

Multielement Analysis of Soft Drinks by X-ray Fluorescence Spectrometry

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Several commercial soft drinks and respective plastic bottles were analyzed for their multielement contents employing the synchrotron radiation total reflection X-ray fluorescence spectrometry technique (SRTXRF). The SRTXRF method has been developed and validated, and about 20 elements were detected in the investigated samples, including some trace elements, which can be toxic for human beings, such as Ti, Cr, Sb, As, and Pb in soft drinks and Al, Sb, As, and Pb in poly(ethylene terephthalate) (PET) containers. Statistical analysis was performed using chemometric techniques (principal component analysis and cluster analysis), and similarities were verified in the multielement contents of the samples. The results demonstrated that the SRTXRF offers a good multielemental approach for the quality control of food products. Moreover, on the basis of enrichment factors, the possibility of the trace elements in the PET container may be leached to the beverages under normal commercial situations and other results were discussed.

KEYWORDS: Synchrotron radiation total reflection X-ray fluorescence spectrometry; trace elements; heavy metals; soft drinks; PET bottles; quality control

INTRODUCTION

Soft drinks are constituted mainly of water, carbon dioxide, and a syrup, whose composition characterizes the beverage flavor. In the mid-1800s, the soft drink forerunner was useful for other purposes: The beverage, made from sparkling water and ginger ale, lemon, or strawberry extracts, was sold in pharmacies to treat several diseases, from arthritis to indigestion. After 1830, soft drinks had their industrial production initiated (1).

In recent years, there has been an increase in consumption, which could be related with the use of poly(ethylene terephthalate) (PET) bottles as soft drink containers (2). Thus, because of the high consumption of soft drinks, quality control is particularly important in this case, inasmuch as this kind of food makes up a significant proportion of trace element daily intake (3); furthermore, trace element concentrations are subject to legislation (4).

Trace elements in beverages may originate from natural sources, such as soil and water; environmental contamination,

including fertilizers and pesticides; industrial processing and containers, such as aluminum cans and, maybe, PET bottles (5, 6). Hence, multielement analysis can be a very valuable tool in the authentication and characterization of beverages as fruit juices (7), teas (8), and alcoholic distillates (9). Moreover, soft drink bottle analyses give information about the polymer additives (allowing to the characterization, constitution, and quality of polymer matrix, indirectly) (10) and trace elements that can be toxic to the human beings (11).

Total-reflection X-ray fluorescence (TXRF) is suitable for this kind of work, because of its advantageous features, namely, multielemental capability, high sensitivity and precision, and short time of analysis (12). Other analytical techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma (ICP) atomic emission spectrometry, and neutron activation analysis also can be used for heavy metal determination; however, all need extensive sample preparation, which is usually troublesome and time consuming and prevents in situ analysis (13, 14).

In the present paper, the analysis of 17 soft drink samples and the respective PET bottles was carried out by synchrotron radiation TXRF (SRTXRF). The obtained data and its interpretation through the statistical tools were used to establish the differences among samples and allowed us to conclude that the technique is feasible for trace element analysis.

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Table 1. ANOVA for Calibration Curve for the Elements $13 \leq Z \leq 42$

source	d.f.	sum of squares	mean square	F	variable	parameter	t	prob. > t
regression	2	60.4664	30.2332	465.277*		$b_0 = -21.168399$	31.5495	0.00001
residual	9	0.58482	0.06498		Z	$b_1 = 1.372323$	26.2378	0.00001
total	11	61.0512			Z ²	$b_2 = -0.022241$	23.3657	0.00001
						$R^2 = 0.9904$		

MATERIALS AND METHODS

Reagents and Equipment. Measurements were performed in an X-ray fluorescence beamline at the National Synchrotron Light Laboratory (Campinas City, Brazil). For the X-ray detection, a Si(Li) detector was employed, with 165 eV resolution at 5.9 keV (Mn K α line). For the excitation, a polychromatic ($E_{\max} = 22$ keV) beam from a storage ring (1.37 GeV and 100 mA) with 2.0 mm width and 1.0 mm height under total reflection conditions was used (15). The spectra were analyzed, and quantitative calculations were performed with the AXIL 3.5 software, analysis of X-rays spectra by iterative least squares fitting (16). The samples and the standards were excited for 100 s. Multielemental standard solutions for calibration by TXRF were prepared by appropriate dilution, with purified water in a Milli-Q system, of Al, Si, K, Ca, Ti, Cr, Fe, Ni, Zn, Ga, Se, Sr, Mo, Cd, Sb, Ba, Pt, Tl, and Pb, covering the range of atomic numbers from 13 (Al) to 82 (Pb). To digest the samples, HNO₃ (65%) and H₂O₂ (30%), both in analytical grade, were used.

Samples. Seventeen commercial soft drink samples and respective PET bottles, from six distinct manufacturers, were analyzed (Tables 4 and 5). Samples were sorted in six groups of soft drinks: orange (O), cola (C), strawberry (S), grape (Gr), guarana (G), and diet guarana (D) soft drinks. Distinct brands were represented by the numbers 1, 2, 3, 4, 5, and 6. All soft drinks were produced in Brazil and analyzed in the commercial period of validity (3 months).

