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Inorganic Chemical Composition by X-Ray Fluorescence Spectrometry of the Mineral Waters from the Minas Gerais Water Circuit, Brazil

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ABSTRACT

The water parks located in the cities of Cambuquira, Caxambu, Conceição do Rio Verde, Lambari and Marimbeiro are part of the Water Circuit of Minas Gerais and have their mineral waters regularly consumed by the local population and tourists motivated by the medicinal use of these waters, characterized as mineral waters. Therefore, the objective of this work was to determine the inorganic chemical composition of the mineral water from these parks, analysing the elements Ag, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K. Mn, Ni, Pb, Se, Ti, V and Zn using the energy dispersive X-ray fluorescence – EDXRF. Despite the proximity to one another, each park has different chemical elements and concentrations. The elements presenting the highest concentrations were the major elements Ca, Fe, K and Mn. However, among the five water parks studied, the Water Park of Caxambu presented the highest concentrations for all the determined elements.

Keywords: **mineral water, inorganic chemical elements, EDXRF.**

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1. INTRODUCTION

The advent of the term hydrotherapy came with the Greek civilization, which introduced water intake as part of medicinal practice. The balneology, the study of the therapeutic use of thermal baths, was established in the 16th century and it was used to treat skin problems through mineral water baths [1].

Presently, the natural radioactive elements and chemical characteristics of mineral waters have determined its use in spas due to the presence of essential minerals for life maintenance, such as K, Ca, Na, Mg and P. Hence, there has been an increase in popularity and demand for spas, bathhouses, geysers and mineral water parks [2-4].

By definition, mineral waters are different from ordinary waters because they come from natural springs with chemical composition properties, which provide them with a medicinal action. According to the Brazilian Mineral Summary of National Department of Mineral Production – DNPM, it is important to characterize and regulate mineral waters, due to the increase of global consumption of these waters by 7 % per year [5].

In order to protect the population from pollution by toxic or poisonous substances and from contamination by pathogenic microorganisms, each country establishes their own maximum permitted values for the chemical elements present in drinking water [5-7].

In Brazil, water potability parameters are regulated by the Ministry of Health and divide the chemical elements into three groups: the major elements that are those present in concentrations higher than 5 mg L^{-1}; the minor elements that are those present in concentration range from 0.01 mg L^{-1} to 5 mg L^{-1} and the trace elements that are those present in concentrations below 0.01 mg L^{-1} [6-8].

The origin of the chemical elements present in mineral waters is associated with the: endogenous factors that consist of the lithological type, rock structure and alteration mantle, which will determine the intensity in which the chemical decomposition will occur in minerals; and the exogenous factors that are related to aquifer characteristics, such as relief, hydrography and climate, which determine the relationship of rainfall and evapotranspiration rates [6, 9].

The water hydro-geochemistry is linked to the interaction between climatic and geological factors. Therefore, when water from precipitation reaches the soil, it is enriched by suspended materials and dissolved substances from both the soil and rocks. Due to the action of gravity, this water initiates the infiltration process on the soil surface until it reaches a less permeable substrate on which it will accumulate and it promotes the denominated recharge process [6, 9, 10-13].

Balneology emerged in Brazil with Portuguese colonization and one of the most famous sites, due to crenotherapy practice and mineral water consumption, is the denominated “Water Circuit of Minas Gerais” which has mineral water parks located in the cities of Cambuquira, Caxambu, Conceição do Rio Verde, Lambari and São Lourenço [14]. Previous work has quantified the concentrations of natural radionuclides ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{210}Po and evaluated the committed effective dose due to mineral water intake from these parks, except for the São Lourenço Water Park [15-17].

Due to the existence of few scientific studies proving the effective use of these mineral waters in health treatments conducted in spas, and the benefit of its use in medical crenology, specified mostly by empirical evidence, a research project was established to study the inorganic chemical composition of the mineral water from the Water Parks of Caxambu, Cambuquira, Marimbeiro, Lambari, and Águas de Contendas, located in the “Water Circuit of Minas Gerais”. For the inorganic chemical composition of these waters, the elements Ag, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, Ti, V and Zn were determined by energy dispersive X-ray fluorescence – EDXR and for the Águas de Contendas and Caxambu Water Parks were analyzed in first-time way the elements Ag, Cd, Co, Cu, Ti and V and for the Lambari, Cambuquira and Marimbeiro Water Parks the elements Ag, Cd, Co, Cu, Se, Ti and V.

