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Quantitative Analysis of Mineral Elements in Commercial Pineapple Juices by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

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Abstract: The consumption of fruit juice in the diet has increased in recent years because it contains mineral food supplements and other essential vitamins. In this study, sugar levels and mineral nutrient concentrations were evaluated in 92 commercial pineapple juice samples from Benin and France using inductively coupled plasma mass spectrometry (ICP-MS). The analysis of the data obtained reveals three ranges of concentrations relative to major elements or macro-elements (Ca, Mg), to minor elements or micro-elements (Mn, Fe, Ni, Cu, Zn), and to trace elements (Mo, V, Co, Cr). The concentrations of macro-elements and micro-elements (expressed in µg/L) vary from 11333 to 278000 for Mg, 95200 to 788000 for Ca, 536 to 25344 for Mn, 142 to 85612 for Fe, 5 to 253 for Ni, 5 to 1256 for Cu, and from 43 to 25862 for Zn. The trace elements were found in the concentration ranges (expressed in µg/L) of: 0.23 - 12.50 for Vanadium, 0.58 - 17.10 for Cobalt, 1.17 - 58.70 for Molybdenum and finally 4 - 70.5 for Chromium. The sugar levels in the various commercial juices collected in Benin and France vary from 11.0 to 18.5 Brix with an average value of 14.0 Brix. Apart from the heterogeneous nature of the juices produced in Benin production units, mineral and sugar levels were generally in accordance with international standards such as CODEX STAN 182-1993. The transformation of pineapple into fruit juice is a credible alternative for the improvement of pineapple exports, if the marketing strategy is better adapted and the local authorities support the manufacturers of the production chain to improve the quality of juices and highlight their excellent nutritional quality.

Keywords: Minerals, Juice, Pineapple, Benin, France, Codex Stan, ICP-MS

1. Introduction

Two varieties of pineapple, namely "Cayenne smooth" and "Sugarloaf", are known to be produced in Benin Republic. The vegetative cycle of pineapple covers a period from 15 to 24 months with their production being concentrated in the southern and central regions of the country, representing 10% of the territorial area inhabited by nearly 60% of the population [1]. Furthermore, an increase in the production and consumption of pineapple has been observed aided by the extension of its cultivation in new geographical areas of the country coupled with the increase in cross-border flows, through informal transactions, to neighbouring countries such as Nigeria, Burkina Faso and Niger. For instance, earlier in 20016, it contributed 1.2% to the Gross Domestic Product

(GDP) and 4.3% to agricultural GDP, or about 13 billions FCFA [1]. Apart from cotton and cashew with higher export potential, pineapple is another crop that can be exported. This is one of the reasons why the government of Benin Republic, in its strategy to fight against poverty, has made the revival of the agricultural sector one of its priorities.

Concerning pineapple, the goal is to increase substantial production of high quality crops and improve the marketing of the fresh fruits and its by-products in order to contribute to the diversification of exports [2]. Despite this renewed interest in this sector in Benin, in terms of its potential socio-economic and financial benefits, that part that has to do with pineapple is facing a number of challenges such as those related to the competitiveness of the commodity in terms of finished products meeting the standard requirements, especially the knowledge of nutritional value, for international market. Consequently, this study was carried out to investigate the concentrations of some minerals in extracted and bottled pineapple juices in Benin in comparison with those for other branded pineapple juices purchased from shopping outlets in France.

2. Materials and Methods

2.1. Sampling of Juices

Samples of pineapple juice were obtained from different processing units in Benin taking into cognisance place and dates of production, nature of the juice (cocktail or pineapple juice), the species of pineapple fruit (Cayenne smooth, Sugarloaf), etc. Samples of packaged and branded juice were also obtained from supermarkets in Pau, France for the purpose of comparison. A total of 85 samples of juice and a sample of pineapple syrup were obtained in Benin with 6 other pineapple juices purchased from supermarket in France were analysed. These samples were classified according to the different criteria that could influence the quality of juice. The inscriptions on the labels on the bottles containing the juice show several varieties but all Benin juices were natural without additives or additions of preservatives or sugar. All the samples for laboratory analyses were properly coded for easy identification. The location of transformation units and cultivation areas of pineapple are shown in figure 1 below.