Preparation of Samples for TRXF Analysis. For each soft drink sample, 5 mL of beverage was used, and for plastic samples, approximately 250 mg was cut in small pieces. The digestion procedure was performed in an open system, heated at a temperature of 120–130 °C, with HNO₃ and H₂O₂ (17, 18), until the solution became clear, and the volume was brought to 10 mL with deionized water. The mixture from the acid digestion deionized water was used as a negative experimental control.

For 1 mL of each digested sample solution, 10 μ L of internal standard (1025 μ g Ga mL⁻¹) was added and an aliquot of 5 μ L was pipetted onto a Perspex disk (polished quartz is used as sample carrier, 3 cm diameter), dried under an infrared lamp (obtaining thus the sample in a shaping thin layer, 5 mm diameter), and irradiated in a spectrometer (SRTXRF system). All of the samples were analyzed in triplicate.

The same procedure was employed to prepare the multielemental standard samples, in five different and well-known concentrations, containing the elements Al, Si, K, Ca, Ti, Cr, Fe, Ni, Zn, Se, Sr, and Mo (K-shell lines) and Mo, Cd, Sb, Ba, Pt, Tl, and Pb (L-shell lines) in which the internal standard (element Ga) was also added. The irradiation time was 100 s for each sample and standards.

Quantitative TXRF Analysis. The samples and standards analyzed, deposited in the Perspex disk, were taken to the spectrometer in order to measure the characteristic X-ray of all elements present in the samples. TXRF calibration was performed using a fitted nondimensional sensitivity curve, with Ga addition as the internal standard to eliminate errors caused by excitation/detection geometry. Using multielemental standards, all sensitivity values in the atomic number range from 13 (Al) to 82 (Pb) were then obtained after fitting.

The quantitative analysis can be made by eq 1, since the sample can be considered as a thin film, whose absorption and enhancement effects are negligible (19).

$$I_i = s_i \cdot C_i \quad (1)$$

where I_i is the fluorescent intensity of element i (cps), s_i (cps μ g⁻¹ mL) is the sensitivity for this element, and C_i is the concentration (in ppm or μ g mL⁻¹).

To correct the geometric effect, gallium was added as an internal standard in each sample and standard. In other words, eq 1 can be rewritten as eq 2:

$$\frac{I_i}{I_{\text{Ga}}} = \frac{s_i}{s_{\text{Ga}}} \cdot \frac{C_i}{C_{\text{Ga}}} \quad (2)$$

Thus, the relative intensity (R_i , in μ g mL⁻¹) can be calculated by eq 3:

$$R_i = \frac{I_i}{I_{\text{Ga}}} \cdot C_{\text{Ga}} \quad (3)$$

then, the relative sensitivity, by eq 4:

$$S_i = \frac{s_i}{s_{\text{Ga}}} \quad (4)$$

and the result is, by eq 5:

$$R_i = S_i \cdot C_i \quad (5)$$

where I_{Ga} (cps) and C_{Ga} (μ g mL⁻¹) are the intensity and concentration of the internal standard Ga in the sample and s_{Ga} (cps μ g⁻¹ mL) is the sensitivity for this element; S_i is the relative sensitivity for element i (nondimensional). Element concentrations can be obtained by eq 5.

Detection Limits. The detection limits (20) were calculated for soft drink and bottle samples, according to the eq 6.

$$\text{DL} = 3 \cdot \sqrt{\frac{BG_i}{t}} \cdot \frac{C_{\text{Ga}}}{I_{\text{Ga}} \cdot S_i} \quad (6)$$

where BG_i is the background area under the element i peak (cps), t is the integration time (100 s), C_{Ga} is the internal standard concentration (10.25 μ g mL⁻¹), I_{Ga} is the internal standard intensity (cps), and S_i is the nondimensional sensitivity for the element i .

RESULTS AND DISCUSSION

Calibrations. The calibration curve for SRTXRF was obtained by X-ray intensities from standard samples [analysis of variance (ANOVA)—Table 1]. Figure 1A,B shows the sensitivity curve for K and L lines, respectively. The curves are described by eqs 7 and 8 for elements whose atomic number ranges are $13 \leq Z \leq 42$ and $42 \leq Z \leq 82$, respectively.

$$\ln S_i = -21.168399 + 1.372323 Z_i - 0.022241 Z_i^2 \quad (7)$$

$$\ln(S_i + 0.5) = 1.24314 \cdot 10^1 - 7.14212 \cdot 10^{-1} Z_i + 1.24994 \cdot 10^{-2} Z_i^2 - 6.88400 \cdot 10^{-5} Z_i^3 \quad (8)$$

In eq 7 (Figure 1A), an absolute maximum can be observed for $Z = 31$, namely, the function is increasing for $Z < 31$ and is decreasing for $Z > 31$. This fact is explained because Ga ($Z = 31$) was used as an internal standard ($S_{\text{Ga}} = 1.0$, theoretical). When $Z = 31$ is substituted in eq 7, a relative sensitivity of 1.000013 was obtained, showing an error of 0.0013%.