2. MATERIALS AND METHODS

2.1. Study areas

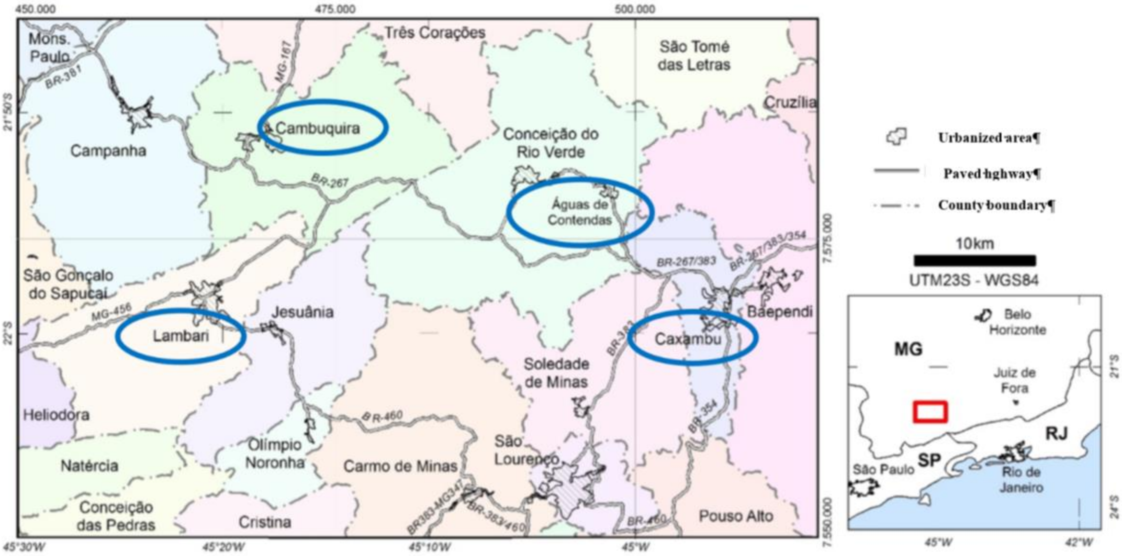
The present work studied the mineral waters of Cambuquira, Caxambu, Conceição do Rio Verde, Lambari and Marimbeiro Water Parks, which together with the cities of Baependi, Cambuquira, Campanha, Carmo de Minas, Caxambu, Cruzilia, Dom Viçoso, Liberdade, Passa

Quatro, São Lourenço, Soledade de Minas and Três Corações are part of the "Water Circuit of Minas Gerais", Figure 1 [18].

2.2. Cambuquira and Marimbeiro

The city of Cambuquira is situated at the coordinates 21° 51' 0.00" S 45° 18' 0.00" W, with elevation of 950.1 m and average annual rainfall of 1338.3 mm. The Cambuquira Water Park, located in the center of the city, has five mineral water springs denominated as: Regina Werneck or Gasosa, Souza Lima or Sulforosa, Fernandes Pinheiro or Férrea, Augusto Ferreira or Magnesiana and Roxo Rodrigues or Litinada [19-20]. There is also another mineral water spring, Laranjal or Dico, located on a private property near Cambuquira Water Park and open to the public [17].

Figure 1: *Map of the Water Circuit of Minas Gerais and the studied areas of Cambuquira, Conceição do Rio Verde, Caxambu and Lambari*.



Source: SIGA, 2018

The Marimbeiro Water Park is located 3 km far from Cambuquira city center and has three mineral water springs: Marimbeiro I, Marimbeiro II and Marimbeiro III [17, 20].

The region is classified as belonging to the geological group Andrelândia – Lambari Complex (also called São João del Rei Complex); both Water Parks are situated on a lithology composed of granatiferous schists with gneiss intercalations, both saprolitized with little associated quartzite; the soil that covers this region is approximately 10 m thick in Cambuquira and approximately 5 m thick, in Marimbeiro. The subterranean hydrological system of the Cambuquira and Marimbeiro Water Parks is part of the Marimbeiro Stream sub-basin, contiguous to the Cambuquira Stream sub-basin and is characterized by the occurrence of fractured hydrogeological domains, which give rise to the mineral springs under study [19-20].

2.3. Caxambu

The city of Caxambu is situated at the coordinates 21° 59' 22.92" S 44° 56' 18.96" W, with elevation of 958.5 m and average annual rainfall of 1725.0 mm. The Caxambu Water Park, located in the center of the city, has eleven mineral water springs, denominated as: Beleza, D. Isabel or Conde D'Eu, D. Leopoldina, Dom Pedro, Duque de Saxe, Ernestina Guedes, Mairink 1, 2 and 3, Venâncio, Viotti and the geyser called Floriano de Lemos. There is also a mineral water spring at Glória Hotel, denominated as Hotel Glória Spring and it is located in front of the Caxambu Water Park [15, 20].

The region is classified as belonging to the geological group Andrelândia – São Vicente Complex. The Water Park location largely determines the presence of a lithology composed of orthogneiss-biotite, thin-banded paragneiss-biotite and granitic leucogneiss. These rocks are cut by alkaline gap dykes and high-radioactive mafic dykes; the soil that covers this region is approximately 10 m thick. The subterranean hydrological system of Caxambu Water Park belongs to the Bengo River sub-basin and it is characterized by the occurrence of fractured hydrogeological domains that give rise to the mineral springs [19-20].

2.4. Conceição do Rio Verde

The city of Conceição do Rio Verde is located at the coordinates 21° 53' 13.92" S 45° 04' 45.12" W, with elevation of 873 m and average annual rainfall of 1489.4 mm. The Águas de Contendas Water Park is located 7 km far from the city and has four mineral water springs, denominated: Ferruginosa, Magnesian, Gasosa I or public spring and Gasosa II [19-21].

The region is classified as belonging to the geological group Barbacena (also denominated Mantiqueira Group) – Lambari Complex, characterized as igneous rocks. The Water Park is located on a lithology composed of biotite gneiss interspersed with biotite gneiss and amphibolite in part mylonitized granules; the soil that covers this region is approximately 4 m thick [20, 22-23]. The subterranean hydrological system of the Water Park belongs to Contendas Riverside sub-basin and it is characterized by the occurrence of two hydrogeological domains, granular and fractured; the mineral water springs come from aquifers of the fractured type [19-20].

