of the data and discriminates samples on the basis of SO_4^{2-} , while PC3 accounts for 12% of the variance of the data and is mainly correlated with the presence of Ba and Sr. Together, 76% of the variability of the original data is thus accounted for. As evident from Figure 2, the samples are clustered in a main group but five are located in different regions of the graph. Samples 23 to 26 are imported: 23 and 24 from France, 25 from Portugal and 26 from Italy. Only sample 22 is from Minas Gerais State, Brazil. Is evident that these samples have different physicochemical compositions, being characterized by relatively high concentrations of salts, mainly HCO_3^- and Sr. Legislation does not specify a value for Sr, and the HCO_3^- ion is an essential component of mineral waters (Decreto-Lei 7841, 1945). These five samples are also rich in F^- , providing a classification as “fluoridated mineral water”, as defined by Brazilian legislation (Portaria DNPM 540, 2014). The concentration of Li is high in samples 22, 24, 25 and 26, also a characteristic of mineral water in accordance with Brazilian legislation (Portaria DNPM 540, 2014). The concentration of Ba in sample 22 is the highest: $386 \pm 5 \mu\text{g L}^{-1}$, but below the maximum specified by Brazilian legislation, i.e., $700 \mu\text{g L}^{-1}$ (RDC N° 274, 2005). The main cluster comprises the majority of the samples that are bottled in the State of Paraná, with the exception of sample 11 from São Paulo State and sample 27 from Italy. This cluster is characteristic of the presence of NO_3^- . Nitrate may have either a mineral or microbiological origin. Its determinable concentration ranges from 0.10 mg L^{-1} - 63.05 mg L^{-1} while samples 01, 15 and 25 are below the LOQ. Only sample 10 (63.05 mg L^{-1}) is above the maximum specified by Brazilian legislation, i.e., 50 mg/L (RDC N° 274, 2005), **but the label states a value of 3.47 mg L^{-1} (Table 3)**. The elevated concentration may be indicative of microbiological contamination which may be harmful to human health (Astel et al., 2014). Samples 01, 10 and 21 are classified as “fluoridated mineral water”, according to their labels; however, in this study, F^- was not detected above 0.02 mg L^{-1} , the minimum, according to Brazilian legislation (Portaria DNPM 540, 2014), needed for water to be classified as such. Since the declared values are close to the

minimum, analyte sorption by the packaging materials may have occurred. It is evident that samples 3 and 4 have the same mineral composition. In reality, these samples are from the same region (Apucarana city, State of Paraná), but on the market they have a different identification and no indication that they are from the same producer. In general, it is clear that information declared on the label is different from that arising from analysis of the samples in this work, but it must also be recognized that as the samples are rich in salts, several factors may lead to changes in the composition, however small, including decomposition of HCO_3^- , sorption of analytes onto the walls of the container material, the time on the market shelf, and proper care during transport and the ambient storage temperature. To make a more qualified analysis of the national samples, a scatter plot based on only national Brazilian samples is presented in Figure 3. Here the PCs account for 73% of the variability of the original data. As in Figure 2, variability in the compositions of samples are evident wherein the difference of mineral content of sample 22 in relation to others is evident. The sample 10 possibly is contaminated and the samples 15 and 17 show F^- content and Na^+ higher concentrations than others. Clearly, the PCA statistical tool can be very useful for identification and comparison of compositions of bottled mineral waters on the market.

Figure 3. Principal component analysis applied to results obtained for the analysis of only national Brazilian samples of bottled mineral water from markets in Curitiba-PR.

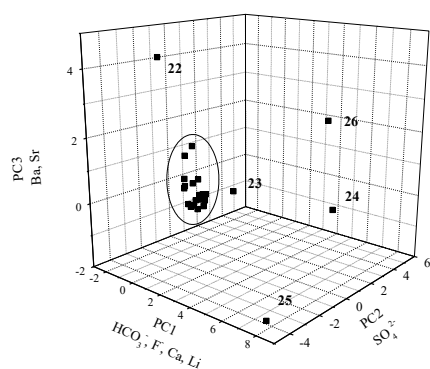


Figure 2. Principal component analysis applied to results obtained for the analysis of twenty-seven samples of bottled mineral water from markets in Curitiba-PR.

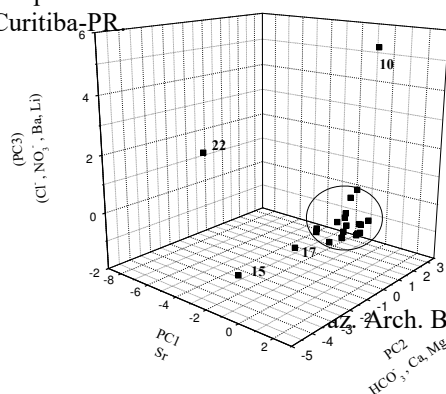


Table 5. Results for physico-chemical parameters and IC (n=3).

