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INORGANIC CHEMICAL ELEMENTS DETERMINED IN MINERAL WATER SPRINGS FROM THE WATER CIRCUIT OF MINAS GERAIS, BRAZIL BY X-RAY FLUORESCENCE SPECTROMETRY

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ABSTRACT

Water Circuit of Minas Gerais (Circuito das Águas de Minas Gerais) is known by its mineral water parks located in the cities of Cambuquira, Caxambu, Conceição do Rio Verde, Lambari and São Lourenço. The mineral water of these parks is consumed regularly by the local population and tourists that are motivated by the medicinal use of the mineral water. One of the characteristics that defines a mineral water is its chemical composition, hence a water is considered mineral due to the chemical elements present in its composition. The objective of this work was to determine the inorganic chemical characterization of the mineral waters from the Water Parks of Cambuquira, Caxambu, Conceição do Rio Verde, Lambari and Marimbeiro analyzing the elements Ag, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K. Mn, Ni, Pb, Se, Ti, V and Zn by energy dispersive X-ray fluorescence spectrometry – EDXRF. Each water park presented different chemical elements with different concentrations, in spite of the parks are located near each other. The elements that presented the highest concentrations in all the samples analyzed were the major elements Ca, Fe, K and Mn. Among the four water parks studied, the mineral waters from Water Park of Caxambu presented the highest concentrations for all the elements determined. This study is part of a research project developed at CMR that studied the natural radionuclides ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{210}Po and the inorganic chemical elements of the mineral waters of the Water Circuit of Minas Gerais.

1. INTRODUCTION

The use of water for the treatment of diseases and as a purifier is reported since the Babylonian times. At first, these treatments consisted in medicinal baths, ablution and compresses; with the Greek civilization, the term hydrotherapy arises, and the intake of waters was introduced as part of the medicinal practice. By the sixteenth century, the balneology was established, associated with the use of mineral waters for the treatment of skin issues, where the high sulfur content in this baths probably was the active agent. [1]

Nowadays, the use of mineral waters in spas is focused on their chemical and natural radioactive characteristics and, the fact that living organisms are constituted by many elements present in these mineral waters (as K, Ca, Na, Mg and P) and these are essential for the life maintenance, the popularity of spas, geysers, mineral water park and bathhouses have increased. With the objective of treating chronic diseases, spas also promote improvement in the lifestyle, with the proposal of improvement as a whole, and not only in the use of mineral waters. [2][3][4]

Mineral waters are defined as those that comes from natural springs with chemical composition properties that give a medicinal action and distinguishes them from ordinary water. According to Brazilian Mineral Summary of National Department of Mineral Production - DNPM [5], the global consumption of mineral water has been increasing around 7% per year, fact that reinforces the importance of the characterization and regulation of these waters.

Although each country establishes their own laws about maximum allowed value of chemical elements present in potable water, the standard defined in these laws is intended to protect the population from contamination by pathogenic micro-organisms and pollution by poisonous or toxic substances, as well as, search for improved characteristics such as color, odor, taste, hardness, turbidity and pH, according to the hydrogeological characteristics of each region.

The regulations of the Ministry of Health that determine these factors of potability of water in Brazil segregate chemical elements in three groups: major, minor and trace elements. Major elements are those present in concentrations higher than 5 mg L^{-1} being Cl^-, Na^+, Ca^{2+}, Mg^{2+} and K^+ the main ions of this group; for minor elements group, the range of ion concentration is from 0,01 to 5 mg L^{-1} and the main ion is Sr^{2+}, but sometimes with the presence of Br^-, I^-, Fe^{3+}, Mn^{2+}, Al^{3+}, among others. Lastly, elements that have concentration lower than 0,01 mg L^{-1} are classified as trace elements, and the elements As^{2+}, Sb^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Ba^{2+}, Cd^{2+} and Hg^{2+} are, among others, the main elements of this group. [6][7][8]

In Brazil, the balneology appeared with the Portuguese colonization and one of the most famous places by the large mineral water consumption and crenotherapy is the “Water Circuit of Minas Gerais”, known by its mineral water parks located in Cambuquira, Caxambu, Conceição do Rio Verde, Lambari and São Lourenço. [9] The mineral waters of these parks, with exception of the Water Park of São Lourenço, were studied in previous works for the natural radionuclide ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{210}Po quantification and as well as the estimated committed effective dose due to the intake of these mineral waters.[10-12]

The objective of this work was to determine the inorganic chemical characterization of the mineral waters from the Water Parks of Cambuquira, Caxambu, Conceição do Rio Verde, Lambari and Marimbeiro analyzing the elements Ag, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, Ti, V and Zn by energy dispersive X-ray fluorescence spectrometry – EDXRF.