2.5. Lambari

The city of Lambari is located at the coordinates 21° 58' 0.12" S 45° 22' 0.12" W, with elevation of 887 m and average annual rainfall of 1654.3 mm. Lambari Water Park has seven mineral water springs from the Mantiqueira Mountains and it is located in the city center. The mineral water springs are denominated: Gasosa, Alcalina, Magnesiana, Ligeiramente Gasosa, Ferruginosa, Picante, and Externa spring, located outside the park [19-20].

The region is also classified as belonging to the geological group Barbacena (also called Mantiqueira) - Lambari Complex, characterized as igneous rocks. The Lambari Water Park is located on a lithology composed of fine-grained biotite gneiss, banded or not, interspersed with amphibolytic biotite gneiss, granite biotite gnite and amphibolytic dioritic gneiss, most of which are saprolitic. However, the soil cover of this region is also approximately 4 m thick [20, 22-23]. The subterranean hydrological system of Lambari Water Park belongs to the Mumbuca River sub-basin and it is characterized by the occurrence of two hydrogeological domains of granular and fractured typologies. The mineral water springs come from fractured aquifers [19-20].

2.6. Sampling

The mineral water samples from each water park were collected as described in Table 1. For inorganic chemical characterization of the elements by energy dispersive X-ray fluorescence – EDXRF analysis, the samples were acidified with 50 % HNO_3 at the time of collection and, posteriorly, 200 mL aliquots were concentrated to 20 mL, in hot plate.

Table 1: Collected and analyzed samples.

	Spring 2015	Autumn 2016	Winter 2016	Spring 2016	Summer 2017	Autumn 2017	Winter 2017
Águas de Contendas				X	X	X	X
Cambuquira		X	X	X	X		
Caxambu	X						
Lambari				X	X	X	X
Marimbeiro		X	X	X	X		

2.7. Energy dispersive X-ray fluorescence – EDXRF

The technique of Energy Dispersive X-Ray Fluorescence (EDXRF) determined the elements: Ag, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, Se, Ti, V and Zn using the equipment EDX-720, from Shimadzu Corporation. The operation of this equipment uses rhodium X-ray tubes, set to a maximum of 1 mA automatically, 5 mm collimator, 15 kV voltage from Na to Sc and 50 kV from Ti to V, liquid N_2 cooling, and Si-Li detector. The results were analyzed using Statistics 6.0, StatSoft Inc. [24].

A 400 μL aliquot of a concentrated sample was placed on a polypropylene film-coated polyethylene backing to prevent sample leakage; [24] the support containing the sample was introduced into the EDXRF and read for 100 s with six repetitions per sample.

2.8. Determination of minimum limit of quantification (MLQ)

The equipment was calibrated with several dilutions of AccUTraceTM reference standard (catalog standard CLP-ICV-01R-5), and a calibration curve was obtained for each analyzed element, determined by Equation 1, as presented in Figure 3:

$$X_i = b \cdot I_i + c \tag{1}$$

Where,

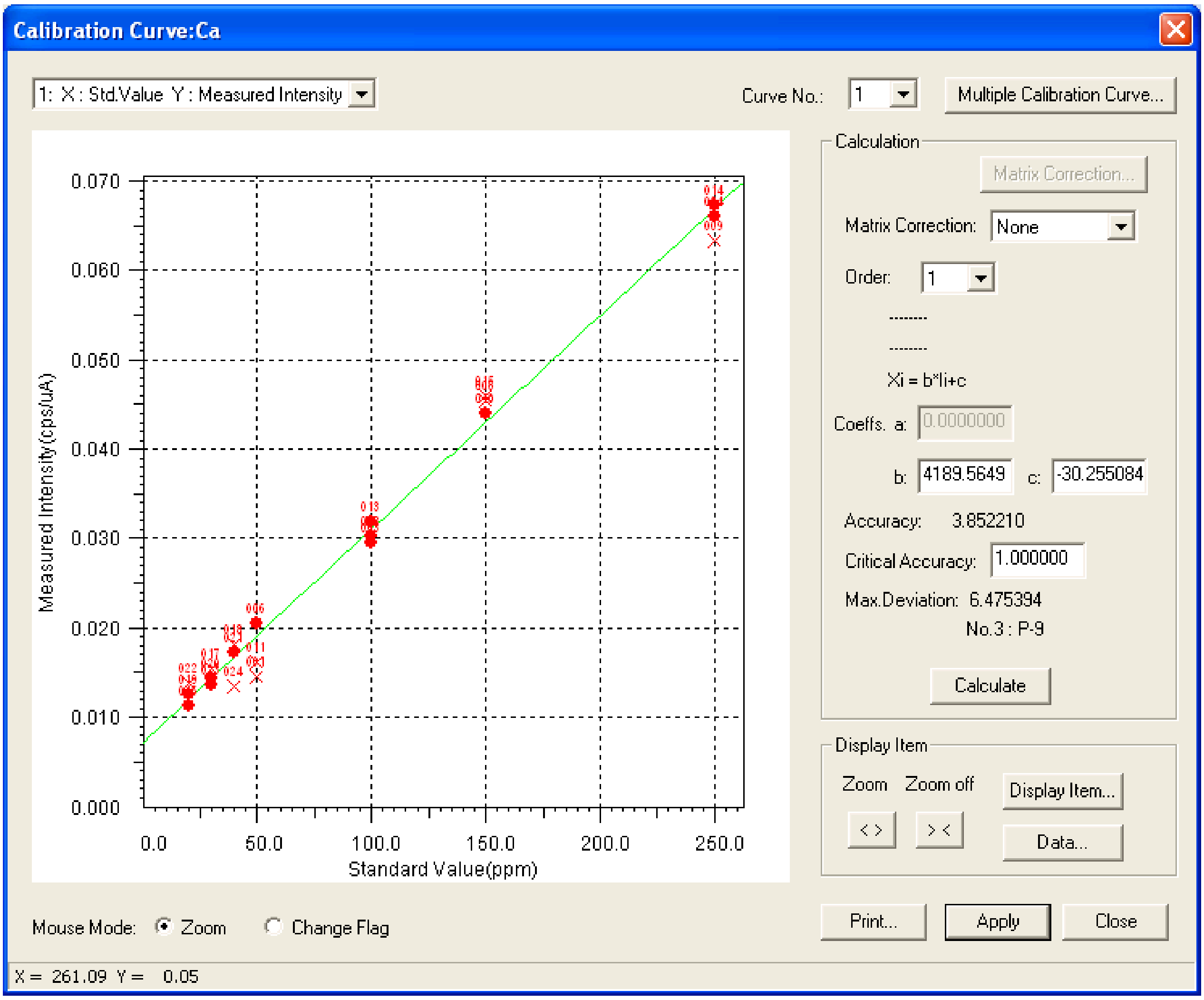
X_i = concentration of the element measured in the sample, in ppm