sample	pH	Cond. ($\mu\text{S cm}^{-1}$)	TDS (mg L^{-1})	HCO_3^- (mg L^{-1})	CO_3^{2-} (mg L^{-1})	F^- (mg L^{-1})	Cl^- (mg L^{-1})	NO_3^- (mg L^{-1})	NO_2^- (mg L^{-1})	SO_4^{2-} (mg L^{-1})	Na^+ (mg L^{-1})	K^+ (mg L^{-1})	NH_4^+ (mg L^{-1})	Mg^{2+} (mg L^{-1})	Ca^{2+} (mg L^{-1})	Hardness (mg L^{-1})
Legislation	-----	-----	-----	-----	-----	⁽¹⁾ 0.02 min. ⁽²⁾ 2.00 max.	-----	⁽²⁾ 50 max.	⁽²⁾ 0.02 max.	-----	-----	-----	-----	-----	-----	-----
01	6.44 ± 0.17	3.7 ± 0.1	1.8 ± 0.1	6.1 ± 0.1	nd	< 0.02	0.20	< 0.10	< 0.01	< 0.10	0.15	< 0.10	< 0.03	0.10	0.15 ± 0.01	0.8
02	6.52 ± 0.20	12.3 ± 0.4	6.1 ± 0.2	6.1 ± 0.2	nd	0.02	0.15	0.18	< 0.01	1.00	0.68	1.55	< 0.03	< 0.10	0.22 ± 0.01	< 0.7
03	7.86 ± 0.08	106.2 ± 1.7	53.1 ± 0.9	63.4 ± 3.5	nd	0.08 ± 0.01	0.56	2.77	< 0.01	0.82 ± 0.01	6.03 ± 0.01	0.19	< 0.03	1.10 ± 0.01	13.67 ± 0.01	38.7
04	7.40 ± 0.06	106.7 ± 1.0	53.3 ± 0.4	69.5 ± 8.9	nd	0.08	0.60 ± 0.01	2.66	< 0.01	0.90	5.94 ± 0.01	0.21 ± 0.01	< 0.03	1.16 ± 0.01	14.35 ± 0.06	40.6
05	6.76 ± 0.11	85.5 ± 2.5	42.8 ± 1.3	48.0 ± 1.8	nd	0.14	1.30 ± 0.01	2.24 ± 0.01	< 0.01	0.43	6.78 ± 0.02	2.78	< 0.03	1.83 ± 0.04	5.81 ± 0.08	22.0
06	8.13 ± 0.04	118.4 ± 1.2	59.1 ± 0.5	75.6 ± 3.5	nd	0.06	< 0.10	0.10	< 0.01	0.17	17.46 ± 0.01	1.71 ± 0.01	< 0.03	0.25	7.77 ± 0.02	20.4
07	7.87 ± 0.02	248.3 ± 4.0	125.8 ± 1.1	167.6 ± 1.8	nd	0.05	0.70	2.64 ± 0.01	< 0.01	0.65	0.98	0.54	< 0.03	16.31 ± 0.06	28.17 ± 0.04	137.5
08	7.29 ± 0.03	51.1 ± 0.1	25.4 ± 0.2	18.4 ± 0.1	nd	0.03	0.98	6.26	< 0.01	0.50	0.89	1.98 ± 0.02	< 0.03	1.81 ± 0.02	3.52 ± 0.04	16.2
09	6.27 ± 0.13	133.2 ± 0.3	16.6 ± 0.1	17.4 ± 1.8	nd	0.03	0.34	2.31	< 0.01	0.15	1.00	1.44	< 0.03	1.40	1.86	10.4
10	7.19 ± 0.03	136.7 ± 0.4	93.4 ± 0.1	12.3 ± 0.2	nd	< 0.02	10.96 ± 0.02	63.05 ± 0.13	< 0.01	< 0.10	7.59 ± 0.01	0.31	< 0.03	5.90 ± 0.02	13.00 ± 0.05	56.8
11	7.92 ± 0.06	161.8 ± 0.5	81.5 ± 0.2	90.0 ± 3.5	nd	0.08	2.31	5.44 ± 0.01	< 0.01	0.24	7.21	1.87	< 0.03	5.01 ± 0.03	15.98 ± 0.10	60.5
12	7.21 ± 0.04	202.9 ± 3.8	101.6 ± 1.5	117.6 ± 1.8	nd	0.25	3.26	0.44	< 0.01	1.78 ± 0.03	10.32 ± 0.01	2.45	< 0.03	5.70 ± 0.01	20.50 ± 0.30	74.7
13	8.00 ± 0.02	181.9 ± 0.6	91.5 ± 0.2	110.4 ± 1.0	nd	0.10	1.78	2.53 ± 0.01	< 0.01	1.04 ± 0.02	5.07 ± 0.01	1.26 ± 0.01	< 0.03	7.78 ± 0.05	18.47 ± 0.07	78.2