In analyses of samples by AXIL software, we employed a criterion described by this way: The count rate for an element i must be, at least, 3-fold the count rate obtained in standard

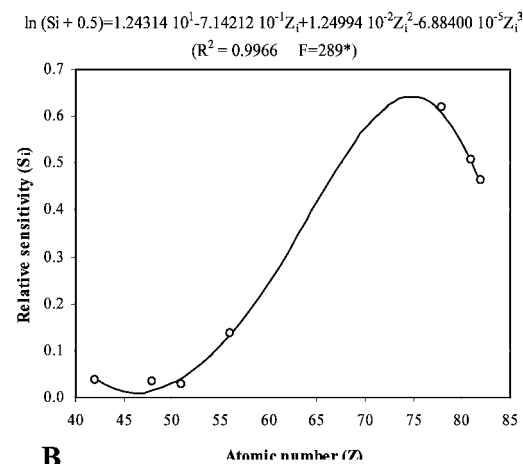
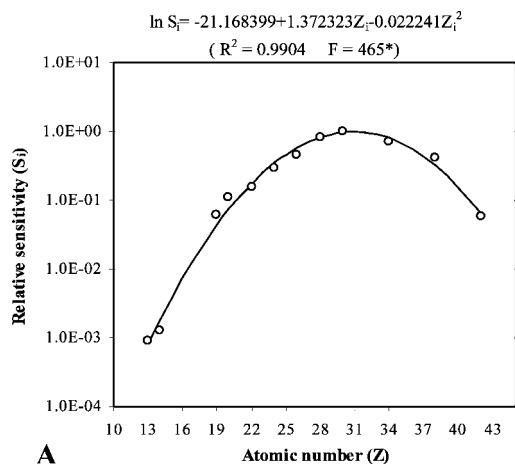


Figure 1. Relative sensitivity (experimental and calculated) for the elements with atomic numbers $13 \leq Z_i \leq 42$ (A) and $42 \leq Z_i \leq 82$ (B).

deviation (SD) for the same element. Furthermore, we also used the χ^2 value, which is decreased when it detects element i and residual value that shows the dispersal of values. These procedures were used to say if there was an element or not.

By eq 4, the experimental detection limits were obtained for each kind of sample and the experimental and calculated detection limit curves (**Figure 2A,B**) were fitted by ANOVA. Comparing detection limits of soft drink samples with bottle ones, a significant difference between elements can be observed. These differences are due to the dilution factors used in order to convert the unit $\mu\text{g mL}^{-1}$ in $\mu\text{g g}^{-1}$ (for polymer samples, dilution factors = 20.0) and also because both samples were diluted (in soft drink samples, dilution factors = 2.0).

TXRF Validation Procedure. The multielement standards Sigma 41,101-8 (for ICP-AAS) and Drinking Water Pollutants (Aldrich) were employed in order to check the accuracy of the procedure developed for element analyses. **Tables 2** and **3** show obtained and standard values for the elements Cr, Mn, Co, Ni, Cu, Zn, As, Se, Ba, and Pb. Measured values showed relative SDs (RSDs) lower than 10% for all of the elements in the analyzed standards.

Element Levels. PET Bottle Samples. A representative spectrum of PET bottle samples is shown in **Figure 3** (G2 sample). The results were obtained from triplicate measurements, and the mean RSD for these samples is 23.56%. P and Si were the elements with the highest average concentrations (521.28 and 352.90 $\mu\text{g g}^{-1}$, respectively). Ni and Cu present lower contents; their average values are 1.21 and 2.17 $\mu\text{g g}^{-1}$, respectively. The elements (**Table 4**) used as catalysts in poly-

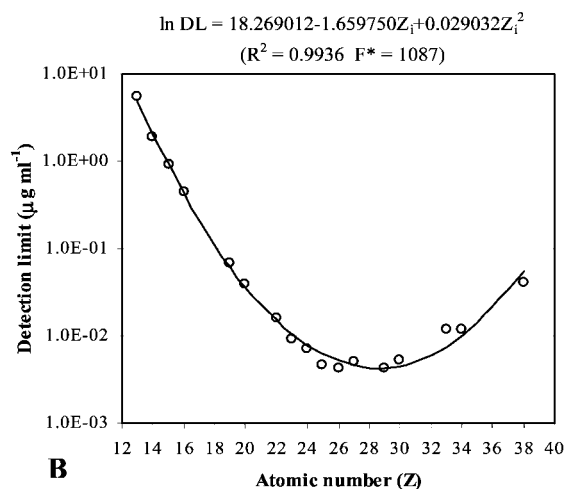
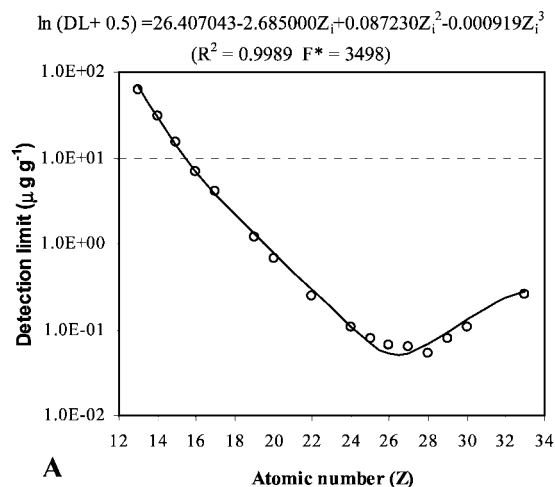


Figure 2. Detection limit curve (experimental and calculated) for the SRTXRF system employed ($13 \leq Z_i \leq 38$)—PET bottles samples (A) and soft drinks samples (B).