b = intensity coefficient of the sample measurement

I_i = sample measurement intensity, in cps

c = intersection point of the curve with the Y axis

Figure 3 : *Example of EDXRF calibration curve of element Ca.*



Source: MENEGHINI *et al.*, 2019

The calibration curves obtained using the reference standard, after the equipment calibration for each analyzed element, representing the lowest values of relative standard deviation and relative error, whose values were used to determine the minimum limit of quantification (MLQ), Table 2.

Table 2: Estimated values for the minimum limit of quantification (MLQ) [25].

Element	MLQ	Calculated Value ± SD	Relative Standard Deviation	Relative Error
Ag	0.25	0.30 ± 0.03	11.5	19.4
As	0.25	0.26 ± 0.04	15.6	3.09
Ba	0.80	0.81 ± 0.08	0.98	1.66
Ca	1.00	1.12 ± 0.13	12.4	11.83
Cd	0.13	0.14± 0.02	16.8	11.4
Co	0.20	0.21 ± 0.04	20.5	1.70
Cr	0.25	0.26 ±0.02	7.28	4.49
Cu	0.63	0.59 ± 0.05	7.80	6.30
Fe	0.30	0.31 ± 0.03	7.80	4.44
K	2.00	2.10 ± 0.13	6.27	4.87
Mn	0.06	0.06 ± 0.01	1.00	1.83
Ni	0.12	0.130 ±0.001	0.71	11.8
Pb	0.02	0.02 ± 0.01	23.9	11.9
Se	0.01	0.012 ± 0.001	14.1	15.5
Ti	0.25	0.28 ± 0.01	3.86	13.7
V	0.20	0.21 ±0.01	5.80	7.10
Zn	0.06	0.04 ± 0.01	10.3	27.5

3. RESULTS AND DISCUSSION

The mean concentrations of Ag, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, Se, Ti, V and Zn elements, in mg L^{-1}, determinated for the mineral water springs analyzed in this study by the EDXRF technique for each Water Park, are presented in Table 3 together with the Maximum Allowed Values (MAV) from the Ministry of Health and CONAMA (National Council Environment). Only the Cu element presented values below the MLQ in all the mineral samples analyzed.

At Cambuquira Water Park, Ag, As, Cd, Cr, Ni, Pb, Se, Ti and Zn elements presented values below the MLQ in all springs and collections. The lowest mean concentration values were obtained for the elements Co (0.22 ± 0.03 mg L^{-1}) in Gasosa II spring, Mn (0.23 ± 0.04 mg L^{-1}) in Laranjal or Dico spring and V (0.30 ± 0.04 mg L^{-1}), in Litinada spring. The highest mean concentrations were obtained for the elements Ca (209 ± 15 mg L^{-1}), K (29.3 ± 3.2 mg L^{-1}) and Fe (21.5 ± 2.4 mg L^{-1}) in Laranjal or Dico spring.

At Marimbeiro Water Park, Ag, As, Cd, Cr, Ni, Pb, Se, Ti and Zn elements presented values below the MLQ in all springs and collections. The lowest mean concentration values were obtained for the elements Mn (0.22 ± 0.04 mg L^{-1}) in Marimbeiro II, and Co (0.39 ± 0.02 mg L^{-1}) and V (0.40 ± 0.03 mg L^{-1}), in Marimbeiro I. The highest mean concentration values were obtained for the elements Ca (105 ± 19 mg L^{-1}) and K (29.4 ± 2.6 mg L^{-1}), both in Marimbeiro III and Fe (8.44 ± 1.07 mg L^{-1}), in Marimbeiro II.