2. METHODS

2.1. Study Area

The study area of this work is located in the Water Parks of the cities of Cambuquira, Caxambu, Conceição do Rio Verde and Lambari, in the state of Minas Gerais. These cities are part of the Water Circuit of Minas Gerais, which is formed by the cities of Baependi, Cambuquira, Campanha, Carmo de Minas, Caxambu, Cruzília, Dom Viçoso, Liberdade, Passa Vinte, São Lourenço, Soledade de Minas and Três Corações, Figure 1. [13]

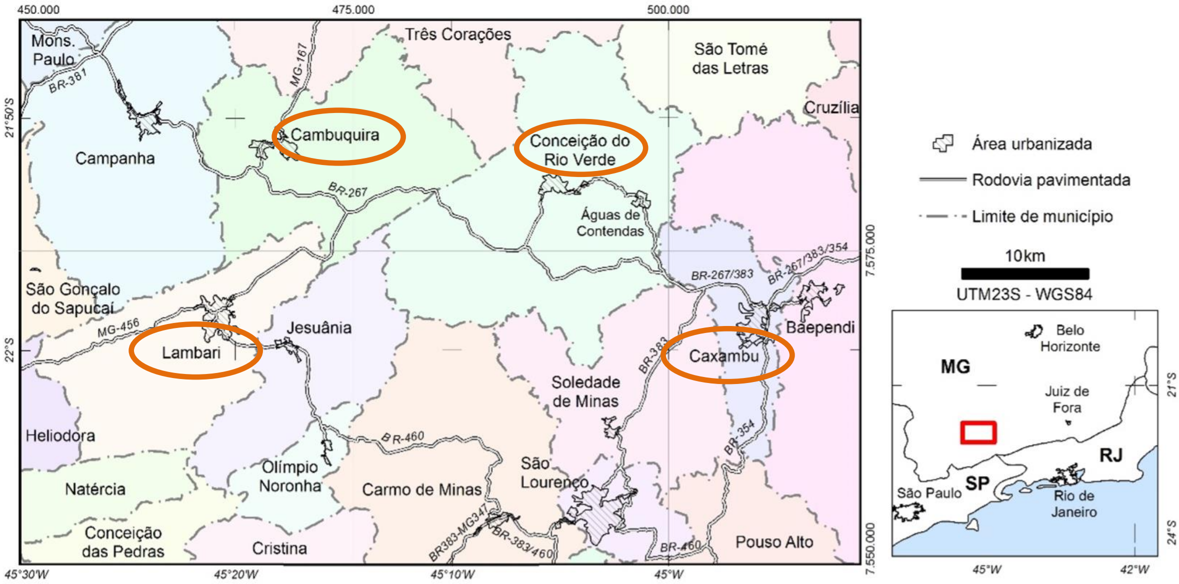

Figure 1: Map of the Water Circuit of Minas Gerais
Fonte: CIRCUITO DAS ÁGUAS DE MINAS GERAIS, 2018. [10]

The climate in the study regions is classified as subtropical humid climate, Cwa type, with dry winter and rainy summer. The temperature in the hottest month, January, is above 22 °C and in the coldest month, July, below 18 °C. [14]

2.1.1. Cambuquira and Marimbeiro

The city of Cambuquira coordinates 21° 51' 0,00" S 45° 18' 0,00" W, altitude of 950,1 m and and with average annual rainfall of 1338,3 mm, has The Parque das Águas of Cambuquira located in the center of the city with five mineral water springs called: Regina Werneck or Gasosa spring, Souza Lima or Sulforosa spring, Fernandes Pinheiro or Férrea spring, Augusto Ferreira or Magnesiana spring and, Roxo Rodrigues or Litinada spring. [14][15][16] There is also another spring of mineral water in a private property, open to the population, located near the Parque das Águas of Cambuquira and named Laranjal or Dico spring.

The Parque das Águas of Marimbeiro is located 3 km from the center of the city of Cambuquira and has three mineral springs called: Spring 1, Spring 2 and Spring 3.