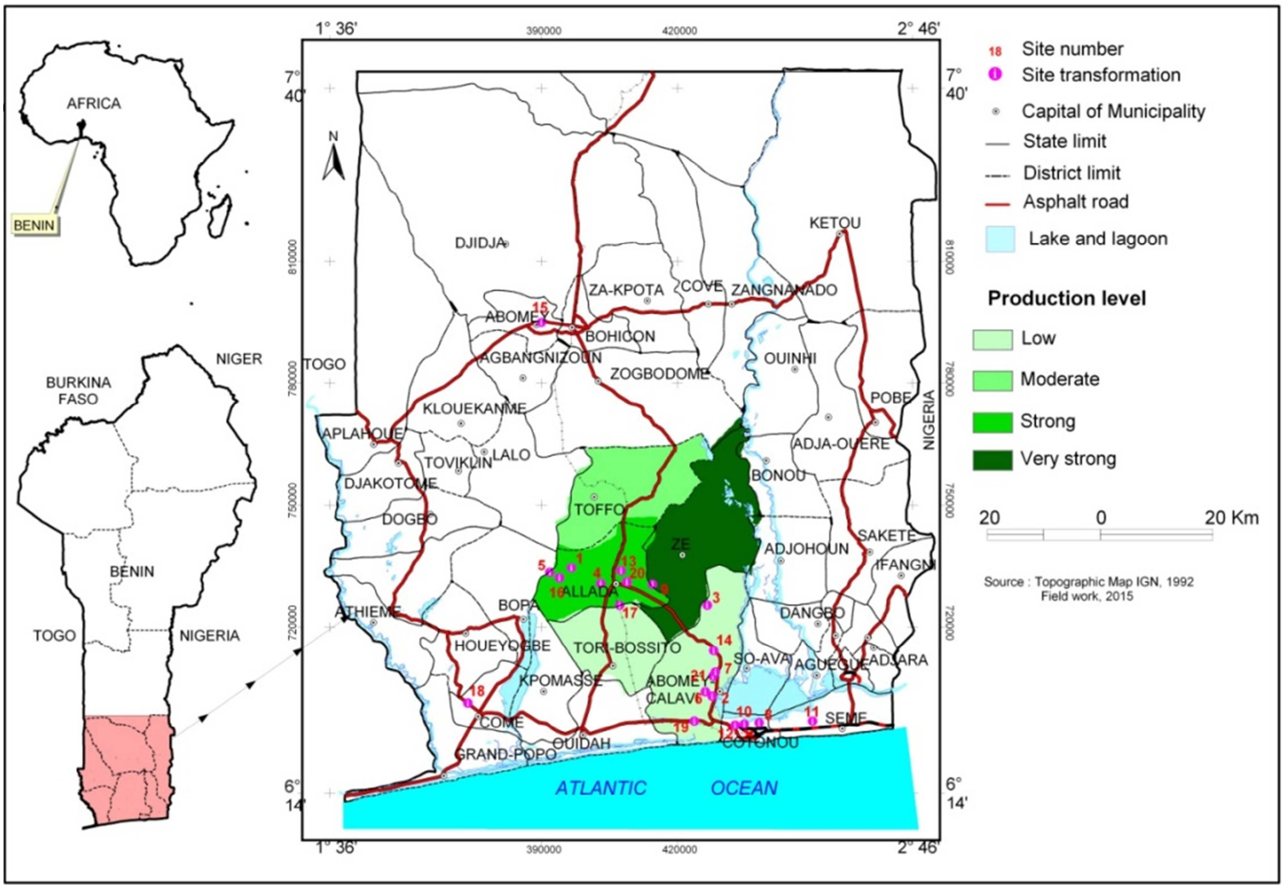

Figure 1. Location of growing areas of pineapple and juices production units in Benin.

The distribution of juices according to the nature of the fruit (pineapple and/or watermelon) gives us three groups namely: 100% pineapple juice (84 samples), PAS Pineapple and Watermelon cocktail (5 samples) and FRE cocktail (3 samples).

2.2. Choice of Sample Mineralization and Quantification Method

The processing of juice samples for the determination of concentrations depends on the chemical forms concerned (soluble, total, species derived from the mineral element) and the mineral elements. Different authors have used hydrostatic atomic fluorescence spectrometry [3], optical emission spectrometry with an inductively coupled plasma source [3] or mass spectrometry inductively coupled plasma source (ICP-MS) [3, 4, 5, 6] without special treatment of samples other than dry or wet incineration for determination of chemical elements in juices. In this study, juice samples were mineralized to destroy organic matter [3] due to high viscosity and high content of dissolved solids; this made it possible to avoid non-spectral difficulties (mainly matrix effects) and spectral interferences in the spectrometric measurements. Digestion of the fruit juice samples was done by DigiPrep digestion blocks with concentrated nitric acid (HNO_3) and 30% hydrogen peroxide (H_2O_2) [5] in a programmable oven with two levels of temperature (45 C and 90 C). An ELAN DRC Perkin Elmer apparatus equipped with a nebulizer was used with a Meinhart silica cyclonic chamber for spraying and continuous nebulization. The operating conditions were optimized daily using a standard 8-level aqueous solution (for calibration of the apparatus) containing: 0; 0.05; 0.1; 0.5; 1; 5; 20 and 100 ppb and internal standards for the control of isotope intensities. The internal standards used were indium (In), bismuth (Bi) and scandium (Sc) with 5ppb concentrations. Two types of reference materials (SRM NIST 1640a and SRM SLRS-5) were used to determine the percentages of recuperation.

First, we used the semi-quantitative method available with Perkin-Elmer ICP-MS instrumentation (Perkin-Elmer total Quant III) which allowed us to identify the levels of concentrations in juices from Benin and juices purchased in supermarkets in France. After, we use the quantitative method to detect the real contamination level of our samples. The method of analysis was "Total Quant": this is a unique software feature for ELAN ICP-MS systems to quantify 81 elements in a sample by interpreting the full mass spectrum. Total Quant is an ideal tool for semi-quantitative analysis during the development of the method; it is also used for the characterization of the final material. When using Total Quant, the spectral interpretation is performed automatically by the software, and the intensities were assigned to elements after correction of the interference on the individual isotopes. The intensities were compared to a stored response table to convert them into concentrations. Total Quant gives quantitative results typically +/- 25% of the real value in simple matrices.

This precision has been improved by the use of an external standard that corrects the "response table" used by the software. Internal standards, added to the sample and standard solutions, are mainly used in measurements made by plasma-based instruments to compensate for possible variations in ICP-MS performance.

2.3. Statistical Analysis

Statistical analyses were carried out with the aid of Statistical Package for Social Science (SPSS) Version 20.0 and Minitab Version 16.0. The statistical tools were those for calculation of the dispersion characteristics and plotting of the moustache boxes and logit including analysis of variance. The data were pre-processed using the whisker boxes to identify recording errors and concentration differences between different processing units.