Table 2. Comparison of Obtained and Certified Values of Multielemental Standard Sigma 41,101-8 for ICP-AAS

element	measured value ($\mu\text{g mL}^{-1}$)	certified value ($\mu\text{g mL}^{-1}$)	RSD (%)
Cr	6.62 ± 0.84	6.25	6
Mn	9.59 ± 0.71	9.37	2
Co	32.15 ± 1.93	31.25	3
Ni	27.06 ± 1.06	25.00	8
Cu	16.46 ± 0.45	15.63	5
Zn	16.59 ± 0.38	12.50	9

Table 3. Comparison of Obtained and Certified Values of Multielemental Standard "Drinking Water Pollutants" (Aldrich)

element	measured value ($\mu\text{g mL}^{-1}$)	certified value ($\mu\text{g mL}^{-1}$)	RSD (%)
Cr	8.87 ± 0.17	9.09 ± 0.45	2
As	8.81 ± 0.88	9.09 ± 0.45	3
Se	4.14 ± 0.37	4.54 ± 0.23	9
Ba	90.72 ± 5.72	90.91 ± 4.55	0
Pb	9.98 ± 0.75	9.09 ± 0.45	10

(ethylene terephthalate) polymerization (21), namely, Mn, Co, and Sb, were detected in almost all samples (Co was not detected in the C1 sample). Also, Pb and As were detected; these elements may present a toxic effect, depending on their concentration and bioavailability, and these potentially toxic

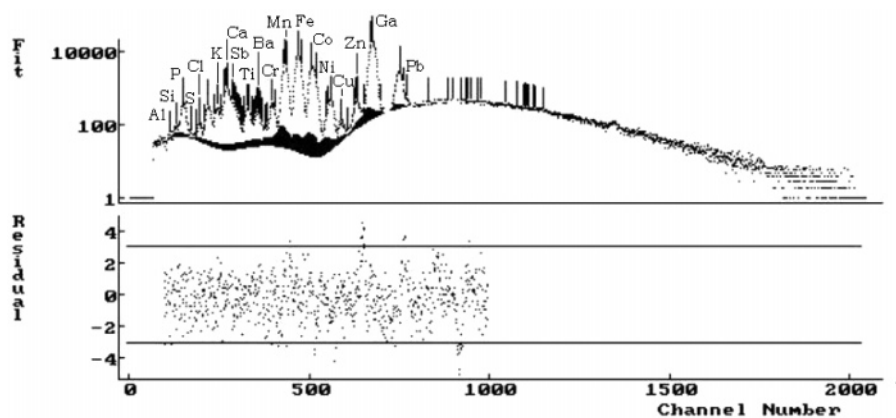


Figure 3. X-ray fluorescence spectrum of PET bottle (sample G2).

Table 4. Elemental Concentrations ($\mu\text{g g}^{-1}$) Obtained for PET Bottles Analyzed by X-ray Fluorescence