14	8.49 ± 0.01	295.3 ± 1.2	148.9 ± 0.4	190.1 ± 6.1	3.0	0.04	1.61 ± 0.01	4.56 ± 0.01	0.01	0.88 ± 0.01	1.37 ± 0.01	0.86	< 0.03	18.33 ± 0.01	32.56 ± 0.03	156.8
15	8.11 ± 0.03	233.7 ± 0.6	116.4 ± 0.4	124.7 ± 3.5	nd	0.38	2.61 ± 0.01	< 0.10	< 0.01	12.06 ± 0.03	33.30 ± 0.07	1.20 ± 0.09	< 0.03	0.44	16.17 ± 0.09	42.2
16	7.80 ± 0.02	234.0 ± 2.0	117.0 ± 1.1	121.6 ± 1.8	nd	0.05	3.39 ± 0.01	20.68 ± 0.02	0.04	0.70	7.28	0.91	< 0.03	8.49 ± 0.10	26.38 ± 0.02	100.8
17	8.79 ± 0.03	217.0 ± 1.0	107.8 ± 0.3	128.8 ± 0.8	3.0	0.22	0.64	2.88	< 0.01	0.54	35.71 ± 0.06	0.46	< 0.03	2.53 ± 0.01	8.83 ± 0.02	32.5
18	8.18 ± 0.05	284.7 ± 1.5	143.1 ± 0.5	159.5 ± 6.1	nd	0.06	3.84 ± 0.02	16.39 ± 0.08	< 0.01	2.16 ± 0.02	8.90 ± 0.01	0.62 ± 0.01	< 0.03	9.89	32.68 ± 0.13	122.3
19	8.44 ± 0.05	333.7 ± 0.6	166.3 ± 0.3	218.8 ± 3.5	3.0	0.03	1.40 ± 0.01	3.18 ± 0.02	0.01	0.19	2.19 ± 0.01	0.86 ± 0.01	< 0.03	20.52 ± 0.03	37.12 ± 0.13	177.2
20	8.19 ± 0.03	360.0 ± 4.6	180.2 ± 2.2	256.6 ± 1.8	nd	0.04	0.90 ± 0.01	1.02 ± 0.01	< 0.01	0.68 ± 0.01	1.61	0.83	< 0.03	26.14 ± 0.05	41.17 ± 0.08	210.5
21	7.76 ± 0.06	326.3 ± 7.4	163.2 ± 3.6	228.0 ± 4.7	nd	< 0.02	1.74	5.53 ± 0.03	0.01	0.25 ± 0.01	1.18 ± 0.01	0.37	< 0.03	21.41 ± 0.03	37.78 ± 0.08	182.5
22	7.44 ± 0.02	492.0 ± 0.6	247.0 ± 1.1	325.1 ± 3.5	nd	0.16 ± 0.01	1.56 ± 0.01	1.74 ± 0.02	< 0.01	1.91 ± 0.01	38.27 ± 0.18	38.24 ± 0.16	< 0.03	13.29 ± 0.19	32.28 ± 0.16	135.4
23	5.53 ± 0.01	718.0 ± 5.0	360.2 ± 2.0	398.7 ± 2.0	nd	0.11 ± 0.01	20.80 ± 0.06	5.26 ± 0.10	< 0.01	29.10 ± 0.11	11.18 ± 0.02	0.89 ± 0.06	< 0.03	3.61 ± 0.01	157.37 ± 0.34	407.9
24	8.89 ± 0.05	1129 ± 8	566.4 ± 1.6	708.4 ± 1.1	30.2	1.22 ± 0.04	51.19 ± 0.10	2.81 ± 0.08	< 0.01	25.73 ± 0.06	174.28 ± 0.04	12.03 ± 0.08	< 0.03	84.34 ± 0.22	170.69 ± 0.16	773.6
25	6.42 ± 0.03	2620 ± 10	1308 ± 5	1294.1 ± 2.5	nd	0.56 ± 0.01	25.79 ± 0.01	< 0.10	< 0.01	4.17 ± 0.01	553.12 ± 0.74	30.51 ± 0.27	< 0.03	22.02 ± 0.88	139.88 ± 2.32	440.0
26	5.46 ± 0.02	1110 ± 11	551.0 ± 1.6	220.8 ± 1.1	nd	0.58 ± 0.03	50.86 ± 0.48	3.24 ± 0.14	< 0.01	420.71 ± 2.77	33.79 ± 0.05	2.37 ± 0.04	< 0.03	47.79 ± 0.90	173.44 ± 2.77	629.9
27	8.25 ± 0.03	245.0 ± 3.6	124.5 ± 2.5	104.3 ± 2.0	nd	0.04	6.89 ± 0.03	3.10 ± 0.01	< 0.01	20.85 ± 0.06	7.90 ± 0.01	0.84	< 0.03	6.22 ± 0.06	30.68 ± 0.03	102.2