3. Results and Discussion

3.1. Sugar Levels in Pineapple Juice

Small producers in Benin are presently struggling to meet the criteria set for standard products particularly for export. This can be seen in the fact that the yields and volume of pineapple were high but less than 2% of the pineapple produced is exported [4]. It is important to state that the conversion of pineapple into fruit juice is an opportunity for producers from Benin to be able to export more pineapple in strict compliance with standards, in this case, the sugar levels expressed in Brix degree. The amount of sugar was determined using a prism from the refractive index. It expresses the amount of dry matter (in grams) per 100 grams of liquid. According to French Directive 93/77 of 21 September 1993 and CODEX STAN 247-2005, the minimum and maximum sugar levels in Brix degree of a commercial pineapple juice were 12.1 and 12.8 respectively. For *Citrullus lanatus* watermelon juice, the minimum sugar level in Brix degree is 8.0 (CODEX STAN 247-2005). In practice, corrected Brix is used which takes into account that juice acids do not contribute exactly to Brix in the same way as pure saccharose. But in a first approximation, we evaluated the contents without this correction for pineapple juices.

For juice comparison purposes, we determined the sugar content of pineapple juices sampled in manufacturing units in Benin and some samples purchased in supermarkets in France. For all these juices, the average total solid content was 14.0 Brix (Table 1), which was above 12.8 Brix, the international reference value. According to the results of the 92 samples presented in the following Table 1, the sugar levels vary from 11.0 to 18.5 Brix.

Table 1. *Dispersal characteristics of total dissolved solids levels (sugar) in pineapple commercial juices.*

Variable (Brix)	Mean value	SD	Minimum	Maximum	Percentiles		
					25	50	75
Total dissolved solids	14.0	1.8	11.0	18.5	13.0	15.0	15.0

SD: Standard Deviation

These results are in agreement with those of Miele et *al*., (2014) [2] for grape juices produced by biological processes. The first quartile was 13.0, which means that at least 75% of the samples have a sugar concentration higher than Codex

Standard (CODEX STAN 247-2005) for pineapple juice, and all the watermelon-based juices are also in compliance with the corresponding standards (8 Brix).

Table 2. *Average total dissolved solids (sugars) in commercial pineapple juice and syrup per unit (Brix).*

Unit	**ALA**	**ALO**	**BRA**	**CHA**	**FRE**	**FRU**	**INN***	**JAF***	**JUA**	**JUD**	**JUS**
Rate	14.2	15.2	14.7	14.7	11.8	14.1	11.3	12.3	14.8	15.2	13.7
Unit	*JUV*	*LAS*	*OJA*	*PAS*	*SAN*	*SIR***	*TRO*	*VIB**	*VIP*	*VIT*	*MEAN*
Rate	12.7	13.3	13.4	12.1	16.0	12.6	15.2	11.3	13.1	15.3	*14.0*

* Juices from France ** Syrup R^2 (Adjusted) = 54.07% $p < 0.001$.

All the units produce juices according to the international standards in the matter with the exception of the FRE, VIB and INN juices, which have (unadjusted) rates slightly lower than the standards because of the dilution of the French commercial juices (Table 2). Also, according to that standard, fruit juices and nectars must have the characteristic colour, aroma and flavour of the juice of the variety of fruit from which they were obtained. This requirement is also satisfied for pineapple juices made in Benin and those obtained from French supermarkets.

3.2. Concentration Ranges of Minerals in Commercial Juices

The results in Tables 3 and 4 shows three ranges of concentrations. These are: major elements or macro-elements (Ca, Mg), minor elements or micro-elements (Mn, Fe, Ni, Cu, Zn) and trace elements (Mo, V, Co, Cr). However, the exploratory factor analysis identified four groups of variables that covariate with two representations that gather the parameters into two main groups, namely macro and micro-elements on one side and trace elements and degree Brix on the other side.

Table 3. *Concentration ranges (μg/L) of major minerals and micro-elements in pineapple juice and syrup.*

	Variables (μg/L)						
	Mg	***Ca***	***Mn***	***Fe***	***Ni***	***Cu***	***Zn***
Average	193558	223616	9551	5811	80	341	1313
SD	36443	105092	4960	15809	38	151	3152
Minimum	111333 (JAF1)	95200 (JAF2)	536 (VIP3)	142 (VIT5)	5 (VIP3)	5 (VIP3)	43 (VIP3)
Maximum	278000 (JUA1)	788000 (JUD3)	25344 (FRU5)	85612 (OJA1)	253 (OJA3)	1256 (JUS2)	25862 (JUD3)
Percentiles							
25	172000	163250	5872	1486	50	252	591
50	201000	219500	8707	1861	80	325	712
75	210750	252500	11904	2606	96	418	969

All major and trace elements have concentrations above the quantification threshold with the exception of vanadium contained in 14 samples (Table 4) the concentrations which were below the quantification threshold corresponding to about 25% of the samples (1st quartile). Metal concentrations in fruit juice samples varied widely depending on the units that produced them (Table 3 and 4). Concentrations ranged from 11333μg/L (JAF1) to 278000μg/L (JUA1) for Mg, from 95200μg/L (JAF2) to 788000μg/L (JUD3) for Ca, from 536μg/L (VIP3) to 25344μg/L (FRU5) for Mn, from 142μg/L (VIT5) to 85612μg/L (OJA1) for Fe, from 5μg/L (VIP3) to 253μg/L (OJA_3) for Ni, from 5μg/L (VIP_3) to 1256μg/L (JUS_2) for Cu and from 43μg/L (VIP_3) to 25862μg/L (JUD_3) for Zn. These strong variations explain the high values obtained for standard deviation for Zn. The mean concentrations obtained show the predominance of Ca with an average value of 223616μg/L followed by Mg with an average concentration of 193558μg/L. Mean concentrations of Mn, Fe, Ni, Cu and Zn were 4960, 15809, 38, 151 and 3152μg/L respectively.