sample ^a	Al	Si	P	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Sb	Ba	Pb
G1	138.8	130.9	685.6	14.01	23.43	34.80	75.29	1.346	3.279	0.416	13.89	29.71	0.246	4.853	3.012	ND	65.39	10.64	2.75
G2	165.8	249.3	790.0	15.49	36.13	49.52	107.4	2.030	9.162	98.91	140.8	48.16	0.341	1.385	3.916	ND	80.30	14.11	4.75
G3	242.8	306.3	450.0	19.83	21.73	36.02	72.87	2.213	3.063	6.361	18.99	27.24	1.396	4.351	4.725	1.817	84.28	11.65	ND
G4	181.2	79.54	357.8	16.00	14.54	34.55	82.68	1.774	2.615	0.334	19.32	0.518	0.853	8.464	5.182	1.344	55.38	11.17	ND
G5	113.1	84.50	479.3	37.46	24.06	53.29	130.9	2.475	3.470	1.988	42.64	13.73	2.926	5.720	4.397	ND	58.96	10.87	5.558
Gr1	296.3	227.1	816.4	22.95	22.47	30.63	141.4	4.451	5.361	65.24	49.02	26.35	ND	0.569	3.889	ND	97.12	12.41	3.745
D2	157.6	104.1	423.2	ND	14.88	25.76	74.80	4.881	4.060	19.28	164.4	41.18	ND	0.236	5.516	1.837	32.76	10.79	ND
D6	ND	ND	395.9	18.11	17.88	54.23	74.98	1.423	2.979	1.349	21.19	12.20	2.646	5.126	4.581	1.413	52.29	8.11	ND
C1	86.34	76.56	498.2	12.34	8.888	41.99	69.90	ND	3.583	0.458	16.33	ND	0.141	0.702	6.033	1.420	85.16	11.68	ND
C2	<133.3 ^b	538.1	345.4	ND	<9.599	60.94	87.77	3.517	2.965	36.18	35.16	58.77	ND	0.589	5.777	3.199	138.3	14.53	ND
C3	136.1	598.5	249.3	ND	ND	40.58	80.52	2.482	1.379	0.448	18.84	9.042	ND	0.232	1.183	4.463	26.52	14.37	ND
C5	300.9	1050	1365	125.4	121.5	127.8	329.5	ND	5.390	115.9	52.96	59.85	ND	2.175	9.250	ND	115.0	31.31	9.169
O1	149.9	651.5	428.8	14.76	24.12	43.01	77.79	1.817	2.389	0.688	13.21	20.04	1.161	0.424	3.722	ND	24.71	11.07	3.941
O2	158.2	130.7	570.3	16.61	14.04	44.93	109.69	1.644	3.611	23.62	18.55	42.33	1.452	0.457	4.166	ND	50.99	16.71	4.220
O3	ND	288.3	140.7	ND	<4.839	49.69	75.98	2.819	1.910	0.667	18.91	15.37	ND	0.377	2.398	2.113	62.51	12.25	ND
O5	151.8	778.1	441.7	16.68	23.11	58.02	97.98	2.174	3.259	1.009	26.67	11.16	1.280	0.556	7.186	ND	74.60	11.56	2.410
S2	91.65	352.7	424.1	6.485	21.80	24.65	57.29	1.488	2.679	41.00	20.51	22.35	0.863	0.675	3.851	1.691	40.51	8.466	<0.303
mean	169.3	352.9	521.3	25.90	27.80	47.70	102.7	2.400	3.600	24.30	40.70	27.40	1.200	2.200	4.600	2.100	67.30	13.00	4.600
min	86.34	76.56	140.7	6.485	8.888	24.65	57.29	1.346	1.379	0.334	13.21	0.518	0.141	0.232	1.183	1.344	24.71	8.112	2.410
max	300.9	1050	1365	125.4	121.5	127.8	329.51	4.881	9.162	115.94	164.4	59.85	2.926	8.464	9.250	4.463	138.3	31.31	9.169
SD	66.82	290.7	277.7	30.76	27.75	23.29	62.55	1.076	1.765	36.55	44.02	17.99	0.905	2.528	1.846	1.037	30.78	5.169	2.115
CV (%)	39.47	82.37	53.28	118.9	99.97	48.85	60.88	44.17	49.06	150.1	108.2	65.71	74.79	116.5	39.83	48.35	45.71	39.64	46.31

^a Samples were sorted in six groups of soft drinks: orange (O), cola (C), strawberry (S), grape (Gr), guarana (G), and diet guarana (D) soft drinks. Distinct manufacturers were represented by the numbers 1, 2, 3, 4, 5, and 6. ^b Lower than experimental detection limit for sample; ND, nondetected element.

impurities can be allowed to migrate from the polymeric packaging material into the foodstuff. On the basis of European legislation (EU directive 94/62/EC), the contents of Pb, Cd, Cr, and Hg materials must be up to $100 \mu\text{g mL}^{-1}$. So, all samples analyzed herein are in accordance with that (22).

However, reliable elemental trace analyses in polymers are difficult, and the decomposition step is usually the limitation process. In this case, the determination of volatile elements, such as Hg and As, can be affected by loss of substance during the sample treatment step and special precautions have to be taken for analysis of volatile elements (22). Hg was not detected in the sample analyzed, while As was detected in our experimental conditions using concentrated nitric acid/ H_2O_2 in an open vessel method. Feng and co-workers (17) obtained good results for total arsenic determination employing a similar digestion procedure. For measurement of the Hg concentration, special procedures are necessary, such as 3% HNO_3 acidic spike solution, stored in a Teflon-PFA bottle with controlled sample decomposition (22).

On the basis of Tukey's test to check statistically significant differences among samples (significance level $P < 0.05$) (23), we found that G5, O5, D2, and G1 samples are similar statistically: G5 and O5 associate with G3; D2 associates with

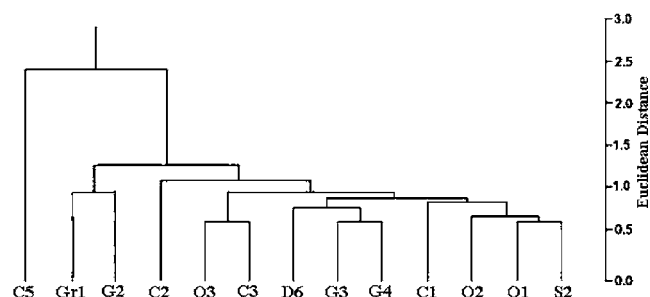


Figure 4. Cluster analysis for 13 PET bottles samples analyzed.