At Caxambu Water Park, Cr and Ni elements presented values below MLQ, in all springs. The lowest mean concentration values were obtained for the elements Se (0.024 ± 0.001 mg L^{-1}), in Ernestina spring, Pb (0.06 ± 0.01 mg L^{-1}), in Beleza spring and Mn (0.15 ± 0.01 mg L^{-1}), in D. Leopoldina spring. The highest mean concentrations were obtained for the elements Ca (318 ± 5 mg L^{-1}) and K (246 ± 3 mg L^{-1}), in Geyser spring and Fe (8.28 ± 0.96 mg L^{-1}), in Hotel Glória spring.

At Águas de Contendas Water Park, the lowest mean concentration values were obtained for the elements Se (0.027 ± 0.002 mg L^{-1}) and Pb (0.10 ± 0.01 mg L^{-1}), both in Ferruginosa spring, and for Mn (0.078 ± 0.001 mg L^{-1}) in Magnesiana spring. The highest mean concentrations were obtained for the elements Fe (36.7 ± 0.9 mg L^{-1}), Ca (21.6 ± 0.7 mg L^{-1}) and K (7.57 ± 0.32 mg L^{-1}), in Gasosa II spring.

For Lambari Water Park, Fe and Mn elements presented values below the MLQ in all springs and collections. The lowest mean concentration values were obtained for the elements Ti (0.024 ± 0.004 mg L^{-1}), in Alcalina spring, Se (0.10 ± 0.03 mg L^{-1}), in Externa spring and Pb (0.13 ± 0.03 mg L^{-1}), in Gasosa spring. The highest mean concentration values were obtained for the elements Ca (8.15 ± 0.30 mg L^{-1}) and K (5.68 ± 0.47 mg L^{-1}), both in Picante spring and Ba (5.34 ± 0.08 mg L^{-1}), in Externa spring.

Comparing the mean concentration results obtained for the chemical elements present in the mineral waters of the parks studied with the limits established by the Ministry of Health and CONAMA, it could be verified that all of them exceeded the limits, except for the element Zn, proving the mineral characteristic of these waters. The probable origin of the studied elements in these mineral waters is attributable to the local geology and the differences determined in the concentrations values due to the aquifer recharge rate and the percolation time, among others.[6-7]

Table 3: Mean values of the analyzed chemical elements, mg L^{-1}, in the mineral water springs [25].