The region is classified as belonging to the Andrelândia Group – Lambari Complex (also called as São João del Rei Complex). The location of the Parque das Águas of Cambuquira and Marimbeiro, in the most part, determines the presence of a lithology composed of granatiferous schists with interleaves of gneiss, both saprolitized with little associated quartzite. However, the soil cover of the region is approximately 10 m thick in Cambuquira and approximately 5 m thick in Marimbeiro. [14][15]

The subterranean hydrological system of the Marimbeiro Stream sub-basin contiguous to Cambuquira Stream sub-basin, in which the Parque das Águas of Marimbeiro and Cambuquira forms part, is characterized by the occurrence of the fractured hydrogeological domains which gives rise to the mineral water springs under study. [14][15]

2.1.2. Caxambu

The city of Caxambu coordinates 21° 59' 22,92" S 44° 56' 18,96" W, altitude of 958,5 m and and with average annual rainfall of 1725,0 mm, has The Parque das Águas of Caxambu located in the center of the city with twelve mineral water springs called: Beleza spring, D. Isabel or Conde D'Eu spring, D. Leopoldina spring, Dom Pedro spring, Duque de Saxe spring, Ernestina Guedes spring, Mairink 1 spring, Mairink 2 spring, Mairink 3 spring, Venâncio spring, Viotti spring and Floriano de Lemos Geyser. There is also another spring of mineral water in the Gloria Hotel, Gloria Hotel spring, located in front of the Parque das Águas of Caxambu.

The region is classified as belonging to the Andrelândia Group – São Vicente Complex. The location of the Parque das Águas of Caxambu, in the most part, determines the presence of a lithology composed of orthogneiss-biotite, thinly banded paragneiss-biotite and granitic leucogneiss, these rocks are cut by dikes of alkaline gap and mafic dikes with high radioactivity. However, the soil cover of the region is approximately 10 m thick. [14][15]

The subterranean hydrological system of the Bengo Riverside sub-basin, in which the Parque das Águas of Caxambu forms part, is characterized by the occurrence of the fractured hydrogeological domains which gives rise to the mineral water springs under study. [14][15]

2.1.3. Conceição do Rio Verde

The city of Conceição do Rio Verde coordinates 21° 53' 13,92" S 45° 04' 45,12" W, altitude of 873 m and with average annual rainfall of 1489,4 mm, has The Parque das Águas of Águas de Contendas is 7 km far from the city with four mineral water springs called: Ferruginosa spring, Magnesiana spring, Gasosa I spring or Public spring and Gasosa II spring. [14-16]

The region is classified as belonging to the Barbacena Group (also called as Mantiqueira Group) - Lambari Complex, characterized as igneous rocks. The location of the Parque das Águas of Águas de Contendas determines the presence of a lithology composed of biotite-gneiss interspersed with biotite-gneiss and amphibolytic in part milonitized granules. However, the soil cover of the region is approximately 4 m thick. [15][17][18]

The subterranean hydrological system of the Contendas Riverside sub-basin, in which the Parque das Águas of Águas de Contendas forms part, is characterized by the occurrence of two hydrogeological domains, granular and fractured. However, the mineral water springs under study come from aquifers of the fractured type. [14][15]

2.1.4. Lambari

The city of Lambari coordinates 21° 58' 0,12" S 45° 22' 0,12" W, altitude of 887 m and and with average annual rainfall of 1654,3 mm, has The Parque das Águas of Lambari is located in the center of the city with seven mineral springs, whose waters come from Serra da Mantiqueira. The springs of mineral water are called: Spring 1 - Gasosa, Sprin 2 - Alkaline, Spring 3 - Magnesiana, Spring 4 – Ligeiramente Gasosa, located in the central pavilion; Spring 5 - Ferruginosa, Spring 6 - Picante, located in proper pavilions and; External spring, located on the outside of the park in its own pavilion. [14][15]

The region of the city of Lambari is also classified as belonging to the Barbacena Group (also called as Mantiqueira) - Lambari Complex, characterized as igneous rocks. The location of the Parque das Águas of Lambari determines the presence of a lithology composed of fine-grained biotite-gneiss, banded or not, interspersed with amphibolytic biotite-gneiss, biotite-granada gneiss and amphibolytic dioritic gneiss, in which the majority are saprolitized. However, the soil cover of the region is also approximately 4 m thick. [15][17][18]

The subterranean hydrological system of the Mumbuca Riverside sub-basin, in which the Parque das Águas de Lambari forms part, is also characterized by the occurrence of two hydrogeological domains of granular and fractured typologies. However, the mineral water springs under study also come from aquifers of the fractured type.