nd: not detected; legislation: Portaria N° 540 de 18/12/2014¹, RDC N° 274 de 22/09/2005², Portaria N° 2914 de 12/12/2011³.

Table 6. Results for cations determined by ICP OES, CVG-ICP OES and ICP-MS (n=3).

sample	Al ($\mu\text{g L}^{-1}$)	As ($\mu\text{g L}^{-1}$)	Ba ($\mu\text{g L}^{-1}$)	Cd ($\mu\text{g L}^{-1}$)	Cr ($\mu\text{g L}^{-1}$)	Cu ($\mu\text{g L}^{-1}$)	Fe ($\mu\text{g L}^{-1}$)	Hg ($\mu\text{g L}^{-1}$)	Li ($\mu\text{g L}^{-1}$)	Mn ($\mu\text{g L}^{-1}$)	Ni ($\mu\text{g L}^{-1}$)	Pb ($\mu\text{g L}^{-1}$)	Sb ($\mu\text{g L}^{-1}$)	Se ($\mu\text{g L}^{-1}$)	Sr ($\mu\text{g L}^{-1}$)	V ($\mu\text{g L}^{-1}$)	Zn ($\mu\text{g L}^{-1}$)
Legislation	⁽²⁾ 200 max	⁽²⁾ 10 max.	⁽²⁾ 700 max.	⁽²⁾ 3 max.	⁽²⁾ 50 max.	⁽²⁾ 1000 max.	-----	⁽²⁾ 1.0 max.	⁽¹⁾ 10 min.	⁽²⁾ 500 max.	⁽²⁾ 20 max.	⁽²⁾ 10 max.	⁽²⁾ 5 max.	⁽¹⁾ 6 min. ⁽²⁾ 10 max.	-----	⁽¹⁾ 30 min.	⁽³⁾ 500 max.
01	< 10	< 1.0	5	< 1.0	< 1.0	< 10	< 10	< 0.2	< 10	1.9 \pm 0.1	< 10	< 1.0	< 1.0	< 1.0	< 5	< 10	< 10
02	< 10	< 1.0	58 \pm 3	< 1.0	< 1.0	< 10	< 10	< 0.2	< 10	1.1 \pm 0.1	< 10	< 1.0	< 1.0	< 1.0	< 5	< 10	< 10
03	< 10	< 1.0	< 1	< 1.0	< 1.0	< 10	< 10	< 0.2	< 10	< 1	< 10	< 1.0	< 1.0	< 1.0	< 5	10 \pm 1	< 10
04	< 10	< 1.0	< 1	< 1.0	< 1.0	< 10	< 10	< 0.2	< 10	< 1	< 10	< 1.0	< 1.0	< 1.0	< 5	10 \pm 1	< 10
05	< 10	< 1.0	76 \pm 5	< 1.0	< 1.0	< 10	< 10	< 0.2	< 10	< 1	< 10	< 1.0	< 1.0	< 1.0	137 \pm 5	< 10	< 10
06	< 10	< 1.0	1	< 1.0	4.9 \pm 0.1	< 10	< 10	< 0.2	< 10	< 1	< 10	< 1.0	< 1.0	< 1.0	333 \pm 10	< 10	< 10
07	< 10	< 1.0	16 \pm 1	< 1.0	< 1	< 10	< 10	< 0.2	< 10	< 1	< 10	< 1.0	< 1.0	< 1.0	< 5	< 10	< 10
08	< 10	< 1.0	80 \pm 4	< 1.0	1.9 \pm 0.1	< 10	< 10	< 0.2	< 10	8.9 \pm 0.2	< 10	< 1.0	< 1.0	< 1.0	33 \pm 2	< 10	< 10
09	< 10	< 1.0	63 \pm 2	< 1.0	< 1	< 10	< 10	< 0.2	< 10	2.0 \pm 0.1	< 10	< 1.0	< 1.0	< 1.0	7	< 10	< 10
10	< 10	< 1.0	100 \pm 5	< 1.0	< 1	< 10	< 10	< 0.2	< 10	4.3 \pm 0.2	< 10	< 1.0	< 1.0	< 1.0	56 \pm 5	< 10	14 \pm 1
11	< 10	< 1.0	7	< 1.0	2.3 \pm 0.1	< 10	< 10	< 0.2	< 10	< 1	< 10	< 1.0	< 1.0	< 1.0	86 \pm 3	21 \pm 1	< 10
12	< 10	< 1.0	19 \pm 1	< 1.0	< 1	< 10	< 10	< 0.2	< 10	< 1	< 10	< 1.0	< 1.0	< 1.0	128 \pm 12	< 10	< 10
13	< 10	< 1.0	75 \pm 2	< 1.0	1.5 \pm 0.1	< 10	< 10	< 0.2	< 10	2.1 \pm 0.1	< 10	< 1.0	< 1.0	< 1.0	100 \pm 4	< 10	22 \pm 1
14	< 10	< 1.0	22 \pm 1	< 1.0	< 1	< 10	< 10	< 0.2	< 10	< 1	< 10	< 1.0	< 1.0	< 1.0	< 5	< 10	< 10
15	< 10	1.1 \pm 0.1	6	< 1.0	< 1	< 10	< 10	< 0.2	< 10	< 1	< 10	< 1.0	< 1.0	< 1.0	316 \pm 13	< 10	< 10
16	< 10	< 1.0	3	< 1.0	< 1	< 10	< 10	< 0.2	< 10	< 1	< 10	< 1.0	2.3 \pm 0.2	< 1.0	121 \pm 8	19 \pm 1	< 10
17	< 10	2.4 \pm 0.1	1	< 1.0	< 1	< 10	< 10	< 0.2	< 10	< 1	< 10	< 1.0	< 1.0	3.4 \pm 0.2	30 \pm 5	150 \pm 5	< 10
18	< 10	< 1.0	1	< 1.0	< 1	< 10	< 10	< 0.2	< 10	< 1	< 10	< 1.0	< 1.0	< 1.0	62 \pm 5	24 \pm 2	< 10
19	< 10	< 1.0	34 \pm 2	< 1.0	< 1	< 10	< 10	< 0.2	< 10	< 1	< 10	< 1.0	< 1.0	< 1.0	< 5	< 10	< 10
20	< 10	< 1.0	37 \pm 4	< 1.0	< 1	< 10	< 10	< 0.2	< 10	< 1	< 10	< 1.0	< 1.0	< 1.0	25 \pm 2	< 10	< 10
21	< 10	< 1.0	9	< 1.0	< 1	< 10	< 10	< 0.2	< 10	< 1	< 10	< 1.0	< 1.0	< 1.0	< 5	< 10	< 10
22	20 \pm 0.2	< 1.0	386 \pm 5	< 1.0	< 1	< 10	< 10	< 0.2	10 \pm 1	1.1 \pm 0.1	< 10	< 1.0	1.0 \pm 0.1	< 1.0	35 \pm 1	< 10	< 10
23	13 \pm 0.5	< 1.0	26 \pm 1	< 1.0	1.3 \pm 0.1	< 10	< 10	< 0.2	< 10	< 1	< 10	< 1.0	< 1.0	1.5 \pm 0.1	600 \pm 15	10 \pm 1	< 10
24	10 \pm 0.1	6.1 \pm 0.2	2	< 1.0	< 1	< 10	< 10	< 0.2	387 \pm 8	0.9	< 10	< 1.0	< 1.0	6.4 \pm 0.3	1127 \pm 20	10 \pm 1	< 10
25	30 \pm 1	1.4 \pm 0.1	2	< 1.0	< 1	< 10	< 10	< 0.2	863 \pm 10	155.6 \pm 5	< 10	< 1.0	< 1.0	< 1.0	959 \pm 12	10 \pm 1	< 10
26	14 \pm 0.1	2.4 \pm 0.1	15 \pm 1	< 1.0	1.3 \pm 0.1	< 10	10 \pm 1	< 0.2	57 \pm 5	< 1	< 10	< 1.0	< 1.0	< 1.0	2364 \pm 18	11 \pm 1	< 10
27	10 \pm 0.3	< 1.0	74 \pm 1	< 1.0	< 1	< 10	21 \pm 1	< 0.2	< 10	< 1	< 10	< 1.0	< 1.0	1.2 \pm 0.1	246 \pm 5	< 10	37 \pm 2

nd: not detected; legislation: Portaria N° 540 de 18/12/2014¹, RDC N° 274 de 22/09/2005², Portaria N° 2914 de 12/12/2011³.