Table 4. *Concentration ranges (μg/L) for trace elements in pineapple juices and syrups.*

Parameters		**V**	**Cr**	**Co**	**Mo**
Number of samples	Valid*	78	90	92	92
	Not detected	14	2	0	0
Average		1.23	18.26	5.94	24.74
SD		1.85	15.99	2.56	13.25
Minimum		0.23	1.40	0.58	1.17
Maximum		12.50	70.50	17.10	58.70
Perentiles					
	25	0.47	8.22	4.40	15.20
	50	0.69	13.10	5.61	19.05
	75	1.22	22.53	6.87	31.88

*Samples with concentrations below the limit of quantification were not considered in the statistical analysis.
SD: Standard Deviation.

Elements such as vanadium (V), cobalt (Co), molybdenum (Mo) and chromium (Cr) were relatively in low concentrations or absent in the analysed fruit juices. These trace elements were found in the following ranges: from 0.23µg/L (CHA1) to 12.50µg/L (JUD3) for V, from 0.58µg/L (CHA4) to 17.10µg/L (JUD3) for Co, and finally from 1.17µg/L (CHA4) to 58.70 (CHA5) for Mo, and 1.40µg/L (FRE4) to 70.50µg/L) for Cr. Mean values were 1.24µg/L, 18.26µg/L, 5.95µg/L, 24.74µg/L and 15.23µg/L for V, Co, Mo and Cr respectively.

A classification of the elements in descending order of the concentrations gives Mg>Ca>Mn> Fe> Cu> Zn> Ni for the major and minor elements and Mo> Cr Co> V for the trace elements. These results are consistent with a synthesis of scientific results from different authors [3, 4, 6, 9, 10, 13, 14, 17] who obtained the ranges of concentrations of the following elements: Mg (7000µg/L - 750000µg/L); Ca (140µg/L - 980100µg/L), Mn (60µg/L - 23000µg/L); Fe (9µg/L - 179200µg/L); Ni (40µg/L - 73370µg/L); Cu (ND – 490µg/L); Cr (ND - 2767µg/L) and Zn (40µg/L - 545900µg/L) where ND means "not detected".

The mean concentration of Mg was close to that obtained by [9], whereas that of Zn was close to the value obtained by [10] in pineapple juices but widely differed from those of [11]. The highest grades were obtained by [11] for Fe, Ni and Zn. Concentrations for Ni were slightly lower in commercial pineapple juices from Benin whereas Cu shows slightly higher values compared to the literature with the exception of [8] which obtained a high value (2910µg/L) for grape juice cultivated according to biological processes.

All things considered, the major elements (Mg and Ca) and the minor elements with Mn and Fe at the upper end were strongly present in the juices. The mean value of Ni (which was equal to the median) was greater than the maximum value of the literature [3, 4, 5, 6, 9, 10].

On the other hand, the Ca and Mg content were higher than those obtained by [8] in grape juice, the same was true for Fe, Mn and Zn. On the other hand, Cu values were lower than those obtained by [8]

The concentrations of Ca were generally distributed around the median value (219500µg/L) which was close to the mean value (223616µg/L) with the exception of JUD2 (593000µg/L), JUD3 788000µg/L) and VIP3 (755000µg/L) which were well above the two reference values (Figure 2).

The distribution of Mg concentrations around the median (201000µg/L) and the mean (193558µg/L) was more uniform than that of Ca. Some samples slightly deviate JUA1 (278000µg/L), CHA1 (268000µg/L), CHA2 (276000µg/L) and OJA4 (273000µg/L) at the upper end of the mustache box and JAF1 the lower end of the mustache box (Figure 2). The best rates of Mn (Figure 3) could be explained by the processes applied by the FRU unit which displays the highest Mn values for FRU4, FRU5 and FRU6, with the respective concentrations 25225µg/L, 25344µg/L and 24981µg/L, followed closely by VIB juice (VIB2, 19950µg/L) while the median value was 8707µg/L and the mean value was 5811µg/L.