2.2. Sampling

Samples of mineral water from each spring and Water Park were collected in the seasons and years presented in Table 1; at the time of collection they were acidified with 50 % HNO_3 and for the inorganic chemical characterization of the elements, using X-ray fluorescence analyses, 200 mL aliquots were concentrated to 20 mL, in hot plate.

Tabel 1: Analyzed samples

	Seasons							
Water Parks	Spring 2015	Summer 2016	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		

2.3. Analytical Methods

The elements: Ag, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, Se, Ti, V, Zn were determined by Energy Dispersive X-Ray Fluorescence (EDXRF). For this analysis, the equipment used was the brand Shimadzu Corporation, model EDX-720 from the Center of Lasers/ Center of Chemistry and Environment (CLA/ CQMA – IPEN). The equipment operates by means of Rhodium X-ray tubes automatically adjusted to a maximum of 1 mA; 15 kV voltage from Na to Sc and from 50 kV from Ti to V; 5 mm collimator; cooling with liquid N_2; and Si-Li detector. The results analysis was performed by the Statistics 6.0 program, StatSoft Inc. [19]

An aliquot of 400 µL of concentrated sample was placed in polypropylene film-coated polyethylene support to prevent sample leakage.[19] Subsequently, the carrier containing the sample was read for 100 s with six replicates per sample. Due to the sample being liquid, it was not possible to apply vacuum, thus, of all the elements analyzed by the equipment only 17 elements were determined, Figure 1.

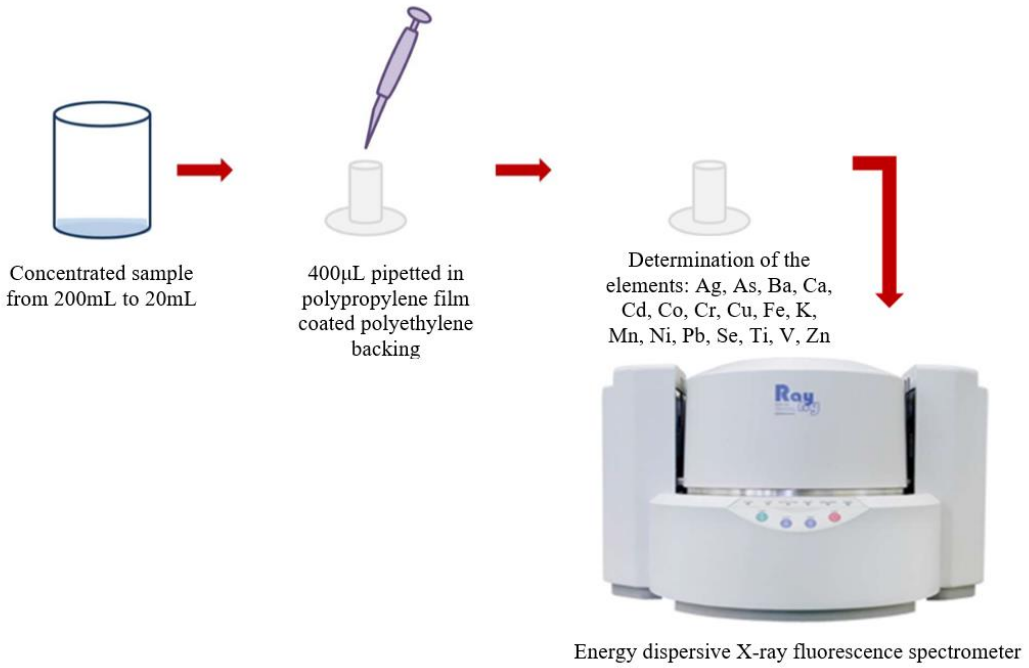

Figure 1: Flowchart of the experimental procedure for dispersive energy X-ray fluorescence spectrometry (EDXRF)
Fonte: WAKASUGI, 2018. [17]

2.3.1. Determination of minimum limit of quantification (MLQ)

In order to perform the analysis of these samples, several dilutions of the reference liquid standard AccUTraceTM Reference Standard (Catalog No. CLP-ICV-01R-5) [19], were used to calibrate the equipment; each analyzed element obtained a calibration curve, Figure 2, determined from the expression (1):

$$X_i = b \cdot I_i + c \quad (1)$$

Where
X_i = concentration of the element measured in the sample, in ppm
b = coefficient of the intensity of the sample measurement
I_i = sample measurement intensity, in cps
c = point of intersection of the curve with the Y axis