CONCLUSIONS

The present study reveals that, in general, the majority of parameters determined in commercial bottled mineral waters from markets in Curitiba-PR-Brazil are below limits specified by Brazilian legislation. Only one sample was detected as having a high concentration of NO_3^- , indicating microbiological contamination; some results for NO_2^- may also reflect the same contamination. Improvements in monitoring throughout the process of filling and points of sale of the samples, with the aim of securing the microbiological quality of bottled mineral waters sold in the region under study may be needed. The comparison of labelled composition to analytical results highlights a difference for most elements, but it should be noted that intrinsic instability as well as other factors such as absorption of components onto container surfaces as well as the length of time spent on the shelf, care during transport, and the ambient storage temperature may alter the composition; perhaps a "best before date" could eliminate such discrepancies. In such cases, a further study of the stability and interaction with the packaging should be performed. Although a perfect division of samples from PR State is not achieved according to their mineral composition, PCA scores clearly delineate the imported samples from those from other states.

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Erratum

In Article “Chemical quality of bottled mineral waters from markets of Curitiba-PR-Brazil”, with the number of DOI: <http://dx.doi.org/10.1590/1678-4324-2016150111>, published in journal Brazilian Archives of Biology and Technology, vol. 59, the 01 page.

That read:

“Éder José dos Santos^{1*}, Dasio Roberto de Oliveira Junior¹, Amanda Beatriz Hermann¹, Ralph Edwatd Sturgeon².

¹ Instituto de Tecnologia do Paraná – TECPAR – Centro de Tecnologia em Saúde e Meio Ambiente, Curitiba, Paraná, Brasil; ²Measurement Science and Standards, National Research Council Canada, Ottawa, Canada.”

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¹ Instituto de Tecnologia do Paraná – TECPAR – Centro de Tecnologia em Saúde e Meio Ambiente, Curitiba, Paraná, Brasil; ²Measurement Science and Standards, National Research Council Canada, Ottawa, Canada.”

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“In Brazil, in accordance with RDC Resolution No. 274/2005 of the Ministry of Health, mineral water is “water obtained directly from natural or groundwater extraction sources”. Concern over the quality of mineral water on the market is highlighted in several articles devoted to this subject. Ikem et al. investigated the chemical quality of twenty-five bottled waters from cities in the state of Alabama, USA, through a one-way parametric analysis of variance (ANOVA) and showed that several samples available on the market had physical-chemical parameters (pH and conductivity) as well as essential and non-essential elements exceeding the EU and US EPA drinking water standards (Ikem et al., 2002).”

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“In these studies, the concentrations of inorganic ions as well as parameters such as pH, electrolytic conductivity and inorganic and total organic carbon were determined. For this purpose, the main analytical techniques employed were ion chromatography (IC), inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS). In Brazil, studies have also highlighted concern over the quality and composition of bottled mineral waters available on the market. Godoy et al. investigated the natural radionuclides ^{228}Ra , ^{226}Ra and ^{210}Pb in Brazilian bottled mineral waters (Godoy et al., 2001).”

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Table 1. ICP OES, CVG-ICP OES and ICP-MS instrumental parameters.

	ICP OES	CVG-ICP OES	ICP-MS
Radiofrequency	40 MHz	40 MHz	27.12 MHz
Forward power	1.25 kW	1.2 kW	1.4 kW
Plasma gas flow rate	15.0 L min ⁻¹	15.0 L min ⁻¹	18.0 L min ⁻¹
Auxiliary gas flow rate	1.5 L min ⁻¹	1.5 L min ⁻¹	1.8 L min ⁻¹
Sheath gas flow	-----	-----	0.21 L min ⁻¹
Carrier gas flow rate	-----	120 mL min ⁻¹	-----
Nebulizer pressure	180 kPa	-----	-----
Nebulizer type	Concentric glass K	-----	-----
Spray chamber	Standard Axial Varian	Standard Axial Varian	-----
Replicate read time	15 s with 4 replicates	15 s with 4 replicates	20 s with 8 replicates
Torch type	1.8 mm I.D. alumina injector tube	Quartz for axial view	Quartz
NaBH ₄ concentration	-----	0.3 % (m/v) in 0.4%, m/v, NaOH	-----
HCl concentration	-----	5 mol L ⁻¹	-----
Analytical lines / isotopes (ICP-MS)	Al: 396.152 nm, Ba: 455.403 nm, Cd: 214.439 nm, Cr: 267.716 nm, Cu: 327.395 nm; Fe: 238.204 nm, Li: 610.365 nm, Mn: 257.610 nm, Ni: 231.604 nm, Sr: 421.552 nm, V: 292.401 nm, Zn: 213.857 nm	Hg: 252.652 nm	^{75}As , ^{121}Sb , $^{206,207,208}\text{Pb}$ and ^{78}Se
Collisional gas CRI	-----	-----	H ₂ (^{78}Se)
Internal standard	-----	-----	^{89}Y , ^{115}In