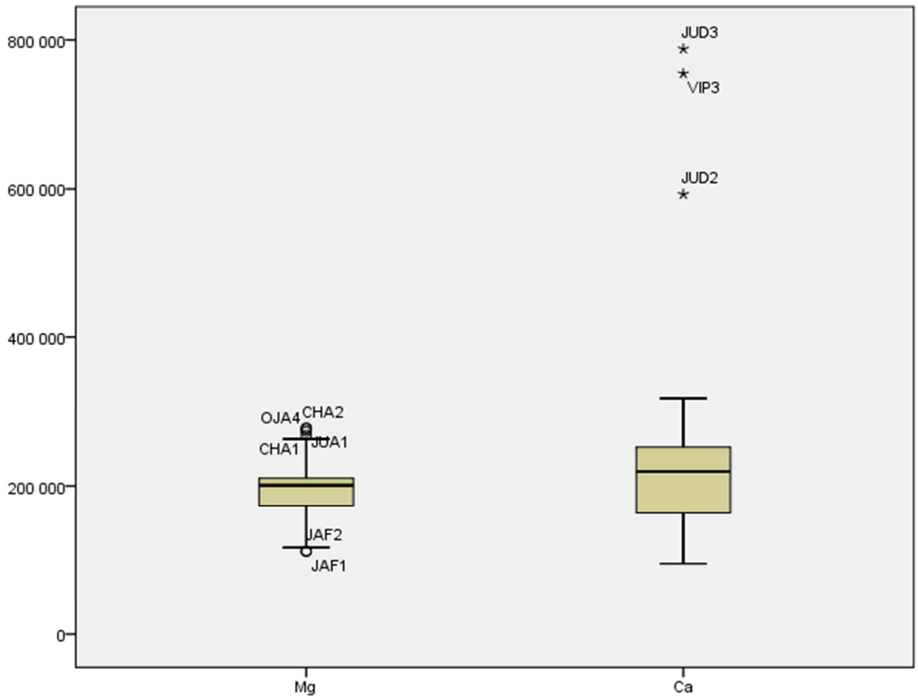

Figure 2. *Mustache box representation of macro-element concentrations (Ca and Mg).*

These strong variations in concentrations could be attributed to juice production processes. Indeed, [6] have noted that laboratory-extracted juices generally contain less Mn than commercially purchased juices and attribute this to extraction processes rather than the acidity of the soils on which the fruits were grown.

Fe concentrations in juices produced by the OJA unit (Figure 3) vary from 41635µg/L (for OJA2) to 85612µg/L (for OJA1) and were significantly higher than those of other processing units; the third quartile (2606µg/L) was much lower (Table 3). All juices in this unit (OJA) exceeded the threshold of 50,000 µg/L prescribed by the beverage quality standards with the exception of OJA2 (Figure 3).

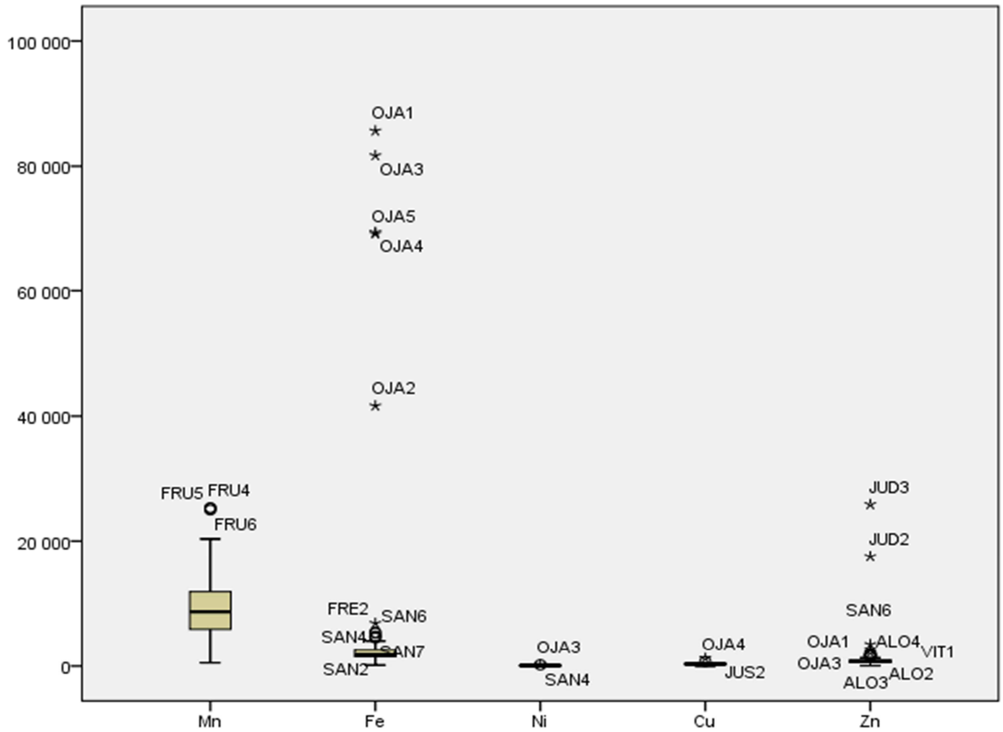

Figure 3. *Box-mustache representation of micronutrient concentrations (Mn, Fe, Ni, Cu and 254 Zn).*

Although Zn levels were relatively low, we observed a heterogeneity of concentrations with JUD2 and JUD3 (17508µg/L and 25862µg/L respectively) well above the average (1313µg/L), followed by SAN6, OJA3 and OJA1 (3501µg/L, 1649µg/L and 2627µg/L) while the 3rd quartile (75% of the values were below this value) is 969µg/L. The relatively low concentration Ni and Cu elements were more homogeneous in pineapple juices with an average of 80µg/L and 341µg/L respectively and a median of 80µg/L and 325µg/L respectively (Table 3). Except OJA3 (253µg/L) and SAN4 (196µg/L) for Ni and OJA4 (4541µg/L) and JUS2 (1256µg/L) for Cu which deviate from the mean and median, all other samples have concentrations concentrated around these two values.

In conclusion Benin's pineapple juices were rich in minerals and especially in Ca, Mg, Mn and Fe. These juices could be used to improve nutritional health in all social strata. Indeed, various authors have shown that maternal and infant mortality and morbidity are directly or indirectly related to malnutrition related to mineral deficiency [11, 12]. The antioxidant properties of certain minerals contained in the fruit juices help protect human health from free radical damage and oxidative stress, and thereby prevent cardiovascular or degenerative diseases, as well as certain cancers. The mineral elements exert primordial functions in the biochemical processes of the organism: they regulate the metabolism, facilitate the release of energy and ensure important functions in the synthesis of bones and tissues [11, 12, 13, 14].