City	Spring	Chemical Elements															
		Ag	As	Ba	Ca	Cd	Co	Cr	Fe	K	Mn	Ni	Pb	Se	Ti	V	Zn
		mg/L ± SD	mg/L ± SD	mg/L ± SD	mg/L ± SD	mg/L ± SD	mg/L ± SD	mg/L ± SD	mg/L ± SD	mg/L ± SD	mg/L ± SD	mg/L ± SD	mg/L ± SD	mg/L ± SD	mg/L ± SD	mg/L ± SD	mg/L ± SD
Águas de Contendas	Ferruginosa	*	*	1.82 ± 0.15	7.17 ± 0.31	*	0.62 ± 0.03	*	18.3 ± 0.8	4.23 ± 0.39	0.30 ± 0.03	0.24 ± 0.07	0.10 ± 0.01	0.027 ± 0.002	0.39 ± 0.01	0.27 ± 0.07	0.26 ± 0.01
	Magnesiana	*	*	1.82 ± 0.04	1.13 ± 0.09	*	0.32 ± 0.03	0.29 ± 0.03	*	*	0.078 ± 0.001	*	0.08 ± 0.01	*	*	*	*
	Gasosa I	0.65 ± 0.02	0.57 ± 0.03	4.53 ± 0.19	7.80 ± 0.34	0.29 ± 0.02	0.63 ± 0.08	0.28 ± 0.01	1.61 ± 0.01	6.03 ± 0.29	0.73 ± 0.05	*	0.11 ± 0.01	*	*	0.47 ± 0.01	*
	Gasosa II	*	0.36 ± 0.36	2.06 ± 0.07	21.6 ± 0.7	*	0.50 ± 0.05	0.42 ± 0.42	36.7 ± 0.9	7.57 ± 0.32	0.32 ± 0.03	*	0.08 ± 0.01	0.029 ± 0.005	*	*	0.19 ± 0.01
Cambuquira	Gasosa I	*	*	2.38 ± 0.25	3.88 ± 0.31	*	0.61 ± 0.06	*	*	4.55 ± 0.42	0.29 ± 0.04	*	*	*	*	0.52 ± 0.03	*
	Gasosa II	*	*	3.61 ± 0.28	4.31 ± 0.31	*	0.22 ± 0.03	*	*	2.46 ± 0.28	*	*	*	*	*	0.31 ± 0.02	*
	Gasosa III	*	*	3.64 ± 0.28	6.53 ± 0.32	*	0.60 ± 0.03	*	*	3.53 ± 0.20	0.30 ± 0.04	*	*	*	*	0.48 ± 0.04	*
	Litinada	*	*	3.91 ± 0.25	10.1 ± 0.4	*	0.48 ± 0.03	*	*	4.40 ± 0.30	0.42 ± 0.04	*	*	*	*	0.30 ± 0.04	*
	Férrea	*	*	3.57 ± 0.27	17.9 ± 2.7	*	0.54 ± 0.05	*	6.58 ± 0.85	12.3 ± 1.8	0.60 ± 0.05	*	*	*	*	0.63 ± 0.02	*
	Magnesiana	*	*	3.72 ± 0.45	55.7 ± 0.3	*	0.60 ± 0.05	*	*	3.80 ± 0.30	0.52 ± 0.03	*	*	*	*	0.46 ± 0.02	*
	Laranjal or Dico	*	*	4.17 ± 0.39	209 ± 15	*	0.46 ± 0.05	*	21.5 ± 2.4	29.3 ± 3.2	0.23 ± 0.04	*	*	*	*	0.70 ± 0.04	*
Caxambu	Hotel Glória	*	*	4.50 ± 0.76	42.7 ± 1	*	0.31 ± 0.06	*	8.28 ± 0.96	37.3 ± 1.0	0.23 ± 0.01	*	0.14 ± 0.02	*	0.54 ± 0.01	*	*
	D. Leopoldina	*	*	1.76 ± 0.07	82.2 ± 0.6	*	0.50 ± 0.08	*	*	58.3 ± 1.4	0.15 ± 0.01	*	0.13 ± 0.01	*	*	*	*
	Venâncio	*	*	1.28 ± 0.17	237 ± 6	*	0.28 ± 0.01	*	3.87 ± 0.58	170 ± 3	0.57 ± 0.05	*	0.18 ± 0.01	*	*	*	*
	Beleza	*	*	3.61 ± 0.31	300 ± 4	0.35 ± 0.05	*	*	6.30 ± 0.26	222 ± 2	0.25 ± 0.01	*	0.06 ± 0.01	0.026 ± 0.001	0.71 ± 0.03	0.57 ± 0.08	*
	Ernestina	*	0.50 ± 0.02	3.29 ± 0.31	223 ± 6	*	0.34 ± 0.04	*	5.71 ± 0.46	174 ± 1	0.26 ± 0.05	*	0.16 ± 0.01	0.024 ± 0.001	*	*	0.26 ± 0.05
	D. Pedro	0.69 ± 0.12	*	2.04 ± 0.06	37.4 ± 0.9	*	0.59 ± 0.08	*	*	28.8 ± 1.2	0.18 ± 0.01	*	0.23 ± 0.03	0.028 ± 0.002	*	0.82 ± 0.09	1.88 ± 0.21
	Geiser	*	*	1.22 ± 0.23	318 ± 5	*	*	*	5.35 ± 0.41	246 ± 3	0.60 ± 0.12	*	0.22 ± 0.05	0.027 ± 0.001	*	*	*
Lambari	Alcalina	*	0.62 ± 0.03	1.56 ± 0.14	7.20 ± 0.34	*	0.31 ± 0.03	0.39 ± 0.02	*	4.43 ± 0.26	0.38 ± 0.05	0.81 ± 0.11	0.14 ± 0.02	0.12 ± 0.02	0.024 ± 0.004	0.39 ± 0.04	0.36 ± 0.03
	Magnesiana	*	0.81 ± 0.08	2.03 ± 0.30	8.13 ± 0.37	*	0.36 ± 0.02	0.66 ± 0.03	*	5.36 ± 0.23	0.16 ± 0.02	*	*	0.13 ± 0.01	0.028 ± 0.001	0.47 ± 0.01	0.30 ± 0.01
	Gasosa	*	1.07 ± 0.27	1.53 ± 0.11	6.85 ± 0.25	0.32 ± 0.03	0.38 ± 0.03	0.37 ± 0.04	*	4.53 ± 0.28	0.15 ± 0.02	*	0.13 ± 0.03	0.11 ± 0.01	0.10 ± 0.01	0.56 ± 0.04	*
	Lig. Gasosa	*	0.78 ± 0.06	1.93 ± 0.14	5.23 ± 0.30	*	0.26 ± 0.03	0.45 ± 0.05	*	4.09 ± 0.26	0.40 ± 0.05	*	*	0.11 ± 0.01	0.05 ± 0.01	0.45 ± 0.07	0.50 ± 0.05
	Picante	0.35 ± 0.05	0.32 ± 0.07	1.83 ± 0.06	8.15 ± 0.30	0.30 ± 0.02	0.42 ± 0.04	*	*	5.68 ± 0.47	0.20 ± 0.02	*	0.14 ± 0.01	0.16 ± 0.02	0.051 ± 0.002	0.33 ± 0.06	0.45 ± 0.04
	Externa	*	0.53 ± 0.07	5.34 ± 0.08	7.07 ± 0.57	*	0.41 ± 0.06	*	*	5.04 ± 0.44	0.34 ± 0.07	*	*	0.10 ± 0.03	*	0.58 ± 0.04	*
Marimbeiro	Marimbeiro I	*	*	3.21 ± 0.38	86.6 ± 8.9	*	0.39 ± 0.02	*	6.69 ± 0.88	25.6 ± 1.7	*	*	*	*	*	0.40 ± 0.03	*
	Marimbeiro II	*	*	3.33 ± 0.39	92,0 ± 15.2	*	0.56 ± 0.05	*	8.44 ± 1.07	27.9 ± 2.3	0.22 ± 0.04	*	*	*	*	0.42 ± 0.02	*
	Marimbeiro II	*	*	3.50 ± 0.26	105 ± 19	*	0.43 ± 0.03	*	8.43 ± 1.07	29.4 ± 2.6	0.25 ± 0.04	*	*	*	*	0.42 ± 0.04	*
Health Ministry and CONAMA	Maximum Allowed Value (MAV)	0.10 ¤	0.01	0.70	—	0.005	—	0.05	0.30	—	0.10	0.07 ◊	0.01	0.01	—	0.05 ¤	5,00