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Collisional gas CRI	-----	-----	H ₂ (⁷⁸ Se)
Internal standard	-----	-----	⁸⁹ Y, ¹¹⁵ In

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“Reagents and samples: All chemicals were of analytical grade, unless otherwise specified. High-purity water (18.2 MΩ cm resistivity) was de-ionized in a Milli-Q system (Bedford, MA, USA). The following Merck reagents (Darmstadt, Germany) were used: NaBH₄ to prepare a 0.3 % m/v solution in NaOH; 65% v/v HNO₃suprapur® ; 37% v/v HCl from which a 5 mol L⁻¹ solution was prepared. Buffer solutions for pH 4.00 and pH 7.00 were supplied by Êxodo (Hortolândia, Brasil). Monoelemental standard solutions containing 1000 µg mL⁻¹ of Al, As, Hg, In, K⁺, Mn, Na⁺, Pb, Se, Sb, Sr, V, Y, Zn, Cl⁻, NO₂⁻ and NH₄⁺ were obtained from AccuStandard (New Haven, USA); those for Ba, Cd, Cr, Ca²⁺, Cu, Fe, Li, Mg²⁺ and Ni from UltraScientific (North Kingstown, USA), while solutions of F⁻, NO₃⁻ and SO₄²⁻ were supplied by FlukaAnalytical (St. Louis, USA). A conductivity standard of 84 µS cm⁻¹ was obtained from Mettler Toledo. Quality control Certified Reference Materials comprising acidified aqueous solutions containing 100 µg mL⁻¹ As, Sb, Ca, Cd, Cr, Cu, Fe, Li, Mg, Mn, Ni, Pb, Se, Sr, V and Zn (QCS-01-5), 100 µg mL⁻¹ of Al, Ba, K and Na (QCS-02-R1-5) and 20 µg mL⁻¹ of Hg (TCLP-02-1) were obtained from AccuStandard. These served as quality control standards.”

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Table 4. Figures of merit and results for analysis of quality control materials and standards (n=7).

Analyte	Linear correlation coefficients	Limit of detection (µg L ⁻¹)	Limit of quantification (µg L ⁻¹)	of expected concentration (µg L ⁻¹)	recovery	RSD, %
Al	0.9998	2	10	10.0	10.0 ± 0.2	2.0
As	0.9997	0.1	1.0	10.0	10.3 ± 0.2	1.9
Ba	0.9999	1	5	10.0	11.0 ± 0.1	0.9
Ca ²⁺	0.9999	10	100	100	106 ± 4	4
Cd	0.9999	0.2	1.0	10.0	9.6 ± 0.1	1.0
Cu	0.9996	1	10	10.0	10.1 ± 0.2	2.0
Cr	0.9999	0.2	1.0	10.0	9.8 ± 0.1	1.0
Cl ⁻	0.9999	30	100	100	101 ± 10	10
F ⁻	0.9993	1	20	10.0	9.1 ± 0.3	3.3
Fe	0.9999	2	10	10.0	10.5 ± 0.1	1.0
Hg	0.9980	0.04	0.2	1.0	0.9 ± 0.03	3.3
K ⁺	0.9999	10	100	100	102 ± 3	3
Li	0.9996	2	10	10.0	11.2 ± 0.2	1.8
Mn	0.9999	0.2	1.0	10.0	10.2 ± 0.2	1.8
Mg ²⁺	0.9999	5	100	100	98 ± 2	2
NO ₃ ⁻	0.9999	5	100	100	89 ± 1	1
NO ₂ ⁻	0.9999	1	10	10.0	10.2 ± 0.3	2.9
NH ₄ ⁺	0.9999	10	30	30.0	33.0 ± 2.1	6.4
Na ⁺	0.9999	10	100	100	100 ± 4	4
Ni	0.9999	2	10	10.0	9.5 ± 0.3	3.2
Pb	0.9995	0.1	1.0	10.0	10.2 ± 0.2	2.0
Sb	0.9996	0.2	1.0	10.0	11.1 ± 0.3	2.7
Sr	0.9997	1	5	10.0	10.0 ± 0.1	1.0
Se	0.9987	0.1	1.0	10.0	10.1 ± 0.1	1.0

SO ₄ ²⁻	0.9999	10	100	100	98 ± 2	2.0
V	0.9999	2	10	10.0	9.0 ± 0.1	1.1
Zn	0.9999	2	10	10.0	9.6 ± 0.3	3.1

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NO ₂ ⁻	0.9999	1	10	10.0	10.2 ± 0.3	2.9
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“Tables 5 and 6 summarize results obtained characterizing the twenty-seven commercial samples purchased for this study. The presence of NH₄⁺ and NO₂⁻ are indicative of microbiological contamination. The concentration of NH₄⁺ was below the limit of quantification but for NO₂⁻ samples 14, 19 and 21 (0.01 mg L⁻¹) concentrations near the maximum limit set by Brazilian legislation were evident whereas that for sample 16 (0.04 mg L⁻¹) exceeded the maximum limit set by RDC N° 274, 2005, i.e., 0.02 mg/L. ”