Micronutrient deficiency is a dangerous form of malnutrition caused by insufficient intake of essential vitamins and minerals. About 30 minerals are known to be essential for life and pineapple juices contain plenty of them. While some of them such as Ca, Mg are needed in more or less significant quantities (macronutrients), others are in the order of trace or ultra-trace (trace elements). Elements such as Cu, Fe, Ni, Zn and Mn were at the upper end of this scale of trace elements and play an important role in biological systems. This was the case of the chemical elements V, Mo, Cr and Co which are necessary to smaller proportions compared to the first ones. The concentrations of these elements in the different samples were low (<80µg/L) but were not uniform from one unit to another; they vary from 0.23µg/L (CHA1) to 12.50µg/L (JUD3) for V, 1.40µg/L (FRE4) to 70.50µg/L (FRU3) for Cr, 0, 58µg/L (CHA4) to 17.10µg/L (JUD3) for Co and from 1.17µg/L (CHA4) to 58.70µg/L (CHA5) for Mo (Table 4). However, some units were distinguished by relatively higher values than others (Figure 4). This was JUD2 and JUD3 for the V and Co, OJA1, OJA3 and OJA4 for the Co, JUS1 and JUS3 for the Cr and CHA6 and CHA5 for the Mb. In isolation we can add to this list FRE2 and JUA2 for the V and ALA1 for the Co.

The ranges of concentrations were in the same order of magnitude compared to previous work [3, 4, 5, 6, 9, 10] except [5] which recorded for Cr values of 2767µg/L and [15], who obtained a value of 370µg/L for Co. However, for V, [7] recorded 5µg/L whereas [15] obtained 52µg/L.

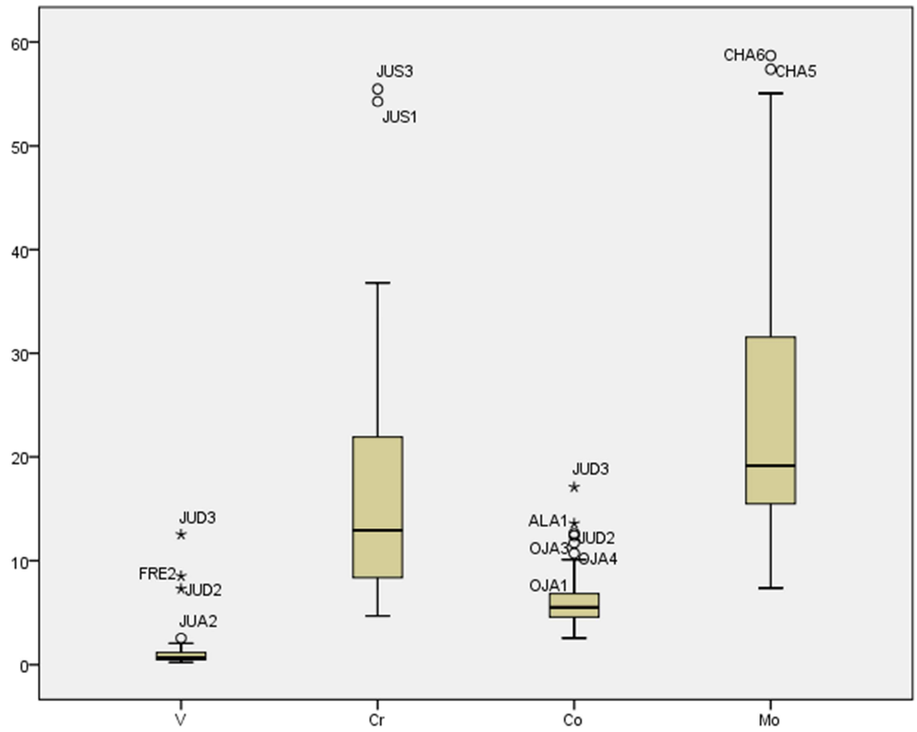

Figure 4. *Box-mustache representation of trace element concentrations.*

The average daily requirements for mineral elements are presented in Table below 5, showing a coherence of nutritional requirements with the composition of pineapple juices in mineral elements.

Table 5. *The average daily needs in mineral elements.*

Elements	Mg	Ca	Mn	Fe	Co	Cu	Zn	Se	V	Ni	Cr	Mo
RDI (mg)	310	1000	10	18	2	0.9	8	8	1.5	0.25	0.025	0.034

RDI: Recommended daily intake

According to the classification of minerals, the macro-elements are those needed in quantity greater than 50 mg/day, among these are calcium and magnesium. The trace elements are those needed in quantity less than 50 mg/day, namely: iron, zinc, copper, manganese, molybdenum, etc. The data obtained show that the consumption of pineapple juice at the rate of one litre per day distributed between meals would effectively meet the daily needs of minerals. Because of the large amounts of essential and physiologically important elements they contain, fruit juices often prove to be rich sources of nutrients and valuable dietary supplements in the event of mineral deficiencies [3, 7, 11, 13-16]. Considering the total concentrations of elements, some studies relating to the elementary analysis of fruit juices reveal that the daily consumption of fruit juice can clearly shelter from the recommended daily doses (RDI) for certain nutritionally important elements required for infants, children, pregnant women and adults [13, 15, 17, 18].