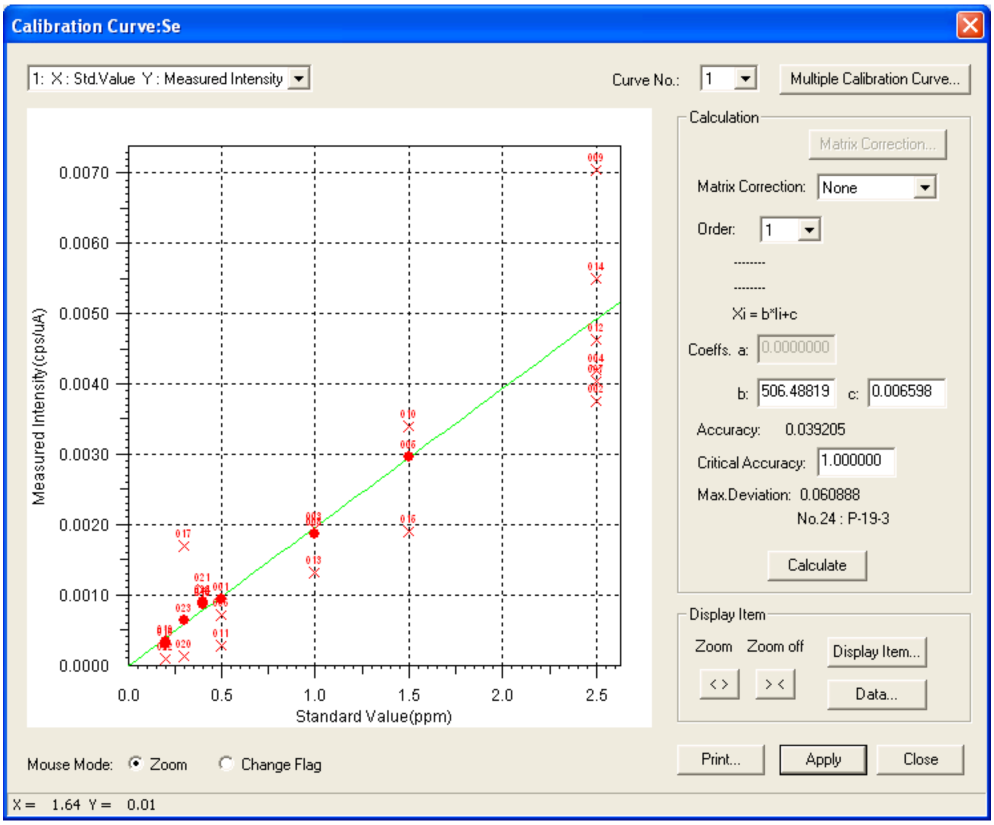

Figure 2: Example of EDXRF calibration curve for element Se

The values obtained after the calibration of the equipment for each of the measured elements were used for the determination of the minimum limit of quantification (MLQ), that represents the lowest values of relative standard deviation and relative error obtained by the calibration curve using the reference standard liquid, Table 2.

Tabel 2: Estimated values for the minimum limit of quantification (MLQ)

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	0.13 ± 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

In Table 3 are presented the mean concentrations, in mg L^{-1}, determined of the elements Ag, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, Se, Ti, V and Zn in the mineral water springs from the Water Parks of Parque das Águas of Águas de Contendas, Cambuquira, Caxambu, Lambari and Marimbeiro, by EDXRF and the Maximum Allowed Values (MAV) for the studied elements from Brazilian Health Ministry and CONAMA (National Council of Environment).

For Parque das Águas of Águas de Contendas, the highest mean values 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 and the lowest mean values for the elements Se (0.027 ± 0.002 mg L^{-1}) and Pb (0.10 ± 0.01 mg L^{-1}) in Ferruginosa spring, and for Mn (0.078 ± 0.001 mg L^{-1}) in Magnesiana spring. The Cu element presented values lower than MLQ in all springs and collections.