* < MLQ — Value not determined ¤ Value attributed only by CONAMA ◊Value of 0.02 mg/L attributed by CONAMA

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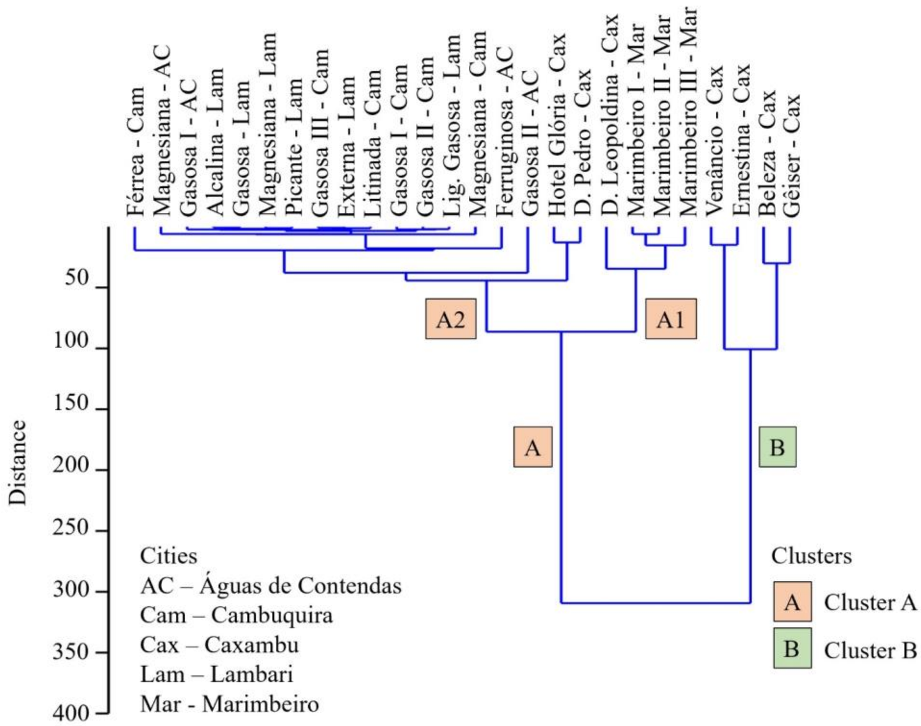
3.1. Statistical analysis

Clusters Statistical Analysis was applied to the results obtained from the mean concentration of the elements determined in the studied mineral waters, Figure 4, with exception for the Cu element that presented values below the MLQ for all samples analyzed. In this analysis, two groups were formed, Cluster A and Cluster B.

Figure 4: *Cluster Analysis for the chemical elements determined in the mineral water samples from the Water Parks.*



Cluster A grouped almost all the mineral water samples analyzed, and Cluster B grouped the mineral waters that presented the highest concentrations for Ca and K elements, the mineral water springs Venâncio, Ernestina, Beleza and Geiser, from Caxambu Water Park.

Cluster A was divided into two major subgroups, A1 and A2. The first one grouped the three Marimbeiro springs and D. Leopoldina, from Marimbeiro and Caxambu Water Parks, respectively. Cluster A2 grouped all the other springs, but it may be observed that Hotel Gloria and D. Pedro springs, from Caxambu Water Park, are isolated from the others that formed a group mixed with the

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springs from Águas de Contendas, Cambuquira, and Lambari Water Parks indicating the great similarity among them, in spite of the Water Parks being located far from each other.

Cluster analysis grouped the majority of the springs by the local geology, Caxambu, Cambuquira and Marimbeiro Water Parks, which belong to the geological group Andrelândia, and Águas de Contendas, plus the Lambari Water Park from Barbacena geological group, but other factors could influence the concentrations of chemical elements, as it was mentioned in previous paragraphs.

Pearson's correlation coefficient analysis was, also, performed with the mean concentrations of the chemical elements determined in the mineral waters from the Water Parks. In this analysis, only the elements with higher concentration and frequency of presence in the studied mineral waters were used. The results are presented in Table 4.

Table 4: Pearson’s correlation coefficients among the Water Parks.

	Águas de Contendas	**Cambuquira**	**Caxambu**	**Lambari**	**Marimbeiro**
Águas de Contendas	1				
Cambuquira	0.997	1			
Caxambu	0.941	0.963	1		
Lambari	0.986	0.994	0.957	1	
Marimbeiro	0.983	0.982	0.960	0.957	1

It may be observed that there is a strong and direct proportional correlation, above ± 0.726, among the studied Water Parks; this similarity might be due to the geological structure characterized by igneous rocks present in the parks.

Another Pearson correlation was performed to verify the correlation among the elements Ba, Ca, Co, K and Mn, Table 5, which were determined in all the springs, with exception of the springs from Caxambu Water Park because, for this park, only one collection was performed, which could lead to errors related to a single measure.