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“Iron is only detected in two imported samples from Italy: $10 \text{ } \mu\text{g L}^{-1}$ (sample 26) and $21 \text{ } \mu\text{g L}^{-1}$ (sample 27), but its concentration is not declared on the sample labels. Selenium is present in the range $1.2 - 6.4 \text{ } \mu\text{g L}^{-1}$ (four samples) and V in the range $10 - 150 \text{ } \mu\text{g L}^{-1}$ (ten samples). Sample 24, imported from France, and sample 17, from Paraná State, are identified as containing the highest concentrations of Se: $6.4 \pm 0.3 \text{ } \mu\text{g L}^{-1}$ and V: $150 \pm 5 \text{ } \mu\text{g L}^{-1}$, respectively. According to Brazilian legislation, these samples should also be classified as mineral waters “seleniada”, i.e., that contain selenium at minimum $6 \text{ } \mu\text{g L}^{-1}$ and maximum of $10 \text{ } \mu\text{g L}^{-1}$, and “vanadica”, i.e., that contain vanadium at minimum $30 \text{ } \mu\text{g L}^{-1}$ (Portaria DNPM 540, 2014 and RDC N° 274, 2005). However, no statement on the label can be found. With respect to trace element content and potential contaminants, all samples should have more information concerning their concentrations.”

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“Although the physico-chemical parameter pH showed values different from those declared on the labels, as summarized in Table 3, these differences were not significant and in these cases the producers indicate that the values correspond to those characterizing the source of the water. These differences are acceptable since chemical transformations may occur over time that could slightly affect the pH. The pH range varies from mildly acidic (5.53 ± 0.01 , sample 23) to slightly alkaline (8.89 ± 0.10 , sample 24). Alkalinity due to the presence of CO_3^{2-} was detected in four samples wherein the reported pH was 8.49 ± 0.01 (sample 14), 8.79 ± 0.03 (sample 17), 8.44 ± 0.05 (sample 19) and 8.89 ± 0.01 (sample 24). Figure 1 shows the correlation between conductivity and total dissolved solids (TDS) parameters which indicates that the higher the sample conductivity, the greater the amount of TDS present. These two parameters are strongly correlated, especially with imported samples 24 (France), 25 (Portugal) and 26 (Italy). Conductivity is in close agreement with declared values except for sample 01 for which a value of $3.7 \pm 0.1 \text{ } \mu\text{S cm}^{-1}$ was determined whereas $153 \text{ } \mu\text{S cm}^{-1}$ declared, and the producer will require notification.”

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“Likewise, the hardness present in the sample can be correlated mainly to the presence of Ca and Mg. Samples 24-26 are again highlighted for their significant values present. The main constituent elements reported on the sample labels include: HCO_3^- , F^- , Cl^- , NO_3^- , SO_4^{2-} , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba, Li and Sr. Principal component analysis (PCA) for the concentrations of these analytes is presented in Figure 2, where PC1 is the first principal component, PC2 is the second and PC3 is the third (Dos Santos et al., 2008, Dos Santos et. al., 2012 and Miller, J. N. and Miller, J. C, 2000). PC1 accounts for 47% of the variance of the data and discriminates samples through the influence of parameters related to HCO_3^- , F^- , Cl^- , Ca^{2+} , and Li. PC2 accounts for 17% of the variance of the data and discriminates samples on the basis of SO_4^{2-} , while PC3 accounts for 12% of the variance of the data and is mainly correlated with the presence of Ba and Sr. Together, 76% of the variability of the original data is thus accounted for. As evident from Figure 2, the samples are clustered in a main group but five are located in different regions of the graph. Samples 23 to 26 are imported: 23 and 24 from France, 25 from Portugal and 26 from Italy. Only sample 22 is from Minas Gerais State, Brazil. Is evident that these samples have different physicochemical compositions, being characterized by relatively high concentrations of salts, mainly HCO_3^- and Sr. Legislation does not specify a value for Sr, and the HCO_3^- ion is an essential component of mineral waters (Decreto-Lei 7841, 1945). These five samples are also rich in F^- , providing a classification as “fluoridated mineral water”, as defined by Brazilian legislation (Portaria DNPM 540, 2014). The concentration of Li is high in samples 22, 24, 25 and 26, also a characteristic of mineral water in accordance with Brazilian legislation (Portaria DNPM 540, 2014). The concentration of Ba in sample 22 is the highest: $386 \pm 5 \mu\text{g L}^{-1}$, but below the maximum specified by Brazilian legislation, i.e., $700 \mu\text{g L}^{-1}$ (RDC N° 274, 2005). The main cluster comprises the majority of the samples that are bottled in the State of Paraná, with the exception of sample 11 from São Paulo State and sample 27 from Italy. This cluster is characteristic of the presence of NO_3^- . Nitrate may have either a mineral or microbiological origin. Its determinable concentration ranges from 0.10 mg L^{-1} - 63.05 mg L^{-1} while samples 01, 15 and 25 are below the LOQ. Only sample 10 (63.05 mg L^{-1}) is above the maximum specified by Brazilian legislation, i.e., 50 mg/L (RDC N° 274, 2005), **but the label states a value of 3.47 mg L^{-1} (Table 3)**. The elevated concentration may be indicative of microbiological contamination which may be harmful to human health (Astel et al., 2014). Samples 01, 10 and 21 are classified as “fluoridated mineral water”, according to their labels; however, in this study, F^- was not detected above 0.02 mg L^{-1} , the minimum, according to Brazilian legislation

(Portaria DNPM 540, 2014), needed for water to be classified as such. Since the declared values are close to the minimum, analyte sorption by the packaging materials may have occurred. It is evident that samples 3 and 4 have the same mineral composition. In reality, these samples are from the same region (Apucarana city, State of Paraná), but on the market they have a different identification and no indication that they are from the same producer. In general, it is clear that information declared on the label is different from that arising from analysis of the samples in this work, but it must also be recognized that as the samples are rich in salts, several factors may lead to changes in the composition, however small, including decomposition of HCO_3^- , sorption of analytes onto the walls of the container material, the time on the market shelf, and proper care during transport and the ambient storage temperature. To make a more qualified analysis of the national samples, a scatter plot based on only national Brazilian samples is presented in Figure 3. Here the PCs account for 73% of the variability of the original data. As in Figure 2, variability in the compositions of samples are evident wherein the difference of mineral content of sample 22 in relation to others is evident. The sample 10 possibly is contaminated and the samples 15 and 17 show F^- content and Na^+ higher concentrations than others. Clearly, the PCA statistical tool can be very useful for identification

and comparison of compositions of bottled mineral waters on the market.”