S2, and G1 associates with O1. As in principal component analysis (PCA) and cluster analysis (CA), we must check the similarities among different samples; those components whose behavior is similar statistically must be withdrawn from the analyses in order to obtain the best results. Then, those samples considered similar statistically (that is, G5, O5, D2, and G1) were withdrawn from other statistical analyses (principal component and cluster analysis). In the chemometric analysis, the PCA validate the CA (24, 25). The PET bottles were grouped by similarity in multielement content and in accordance with the color of the bottles (green or transparent). On the basis of

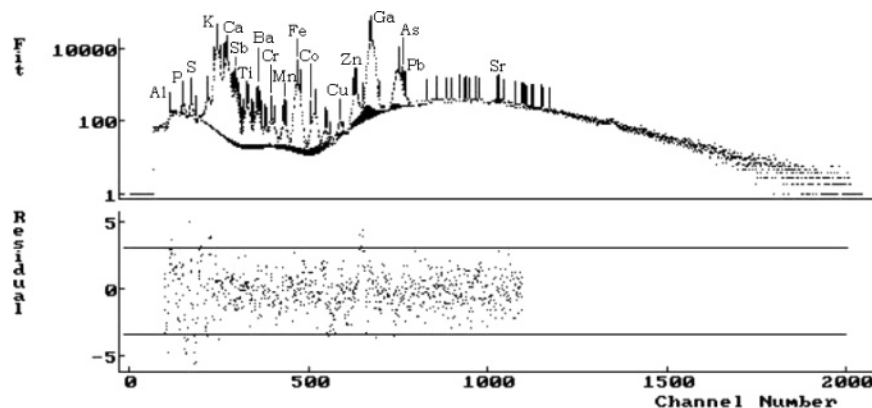


Figure 5. X-ray fluorescence spectrum of soft drink (sample O3).

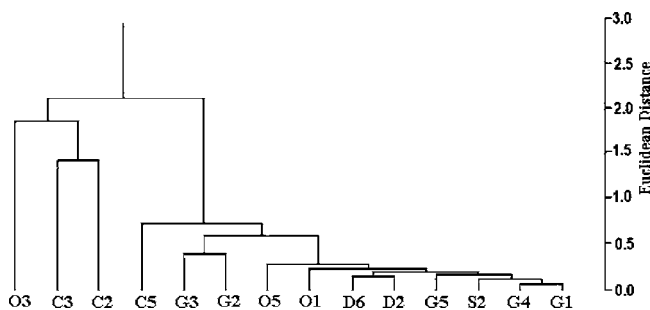


Figure 6. Cluster analysis for 14 soft drinks samples analyzed.

cluster analysis (Figure 4), there was a natural variability of grouping. In the CA, the Euclidean distance (single linkage method) was used as a similarity measurement (26, 27) in relation to element levels. As it can be seen (Figure 4), samples belonging to brands 1 and 2 grouped them in two clusters: C1, O2, O1, S2 and Gr1 with G2; it can indicate a similar production process. Another cluster, that is, D6, G3, and G4, grouped samples whose color PET bottle is green, which can be related to an unknown element that lends the characteristic color observed. The C5 sample appears isolated, probably because of the highest P concentration (Table 4). The PCA confirmed the grouping formed. In this grouping, the variables were as

follows: P concentration (axis X – first component $\lambda_1 = 52.29\%$); Ti concentration (axis Y – second component $\lambda_2 = 13.17\%$), and Pb concentration (axis Z – third component $\lambda_3 = 11.41\%$).

Soft Drink Samples. Several elements were detected in the soft drink samples, including Sb, As, Cr, Pb, and Ti that can be toxic to human beings. Data obtained are listed in Table 5, and Figure 5 shows a spectrum of the O3 sample. The mean RSD was 26.47%. Some soft drink samples had element concentrations above the maximum value allowed by Brazilian law (4). The maximum allowed for Cr is $0.10 \mu\text{g mL}^{-1}$, and samples C3, O3, C2, and C5 showed the following Cr levels: 0.167, 0.214, 0.274, and $0.396 \mu\text{g mL}^{-1}$, respectively; for As, the maximum allowed is $0.200 \mu\text{g mL}^{-1}$, and samples C2 and O3 showed concentrations of 0.246 and $0.249 \mu\text{g mL}^{-1}$; and for Sb, the maximum allowed is $0.200 \mu\text{g mL}^{-1}$, whereas O3, C3, and C2 samples had concentrations of 1.945, 3.152, and $4.106 \mu\text{g mL}^{-1}$, respectively. To assess the toxic effect of these elements, other studies may be carried out, as element speciation (28), for example. On the other hand, for Cu, Zn, Se, and Pb, the maximum value allowed is 5.00, 5.00, 0.050, and $0.200 \mu\text{g mL}^{-1}$, respectively, and the concentrations of these elements in soft drink samples analyzed are in accordance with Brazilian law.

Table 5. Elemental Concentrations ($\mu\text{g mL}^{-1}$) Obtained for Soft Drinks Analyzed by X-ray Fluorescence