In this analysis it could be observed that some elements in the same Water Park presented strong positive correlations with each other, such as Co element in Águas de Contendas Water Park and others presented weak or no correlations, for example, Ba element in Marimbeiro Water Park. An addition, one exception may be observed for the correlations between the Water Parks of Águas de

Contendas and Lambari, where all the Pearson coefficients of these parks are positive and above 0.4, indicating moderate and strong correlations, probably because these Water Parks have the same local geology. Nevertheless, based on local geology, both belong to the geological group Barbacena – Lambari Complex, these strong correlations could be derived, mainly, from the simultaneous dissolution of igneous rocks containing carbonates and silicates, such as calcite, potassium feldspar and garnet, present in aquifer rocks, as well as the dissolution of clayey and silty sediments by the infiltrating waters rich in carbonic acid present in the water parks [20, 27-28].

On the other hand, a strong inversely proportional correlation, below - 0.7 was found between the Águas de Contendas and Cambuquira Water Parks for the analyzed elements. These inversely proportional correlations could be due to the different local geology and groundwater rapid and superficial transit flow replenishment, as well as other factors, such as: the leaching of these elements present in soils and sediments, the process of dissolution of the rocks through which they percolate and are stored, the presence of decomposing plant organic matter in alluvial sediments These facts will help to compose the pH value of mineral waters and influence the degree of dissolution of the aquifer rocks through which they percolate and store, among others [20, 27-29].

4. CONCLUSION

In all the mineral waters analyzed, the major elements Ca, Fe and K presented the highest mean concentrations, except for Lambari Water Park, which presented a higher mean concentration for Ba element and Cu element presented values below the MLQ in all mineral water samples analyzed. Some elements, such as As, Ba and Co when present in mineral waters, may be considered contaminants; the values obtained for these elements were above the MAV, indicating that these values could be related to natural anomalies of aquifers.

The Cluster statistical analysis divided the water samples in two major groups, by similarity of concentration: one of them grouped the samples with the highest concentrations (springs Geiser, Beleza, Venâncio and Ernestina from Caxambu Water Park); the other group, with all the samples of mineral water, demonstrating that, despite the distance between the parks, there is a mineralogical similarity among these regions.

Pearson's correlation coefficient statistical analyzes presented strong and direct proportional correlations among all water parks studied and the same fact occurred among most elements, which presented higher concentration values and frequency in the mineral waters; also, strong inversely proportional correlations were found among a few elements.

Therefore, the results presented demonstrate the importance of the present work and contribute to the Brazilian legislation regarding the potability standards of the mineral waters from the studied water parks, which have attracted many people in recent years, due to the constant increase in mineral water consumption and the demand for hydromineral parks for thermal health treatments.

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Table 5: Pearson's correlation coefficients among Ba, Ca, Co, K and Mn present in the water parks under study.

		Águas de Contendas					**Cambuquira**					**Lambari**					**Marimbeiro**				
		Ba	**Ca**	**Co**	**K**	**Mn**	**Ba**	**Ca**	**Co**	**K**	**Mn**	**Ba**	**Ca**	**Co**	**K**	**Mn**	**Ba**	**Ca**	**Co**	**K**	**Mn**
Águas de Contendas	Ba	1																			
	Ca	0.453	1																		
	Co	0.873	0.787	1																	
	K	0.359	0.995	0.722	1																
	Mn	0.425	0.940	0.805	0.935	1															
Cambuquira	Ba	-0.979	-0.300	-0.810	-0.200	-0.312	1														
	Ca	0.881	0.372	0.857	0.285	0.500		1													
	Co	0.430	0.383	0.656	0.346	0.655	-0.497	0.786	1												
	K	0.554	0.125	0.597	0.062	0.389	-0.668	0.879	0.928	1											
	Mn	0.276	-0.713	-0.129	-0.780	-0.611	-0.447	0.366	0.095	0.449	1										
Lambari	Ba	0.982	0.606	0.949	0.521	0.581	-0.939	0.889	0.514	0.569	0.114	1									
	Ca	0.630	0.974	0.906	0.947	0.941	-0.502	0.570	0.505	0.307	-0.536	0.763	1								
	Co	0.838	0.865	0.962	0.809	0.794	-0.728	0.705	0.442	0.357	-0.287	0.919	0.945	1							
	K	0.613	0.977	0.899	0.952	0.947	-0.485	0.559	0.508	0.303	-0.551	0.749	1	0.937	1						
	Mn	0.449	0.996	0.800	0.991	0.966	-0.306	0.408	0.454	0.191	-0.696	0.606	0.977	0.857	0.981	1					
Marimbeiro	Ba	-0.312	0.666	0.064	0.735	0.538	0.488	-0.438	-0.194	-0.536	-0.995	-0.160	0.480	0.242	0.494	0.642	1				
	Ca	0.956	0.689	0.974	0.611	0.618	-0.882	0.805	0.418	0.440	-0.017	0.987	0.819	0.960	0.806	0.679	-0.022	1			
	Co	0.972	0.568	0.951	0.481	0.588	-0.952	0.941	0.612	0.672	0.171	0.991	0.738	0.855	0.725	0.579	-0.228	0.959	1		
	K	0.660	0.178	0.358	0.115	-0.092	-0.575	0.237	-0.394	-0.221	0.163	0.578	0.250	0.507	0.232	0.114	-0.117	0.673	0.483	1	
	Mn	0.391	0.411	0.267	0.390	0.084	-0.230	-0.080	-0.551	-0.545	-0.314	0.377	0.376	0.503	0.366	0.335	0.368	0.502	0.252	0.874	1

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