For Parque das Águas of Cambuquira the highest mean values were obtained for the elements: Ca (209 ± 15 mg L^{-1}), K (29.3 ± 3.2 mg L^{-}) and Fe (21.5 ± 2.4 mg L^{-1}) in Laranjal or Dico spring, and the lowest mean values were 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 elements Ag, As, Cd, Cr, Cu, Ni, Pb, Se, Ti and Zn presented values lower than the MLQ in all springs and collections.

The highest values for the Parque das Águas of Caxambu were obtained for the elements Ca (318 ± 5 mg L^{-1}) and K (246 ± 3 mg L^{-1}) in Geiser spring, and Fe (8.28 ± 0.96 mg L^{-1}) in Hotel Glória spring, the lowest values were 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 for Mn (0.15 ± 0.01 mg L^{-1}) in D. Leopoldina spring. The Cr, Cu and Ni elements presented values lower than MLQ in all springs.

The highest mean values for the Parque das Águas of Lambari were obtained for the elements Ca (8.15 ± 0.30 mg L^{-1},) and K (5.68 ± 0.47 mg L^{-1}) in Picante spring and Ba (5.34 ± 0.08 mg L^{-1}) in Externa spring, the lowest mean values were 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 for Pb (0.13 ± 0.03 mg L^{-1}) in Gasosa spring. The Cu, Fe and Mn elements presented lower values than MLQ in all springs and collections.

For the Parque das Águas of Marimbeiro the highest mean values were obtained for the elements Ca (105 ± 19 mg L^{-1}) and K (29.4 ± 2.6 mg L^{-1}) in Marimbeiro III spring, and for Fe (8.44 ± 1.07 mg L^{-1}) in Marimbeiro II spring. the lowest mean values were for the elements Mn (0.22 ± 0.04 mg L^{-1}) in Marimbeiro II spring, Co (0.39 ± 0.02 mg L^{-1}) and for V (0.40 ± 0.03 mg L^{-1}) in Marimbeiro I spring. The elements Ag, As, Cd, Cr, Cu, Ni, Pb, Se, Ti and Zn presented values lower than the MLQ in all spring and collections.

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

City	Spring	Chemical Elements															
		Ag mg/L ± SD	As mg/L ± SD	Ba mg/L ± SD	Ca mg/L ± SD	Cd mg/L ± SD	Co mg/L ± SD	Cr mg/L ± SD	Fe mg/L ± SD	K mg/L ± SD	Mn mg/L ± SD	Ni mg/L ± SD	Pb mg/L ± SD	Se mg/L ± SD	Ti mg/L ± SD	V mg/L ± SD	Zn 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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Comparing the mean concentration results obtained for the chemical elements in the mineral water springs of all parks with the limits established by the Brazilian Ministry of Health, for the elements that have limits, it was possible to verify that all of them exceeded this limit, with the exception of the Zn element, proving the mineral characteristic of these waters. Exceeded values show that these waters do not attend the potability standards established by the Brazilian norms that guarantee the safe consumption of these waters.

3.1. Statistical Analysis – Cluster

The statistical analysis of Clusters was applied to the mean concentrations of the chemical elements: Ag, As, Ba, Ca, Cd, Co, Cr, Fe, K, Mn, Ni, Pb, Se, Ti, V and Zn in the mineral waters of the Parques das Águas of Contendas, Cambuquira, Caxambu, Lambari and Marimbeiro, which evidenced the formation of cluster B, with Venâncio, Ernestina, Beleza and Geiser springs belonging to the Parque das Águas of Caxambu and cluster A, with the other springs of the water parks under study, Figure 3. It should be noted that the Cu element was not considered in this analysis because it presented values below the MLQ for all the samples of all the water parks studied.