3.3. Comparative Analysis of Minerals in Commercial Juices from Benin and France

One of the objectives of this research was to analyse the average concentrations per unit of production in order to study the compliance of Benin's juices with international standards with reference values the concentrations of juices sampled in France and analysed in the same conditions. Tables 6 and 7, related to the variation of the composition of juices in minerals according to the production units, present the averages of the results of the analyses by unit of manufacture, by country and the general average of the concentrations in minerals. Overall, the concentrations of macro-elements, micro-elements and trace elements in the juices of Benin units were above these reference values except for Mn. This could be the consequence of the high Brix value which represent the dry matter content and which shows that French commercial juices have been diluted. The reversal of the trend for Mn can be seen through the average concentration of Mn in Benin juices equal to 9472µg/L, which was lower than that in French commercial juices, which was 11343µg/L and the average which was equal to 9551µg/L. This is explained by the high values of this element in commercial VIB juice from France with an average of 19631µg/L, which was closely followed by FRU juice from Benin with an average of 18515µg/L. Moreover, the vanadium level in the juices was less than 10µg/L, the Cobalt 15µg/L and the Molybdenum 50µg/L except the

TROP juices with an average molybdenum content of 53.55µg/L. It should also be noted that the FRU juice contains practically no vanadium (the content of which was below the threshold of quantification).

3.4. Analysis of the Homogeneity of Commercial Juices in Relation to Mineral Composition

The homogeneity analysis will consist in studying the variability of the results averages of the quantitative analysis of minerals and sugar levels around the median value for the juices of each unit of production in relation to the sampling parameters, the date of production, the area of cultivation and/or production of the juice, which were generally close, will also be discussed. According to [17], pineapple growing areas in Benin are located in five of the eight Atlantic townships of the Atlantic Department. The same was true of exporters and intermediaries who were located in the pineapple growing areas in the five townships of Abomey-Calavi, Zè, Allada, Tori and Toffo. Wholesalers and retailers were based in five markets: SèmèKraké (in Sèmè-Kpodji), Dantokpa (in Cotonou), Zè, Sékou (Allada) and Sèhouè (Toffo). Sèmè-Kraké and Dantokpa are the main sources of supply for the regional market since they are often visited by local and regional customers from Nigeria, Ghana, Burkina Faso, Mali and Côte-d'Ivoire. The fruit and juice pineapple processors are located in the Atlantic and Littoral Departments; but most of them are not located in the pineapple producing areas, but in the Littoral Department near the regional markets. Table 7 related to the variations in the composition of commercial juices and syrups in mineral elements as a function of the location of the production units shows that the pineapples fruits used in Porto-Novo are very rich in Zn and those of Allada district are particularly rich in Fe. This shows that the nature of the soils of the growing regions influences the composition of the major minerals and micro-elements of the produced juices (Table 9).

Table 6. *Variations in the composition of commercial juices and syrups in mineral elements according to the production units from.*

Variables	JUICE MANUFACTURING UNITS (LABEL)											
(µg/L)	ALA	ALO	BRA	CHA	FRE	FRU	INN**	JAF**	JUA	JUD	JUS	JUV
Macro-elements												
Mg	230500	217500	207333	227667	150200	195833	117500	111667	193333	200667	200667	165000
Ca	231000	239000	248000	241667	150400	263500	129000	95833	156500	525333	227000	168167
Micro-elements												
Mn	11631	6072	9369	8336	3215	18515	5289	9110	10480	10868	15374	7543
Fe	1714	1327	2321	1543	2138	3048	1967	1576	1972	3024	2491	1269
Ni	115	58	50	68	44	130	30	28	116	88	98	65
Cu	419	276	290	272	295	372	378	404	370	476	649	242
Zn	703	1099	645	605	61	643	1107	986	673	14745	1044	755
Trace elements												
V	0.35	0.43	0.49	1.4	3.96	<QL*	0.64	0.92	1.39	7.27	1.23	0.61
Cr	10.41	10.34	10.94	6.18	3.77	64.97	15.7	9.21	7.03	24.47	43.17	6.62
Co	8.80	5.37	4.83	4.31	4.65	6.09	4.66	5.13	6.98	12.53	7.12	4.75
Mo	11.65	16.07	32.10	28.66	13.24	41.92	13.10	10.40	19.68	31.23	30.8	17.48

* Lower than the threshold of quantification ** Juices from France

The one-way ANOVA model was used for statistical processing, and the calibrated averages were significant at $p < 0.001$ (32% $<$ adjusted R^2 $<$ 59%) except for Fe 385 with adjusted $R^2 = 93.05\%$.

Table 7. *Variations in the composition of commercial juices and syrups in mineral elements according to production units.*

Variables	Juice Production Units									Average/country		OverallAverage
(µg/L)	LAS	OJA	PAS	SAN	SYR**	TRO	VIB*	VIP	VIT	BEN	FR	
Macro-elements												
Mg	240333	223800	193167	216333	141667	175000	173500	171429	198167	198827	134222	193558
Ca	244333	257400	160333	244778	143667	270500	169000	257000	205500	231784	131278	223616
Micro-elements												
Mn	12995	11856	7966	4756	3865	14166	19631	9247	11819	9472	11343	9551
Fe	1335	69496	1519	4276	1517	2098	2359	2147	1345	6156	1967	5811
Ni	76	121	76	95	49	99	23	83	75	84	27	80
Cu	333	486	360	416	122	431	509	197	324	347	430	341
Zn	720	1597	770	1324	558	854	926	491	986	1349	1006	1313
Trace elements												
V	0.57	1.14	0.34	1.41	1.26	0.55	1.06	1.35	0.57	1.44	1.12	1.22
Cr	5.9	27.28	16.72	18.99	36.8	9.79	11.05	21.42	16.75	18.99	11.99	17.98
Co	7.48	10.6	6.8	4.48	2.55	3.97	3.00	6.15	5.42	6.49	6.02	5.97
Mo	19.10	21.62	14.40	40.50	7.39	53.55	12.65	24.84	21.00	25.76	23.87	24.74