sample ^a	Al	Si	P	S	K	Ca	Ti	V	Cr	Mn	Fe	Co	Cu	Zn	As	Se	Sr	Sb
G1	ND	2.685	2.023	2.236	1.701	3.105	ND	ND	0.010	ND	0.129	ND	ND	ND	ND	ND	ND	ND
G2	ND	2.858	3.528	5.171	5.173	3.415	ND	ND	0.010	ND	1.427	ND	ND	<0.003 ^b	0.024	0.030	ND	ND
G3	ND	2.970	2.994	3.356	2.546	6.188	ND	ND	<0.004 ^b	ND	0.076	ND	ND	<0.003 ^b	<0.005 ^b	0.019	ND	ND
G4	ND	3.120	0.897	1.189	1.188	2.829	<0.009 ^b	ND	<0.004 ^b	ND	0.063	ND	ND	ND	ND	ND	ND	ND
G5	ND	4.390	3.450	2.003	1.553	2.763	0.026	ND	0.016	<0.002 ^b	0.186	ND	0.008	0.018	ND	ND	ND	ND
Gr1	ND	ND	5.797	3.763	7.743	4.933	0.015	ND	0.020	0.022	0.098	ND	0.035	0.020	ND	ND	ND	ND
D2	ND	5.181	5.302	32.17	1.017	2.264	ND	ND	ND	ND	0.127	ND	ND	0.010	ND	ND	ND	ND
D6	ND	ND	ND	25.62	1.660	1.695	ND	ND	0.009	ND	0.062	ND	ND	ND	ND	ND	ND	ND
C1	ND	ND	28.13	11.03	1.247	1.215	ND	ND	ND	0.015	0.060	ND	ND	ND	ND	ND	0.034	ND
C2	13.84	59.70	299.2	146.2	27.33	30.64	0.366	0.159	0.274	0.141	2.942	0.016	0.048	0.475	0.246	ND	0.141	4.106
C3	24.65	ND	291.7	97.90	17.67	45.89	0.136	ND	0.167	0.081	1.640	0.012	0.043	0.578	0.176	ND	0.188	3.152
C5	ND	ND	33.55	9.409	0.784	1.950	ND	ND	0.396	ND	0.359	ND	ND	ND	ND	ND	ND	ND
O1	6.375	ND	5.798	2.897	28.63	4.645	ND	ND	0.025	0.013	0.099	ND	0.012	0.021	<0.003 ^b	ND	ND	ND
O2	ND	ND	3.283	4.657	11.86	3.177	0.017	0.008	0.030	0.010	0.121	ND	0.022	0.025	ND	ND	ND	ND
O3	69.81	ND	45.10	22.67	226.7	62.07	0.246	ND	0.214	0.202	2.695	0.027	0.070	0.817	0.249	ND	0.265	1.945
O5	<1.692 ^b	<0.779 ^b	3.920	2.096	21.92	4.468	ND	ND	<0.004 ^b	ND	0.139	ND	ND	0.060	ND	<0.005 ^b	ND	ND
S2	ND	ND	1.528	2.495	1.288	2.751	ND	ND	ND	ND	0.053	ND	ND	0.063	ND	ND	ND	ND
mean	28.67	11.56	46.01	22.05	21.18	10.82	0.134	0.084	0.106	0.069	0.604	0.018	0.034	0.209	0.174	0.025	0.157	3.068
min	6.375	2.685	0.897	1.189	0.784	1.215	0.015	0.008	0.009	0.010	0.053	0.012	0.008	0.010	0.024	0.019	0.034	1.945
max	69.81	59.70	299.2	146.2	226.7	62.07	0.366	0.159	0.396	0.202	2.942	0.027	0.070	0.817	0.249	0.030	0.265	4.106
SD	28.43	21.25	98.27	39.70	53.84	17.81	0.146	0.107	0.135	0.076	0.959	0.008	0.022	0.298	0.105	0.008	0.097	1.083
CV (%)	99.18	183.9	213.6	180.0	254.2	164.6	108.3	127.9	127.2	110.1	158.6	42.37	64.42	143.0	60.65	31.75	61.55	35.30

^a Samples were sorted in six groups of soft drinks: orange (O), cola (C), strawberry (S), grape (Gr), guarana (G), and diet guarana (D) soft drinks. Distinct manufacturers were represented by the numbers 1, 2, 3, 4, 5, and 6. ^b Lower than experimental detection limit for sample; ND, nondetected element.

Table 6. Enrichment Factors (E_f) Calculated for Soft Drink/PET Bottles

sample	Al	Cr	Mn	Co	As	Sb
G1	ND ^a	NS ^b	ND	ND	ND	ND
G2	ND	NS	ND	ND	ND	ND
G5	ND	NS	ND	ND	ND	ND
Gr1	ND	NS	NS	ND	ND	ND
D6	ND	NS	ND	ND	ND	ND
C1	ND	ND	8.86	ND	ND	ND
C2	ND	NS	NS	NS	NS	NS
C3	NS	NS	NS	NS	NS	NS
C5	ND	NS	ND	ND	ND	ND
O1	6.98	NS	NS	ND	ND	ND
O2	ND	NS	NS	ND	ND	ND
O3	ND	NS	2.19	NS	NS	NS

^a ND, nondetected element. ^b NS, nonsignificant statistically.

It is shown that aluminum cans are corroded over time by canned beverages, such as soft drinks and beers, due to several factors, such as temperature, pH, and the presence of acidic substances (6, 29). Thus, the same interaction could occur between a soft drink and its PET bottle, since there is a relatively high concentration of several elements in the polymer matrix. Therefore, a prior assessment may be done, through statistical analysis. Enrichment factors (E_f) were calculated for some samples, using select elements. Afterward, values were tested through a hypothesis testing ($\alpha = 0.05$), to verify if they are higher than unity (30). E_f is calculated by:

$$E_f = \frac{(C_d/C_b)_s}{(C_d/C_b)_p} \quad (9)$$

where $(C_d/C_b)_s$ and $(C_d/C_b)_p$ are ratios of the mean concentration of elements in the soft drink and in PET bottle, respectively.