Read:

“Likewise, the hardness present in the sample can be correlated mainly to the presence of Ca and Mg. Samples 24-26 are again highlighted for their significant values present. The main constituent elements reported on the sample labels include: HCO_3^- , F^- , Cl^- , NO_3^- , SO_4^{2-} , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba, Li and Sr. Principal component analysis (PCA) for the concentrations of these analytes is presented in Figure 2, where PC1 is the first principal component, PC2 is the second and PC3 is the third (Dos Santos et al., 2008, Dos Santos et. al., 2012 and Miller, J. N. and Miller, J. C, 2000). PC1 accounts for 47% of the variance of the data and discriminates samples through the influence of parameters related to HCO_3^- , F^- , Cl^- , Ca^{2+} , and Li. PC2 accounts for 17% of the variance of the data and discriminates samples on the basis of SO_4^{2-} , while PC3 accounts for 12% of the variance of the data and is mainly correlated with the presence of Ba and Sr. Together, 76% of the variability of the original data is thus accounted for. As evident from Figure 2, the samples are clustered in a main group but five are located in different regions of the graph. Samples 23 to 26 are imported: 23 and 24 from France, 25 from Portugal and 26 from Italy. Only sample 22 is from Minas Gerais State, Brazil. It is evident that these samples have different physicochemical compositions, being characterized by relatively high concentrations of salts, mainly HCO_3^- and Sr. Legislation does not specify a value for Sr, and the HCO_3^- ion is an essential component of mineral waters (Decreto-Lei 7841, 1945). These five samples are also rich in F^- , providing a classification as “fluoridated mineral water”, as defined by Brazilian legislation (Portaria DNPM 540, 2014). The concentration of Li is high in samples 22, 24, 25 and 26, also a characteristic of mineral water in accordance with Brazilian legislation (Portaria DNPM 540, 2014). The concentration of Ba in sample 22 is the highest: $386 \pm 5 \mu\text{g L}^{-1}$, but below the maximum specified by Brazilian legislation, i.e., $700 \mu\text{g L}^{-1}$ (RDC N° 274, 2005). The main cluster comprises the majority of the samples that are bottled in the State of Paraná, with the exception of sample 11 from São Paulo State and sample 27 from Italy. This cluster is characteristic of the presence of NO_3^- . Nitrate may have either a mineral or microbiological origin. Its determinable concentration ranges from 0.10 mg L^{-1} - 63.05 mg L^{-1} while samples 01, 15 and 25 are below the LOQ. Only sample 10 (63.05 mg L^{-1}) is above the maximum specified by Brazilian legislation, i.e., 50 mg/L (RDC N° 274, 2005), but the label states a value of 3.47 mg L^{-1} (Table 3). The elevated concentration may be indicative of microbiological contamination which may be harmful to human health (Astel et al., 2014). Samples 01, 10 and 21 are classified as “fluoridated mineral water”, according to their labels; however, in this study, F^- was not detected above 0.02 mg L^{-1} , the minimum, according to Brazilian legislation (Portaria DNPM 540, 2014), needed for water to be classified as such. Since the declared values are close to the

minimum, analyte sorption by the packaging materials may have occurred. It is evident that samples 3 and 4 have the same mineral composition. In reality, these samples are from the same region (Apucarana city, State of Paraná), but on the market they have a different identification and no indication that they are from the same producer. In general, it is clear that information declared on the label is different from that arising from analysis of the samples in this work, but it must also be recognized that as the samples are rich in salts, several factors may lead to changes in the composition, however small, including decomposition of HCO_3^- , sorption of analytes onto the walls of the container material, the time on the market shelf, and proper care during transport and the ambient storage temperature. To make a more qualified analysis of the national samples, a scatter plot based on only national Brazilian samples is presented in Figure 3. Here the PCs account for 73% of the variability of the original data. As in Figure 2, variability in the compositions of samples are evident wherein the difference of mineral content of sample 22 in relation to others is evident. The sample 10 possibly is contaminated and the samples 15 and 17 show F^- content and Na^+ higher concentrations than others. Clearly, the PCA statistical tool can be very useful for identification and comparison of compositions of bottled mineral waters on the market.”

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The present study reveals that, in general, the majority of parameters determined in commercial bottled mineral waters from markets in Curitiba-PR-Brazil are below limits specified by Brazilian legislation. Only one sample was detected as having a high concentration of NO_3^- , indicating microbiological contamination; some results for NO_2^- may also reflect the same contamination. Improvements in monitoring throughout the process of filling and points of sale of the samples, with the aim of securing the microbiological quality of bottled mineral waters sold in the region under study may be needed. The comparison of labelled composition to analytical results highlights a difference for most elements, but it should be noted that intrinsic instability as well as other factors such as sorption of components onto container surfaces as well as the length of time spent on the shelf, care during transport, and the ambient storage temperature may alter the composition; perhaps a “best before date” could eliminate such discrepancies. In such cases, a further study of the stability and interaction with the packaging should be performed. Although a perfect division of samples from

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