BEN: Benin country

FR: France country *Samples from France **Syrup sample

Table 8. *Variations in the composition of commercial juices and syrups in mineral elementsaccording to the location of the production units.*

Townships/districts	Ns	Concentrations (in µg/L)							Average (Brix)
		Mg	Ca	Mn	Fe	Ni	Cu	Zn	
ABOMEY	6	193333	156500	10480	1972	116	370	673	14.8
AKASSATO	6	207333	248000	9369	2321	50	290	645	14.7
ALLADA	13	218077	252154	10587	27764	93	379	1025	14.3
AVAKPA	9	216333	244778	4756	4061	93	369	1278	16.0
CALAVI	8	202500	178000	8883	1567	85	375	753	12.7
COME	6	165000	168167	7543	1269	65	242	755	12.7
COTONOU	7	171429	257000	9247	2147	83	197	491	13.1
EKPE	6	217500	239000	6072	1327	58	276	1099	15.2
FR	6	134222	131278	11343	1967	27	370	1006	11.6
LOGBOZOUKPA	6	195833	263500	18515	3048	130	372	643	14.1
PORTO-NOVO	9	177037	285815	6852	2344	62	359	5335	13.1
SEKOU	3	200667	227000	15374	2491	98	649	1044	13.7
SYR* (ABOMEY)	1	141667	143667	3865	1517	49	122	558	12.6
ZE	6	198167	205500	11819	1345	75	324	986	15.3

Ns: Number of samples collected. * Syrup was manufactured in Abomey

Table 9. *Presentation of the samples with their identification codes.*

TOWN/COUNTRY	Ns	SAMPLES IDENTIFICATION NAME
ABOMEY	7	JUA1- JUA6, SYR
AKASSATO	6	BRA1– BRA6,
ALLADA	13	CHA1 – CHA6, OJA1– OJA5, TRO1– TRO2
AVAKPA	9	SAN1– SAN9
CALAVI	8	ALA1– ALA2, PAS1– PAS6
COME	6	JUV1– JUV6
COTONOU	7	VIP1 – VIP7
EKPE	6	ALO1– ALO6
FRANCE	6	JAF1– JAF2, INN1– INN2, VIB1– VIB2
LOGBOZOUKPA	6	FRU1– FRU6
PORTO-NOVO	9	FRE4– FRE5, LAS, JUD1– JUD3
SEKOU	3	JUS1– JUS3
ZE	6	VIT1– VIT6
TOTAL	92	

Ns: Number of samples

In general, juices manufactured in urban areas, far from production sites, were characterized by the lowest sugar levels at the limit of the required threshold (Table 8). These are the cities of Cotonou (13.1 Brix), Porto-Novo (13.1 Brix), Abomey-Calavi (12.7 Brix) and Comé (12.7 Brix) unlike rural areas such as AVAKPA (16.0 Brix). The juice production units of these localities proceeds either to systematic Brix corrections or the fruits were affected by the conditions of transport and conservation before processing into juice. This thesis of degradation of the quality and especially of the sugars the atomic links of which were destroyed is more concordant for several reasons. According to Hotegni *et al.* [11, 12, 17, 20] the poor transportation system and poor storage conditions at the wholesaler and processor level and the lack of transport crates would be one of the major causes of significant fruit loss. According to these authors, pineapple is delivered under uncontrolled conditions in "taxis" or "bachées" by independent drivers hired by buyers. Also, fruits were exposed to sunlight for a few hours, loading in trucks side by side and unconditioned transport conditions would affect fruit quality Crisosto *et al.*, 1995 cited by [7]. However, it is well known that temperature conditions affect the shelf life of fruit Nunes and Edmond 2002 in [7]. According to [12], the optimal storage temperature for a long shelf life of pineapple is 10 °C while the ambient temperature in the region fluctuates between 25 °C and 31 °C.

4. Conclusion

Globally, the major elements (Mg and Ca) and the minor elements (Mn, Fe, Ni, Cu, Zn) were strongly present in pineapple juices made in Benin. For all juice samples, Mn and Fe were the most quantitatively represented micro-elements, while Ni, Cu and Zn were weakly detected, with the exception of juice of the JUAN unit where Zn is strongly detected. It is noted that the soils of culture have a determining role in the composition of the juices as well as the conditions of transport which would affect the quality of the juices, particularly with regard to the low level of Brix degree.

The basic analysis shows that fruit juices in Benin have a varied mineral composition with very high levels of certain elements in some regions. These juices could be used as dietary supplements [8] to stem malnutrition and improve nutritional health in all social strata.

Trace and minor elements such as Co, Cr, Cu, Ni, Zn and Se contained in juices do not contribute significantly to nutritional requirements. The process of concentrating to obtain pineapple syrup appears to cause a loss of sugars and a significant variation in mineral concentrations either by loss or gain. Further work may be carried out in the direction of controlling these factors of influence on the nutritional quality of pineapple juices and syrups.

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