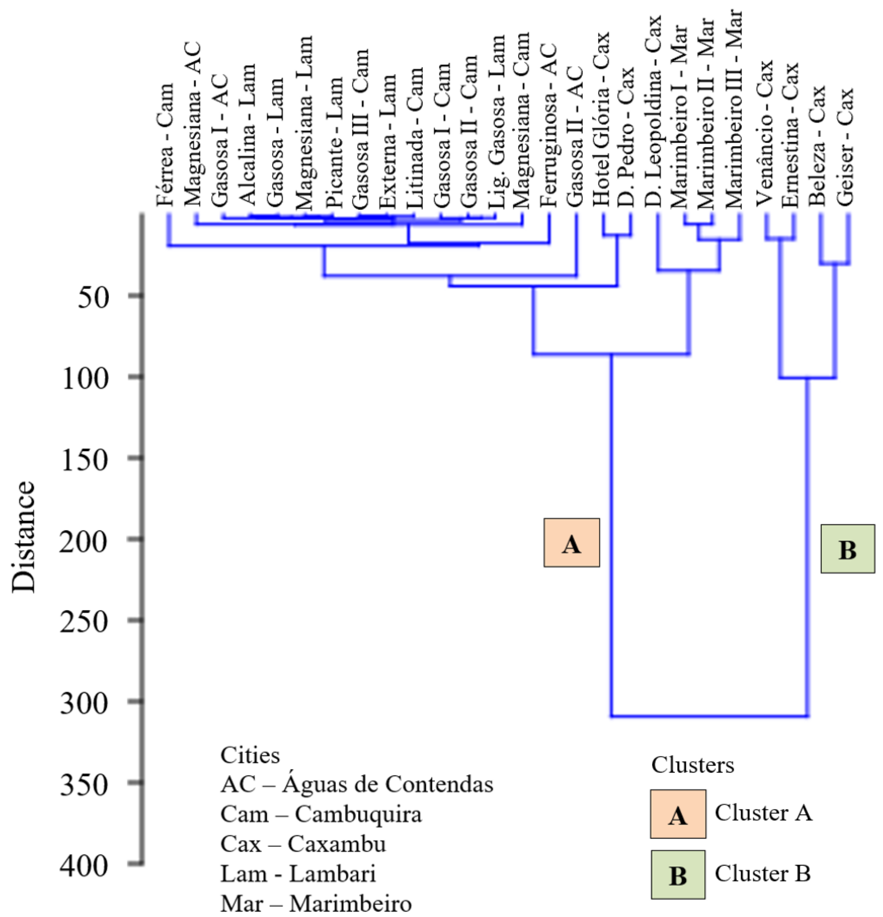

Figure 3: Cluster Analysis for the chemical elements Ag, As, Ba, Ca, Cd, Co, Cr, Fe, K, Mn, Ni, Pb, Se, Ti, V an Zn in mineral water samples from the Parques das Águas of Águas de Contendas, Cambuquira, Caxambu, Lambari and Marimbeiro

Cluster B with the Geiser, Beleza, Venâncio and Ernestina springs presented in decreasing order the highest concentration means for the elements Ca and K; in the same way, the highest concentration value determined for the element Mn was in the Geiser spring, for the elements Cd and Ti in the Beleza spring and, for the elements As, Cr and Zn in the Ernestina spring when compared to the concentration means of cluster A.

Cluster A presented greater similarity among the Gasosa I spring of the Parque das Águas of Águas de Contendas, Alcalina, Magnesiana, Gasosa, Ligeiramente Gasosa, Picante and Externa of the Parque das Águas of Lambari and Gasosa I, Gasosa II, Gasosa III and Litinada of the Parque das Águas of Cambuquira, which presented mean concentration values close to K, Mn and V. However, the highest mean concentration was observed in the Parque das Águas of Lambari for the eled ments Ni and Se in the Alcalina spring and in the Parque das Águas of Cambuquira for the element Co in the Gasosa I spring.

Within the same cluster A, there was also a greater similarity between the Hotel Glória and D. Pedro springs, both belonging to the Parque das Águas of Caxambu and, among the Marimbeiro I, Marimbeiro II, Marimbeiro III, belonging to the Parque das Águas of Marimbeiro, and D. Leopoldina, belonging to the Parque das Águas of Caxambu.

4. CONCLUSIONS

In this work an inorganic chemical characterization of the mineral water springs from the Water Parks of Parque das Águas of Águas de Contendas, Cambuquira, Caxambu, Lambari and Marimbeiro, of “Water Circuit of Minas Gerais” was performed, determining the elements Ag, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, Se, Ti, V and Zn concentration, by EDXRF.

The elements that presented the highest mean concentrations in samples were the major elements Ba, Ca, Fe and K in all the studied parks. The cluster analysis grouped the mineral water samples by similarity of element concentration, even though the parks were located far from each other.

The present work evidence the importance of this study to ensure the potability and the maintenance of the natural characteristics of the mineral water from the “Water Circuit of Minas Gerais” due to the constant increase of mineral water consumption, the demand of hydromineral parks for thermalism and to ensure that the mineral waters made available for consumption in water parks are in accordance with current water potability standards in Brazil.

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