If E_f values are significantly higher than unity, there is a possibility of the element a (in this case, a can be Al, Cr, Mn, Co, As, or Sb) is leached out from the inner wall of the PET bottle (31, 32). Al, Cr, Mn, Co, As, and Sb were chosen due to the possibility of toxic effects and because these elements were detected in both soft drink and polymer samples. The element b is Fe, because this metal was detected in all samples. After the hypothesis testing was carried out, only Mn and Al, in samples O3, O1, and C1 (Table 6), showed that these elements could be leached out from a polymer matrix. The amount of heavy elements found in the PET bottles is high in some cases; yet, the amount carried over into the soft drinks, according to the enrichment factor, is not significant except for Al and Mn in several instances. That is, soft drinks do not appear to be contaminated by the PET bottles elements under normal commercial situations. Other studies in order to assess if elements migrate to the drink components may be carried out, such as the work done by Vela and co-workers (6) and Fordham and co-workers (1995) (33).

As in the PET bottle samples, Tukey's test was done for soft drink samples, and C1, Gr1, and O2 samples were similar statistically; samples were associated with G2 and as it was done for bottle analysis, C1, Gr1, and O2 samples were withdrawn from PCA and CA. The soft drink samples were grouped by similarity in multielement content according to kind of soft drink and no agreement of the brands. On the basis of CA (Figure 6), there was a natural variability of grouping. Two mainly clusters were formed as follows: O3, C3, and C2; another cluster comprises the remaining samples. Ba is an element with high discriminating power in this analysis, because it explains 69.78% of variability in this case. Hence, samples with a high

concentration of Ba, namely, O3, C2, and C3, formed a cluster. Furthermore, in these samples were detected almost all 20 elements seen in soft drinks (see Table 5), what distinguishes those samples. In another cluster, there are samples with a lower number of detected elements and lower variation in their concentration. The PCA is in agreement with CA, and the variables used for this grouping were as follows: Ba concentration (axis X – first component $\lambda_1 = 69.78\%$); Si concentration (axis Y – second component $\lambda_2 = 17.48\%$), and Se concentration (axis Z – third component $\lambda_3 = 5.38\%$). Therefore, in general, it can be observed that grouping soft drink samples according to kind of soft drink and not in agreement of the brands: G5, G4, G3, G2, and G1 (guarana soft drinks); D6 and D2 (diet guarana soft drinks); and O5 and O1 (orange soft drinks). It can be related with common substances added to each kind of soft drink. For example, D6 and D2 samples showed a relatively high concentration of sulfur, an atom that constitutes the saccharin molecule ($C_7H_5NO_3S$), a sweetener added in diet soft drinks. Thus, despite soft drinks being mainly composed of water, sweeteners, acids, flavor, color, and/or fruits juices, the multielement composition of the soft drink and grouping formed in statistical analysis differ, mainly, in agreement with kind of soft drink and ingredients used (for example, guarana is a group, diet guarana another group, and orange soft drinks other), and no relationship was seen among brands.

A brief comparison among obtained results by other authors was done. López and co-workers (28) detected Al in soft drinks, with concentrations ranging 44.6 to 1053.3 $\mu\text{g L}^{-1}$, and in this work, we obtained a range of 6.375–69.806 $\mu\text{g mL}^{-1}$. On the other hand, Abercrombie and Fowler (34) pointed out Al levels ranging from 0.1 to 74.0 $\mu\text{g mL}^{-1}$. Onianwa and co-workers (3) detected heavy metals: Co (0.20–0.27 $\mu\text{g mL}^{-1}$), Cr (0.001–0.09 $\mu\text{g mL}^{-1}$), Cu (0.20–0.40 $\mu\text{g mL}^{-1}$), Fe (0.16–0.67 $\mu\text{g mL}^{-1}$), Zn (0.05–0.18 $\mu\text{g mL}^{-1}$), and Pb (0.02–0.05 $\mu\text{g mL}^{-1}$); results obtained herein are in agreement only for Pb, Cr, and Zn, that is: Pb (0.026–0.062 $\mu\text{g mL}^{-1}$), Cr (0.009–0.396 $\mu\text{g mL}^{-1}$), and Zn (0.010–0.817 $\mu\text{g mL}^{-1}$). Chromium was analyzed in soft drinks, with concentrations ranging from 3.60 to 60.50 $\mu\text{g L}^{-1}$ (35). In these papers, the analyses were carried out by graphite furnace AAS and flame AAS.

Thus, TXRF has advantages as a simultaneous multielemental determination and good analytical features for soft drink and polymer analyses. TXRF is shown to be a useful technique for trace element determination in soft drinks and PET bottles. Because some heavy metals were detected in PET container and there is a possibility that some elements could be leached to the beverages, other studies about this subject are necessary. The quality control of soft drinks is important, because of the high consumption and exposure to toxicant trace elements; sometimes, these elements are above the value allowed by legislation. So, TXRF is a suitable analytical tool for this kind of analysis.

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