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# Analysis of pesticides and quality of citrus fruits in the internal market of Corrientes- Argentina

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## ABSTRACT

Corrientes, among the main citrus producing provinces, contributes 23 % to the national production. The use of very diverse chemical products in the agricultural production to control plagues and diseases, to diminish risks and losses of the agricultural systems, has been a permanent challenge. The use of such products is due to the biocidal properties and their selectivity. The objective was to evaluate the presence of pesticide residues in the juice and parameters of fruit quality by physicochemical characteristics. Three samples were taken in two consecutive years collecting samples by five replicates, evaluating the presence of residues of pyrethroid pesticides (cypermethrin, deltamethrin, alphacypermethrin, lambdacyhalthrine) carbamates (aldicarb, carbofuran) and organochlorines (endosulfan) and the variables: bark thickness, diameter equatorial, fresh mass, content and percentage of juice, total soluble solids, total acidity and maturity index. The fruits did not present detectable toxic residues. The quality parameters of Valencia orange fruit, mandarins Nova, Murcott and lemon Eureka presented adequate fruit size, high amount of juice and °Brix that exceed the standard levels. The highest juice values and maturity index were found in orange and tangerines, which were of interest for both, fresh consumption and industry.

**Key words**: Organoleptic properties, physicochemical properties, waste, contamination

# INTRODUCTION

The Argentine Republic shows a continuous growth of the citrus sector, both in fresh and processed fruits. Corrientes placed as one of the main producing provinces of oranges and tangerines in northeastern Argentina, contributing 23 % of national production [(1)]. The citrus industry in the province focuses on the production of fruit for fresh consumption. The destination to industry is secondary or rather it is a byproduct. The other point is that in the primary production phase there would be a first difference between production for export and domestic market. In principle, in the first case, depending on the region of destination, there are different production requirements to export; Thus. The distinction between one destination and another begins in the field. Depending on the export fruit quality parameters, there may be fruit that does not meet the specifications, therefore, from an export package; certain fruit can be re-destined to the domestic market or industry [(2)]. In turn, the consumption of fruits and vegetables is increasing, due to awareness in healthy diets, some authors say that it is advisable to promote the consumption of fruits and vegetables by eight members of the International Alliance of Associations and Movements "5 a day” (AIAM5) to achieve its objectives to promote the consumption of fruits and vegetables [(3)]. Insufficient intake of fruits and vegetables is a fundamental and common risk factor for several chronic noncommunicable diseases. The low intake of fruits and vegetables causes 1.7 million deaths per year, mostly due to cardiovascular diseases, cancer, respiratory diseases and diabetes. Regular consumption of fruits and vegetables has been associated with a lower risk of disease and mortality [(4)].

On the other hand, the current use of pesticides has provided undoubted improvements in production performance. These compounds comprise a large number of substances, with different levels of persistence and selectivity [(5-7)], which are divided into different classes (herbicides, fungicides, insecticides, etc.). However, the incorrect application of pesticides can leave residues in food, which has led different governments to establish maximum residue limits (MRLs) for food. In Argentina, the General Guidelines for the coordination of safety of products of plant origin, as well as the fruit and vegetable control system and the monitoring program for pesticide residues and microbiological contaminants in fruits and vegetables, are specified by SENASA (8) in pursuit of environmental and food security. Brazil is the largest producer of orange juice and exporter in the world (9,10); In 2012, the export of orange juice from Brazil to the United States was banned, due to the presence of carbendazim (fungicide) residues (11,12).

At present, an attempt is being made to find a viable solution in the biological fight against pests and in the use of low-polluting pesticides. Government initiatives have been developed and implemented, such as production models, based on "good agricultural practices" (GAP) and "food safety", which have had remarkable results in commercial agriculture, especially in horticulture export. In this agricultural activity, the concern of the producers, caused by the possibility that their exportable products are returned by containing pesticide residues, is manifested in safety policies and in a tendency to use compounds with less persistence and residuality, which guarantee the quality established in the markets, as consumers expect a constant supply of clean, high quality, healthy and safe food (13,14).

Among fruits and vegetables, citrus fruits stand out for an important content of flavonoids and phenylpropanoles, as well as ascorbic acid, all of these components being responsible for providing beneficial health-related qualities (15). There are several parameters indicative of fruit quality. Thus the fruits can be classified externally according to their size. On the other hand, the juice content, of total soluble solids, the acidity of the juice as well as the firmness of the pulp, are important attributes of the fruit's internal quality. In the particular case of citrus fruits, to know the degree of maturity and define the moment of its collection, the maturity index is calculated; value resulting from the ratio between the total soluble solids content/100 g of juice, with respect to titratable acidity (2).

Cumulative assessments of acute dietary risk of organophosphates (OP), carbamates (CB) and pyrethroids (PY) were carried out for the Brazilian population, obtaining residue data for 30786 samples of 30 foods from two national monitoring programs. In this study they found that orange juice contains mainly OP (14).

Studies on the cumulative chronic intake of organophosphates, carbamates and pesticides pyrethroids and pyrethrins in the Valencia region, through the consumption of fruits and vegetables, showed that of a total of 752 fruits and vegetables analyzed between 2007 and

2011, residues were found of pesticides in 63 % of the samples from Valencia-Spain. Of these, only 3 % exceeded the maximum residue limits established by law. The most frequent of the pesticides detected were carbendazim, chlorpyrifos and lambdacyhalothrina. The accumulated chronic intake of pesticide residues analyzed would be relatively low compared to the acceptable daily intake. Therefore, the safety of Valencian consumers seems to be under control in terms of chronic cumulative pesticide intake, through the consumption of fruits and vegetables [(16)].

The objective of this work was to evaluate the presence of pyrethroid, carbamate and organochlorine pesticide residues; as well as the quality through its physical and chemical characteristics of the fruits of orange, tangerine and lemon that enter the internal market of the city of Corrientes and establish associations between the different properties analyzed.

# MATERIALS AND METHODS

Different samples were taken, coming from different areas adjacent to the Correntina capital (Argentina), San Lorenzo, Saladas Department, Santa Rosa, Concepción Department, Mocoretá (Corrientes) and Posadas (Misiones), which entered the Market sales lines Central, destined for internal consumption. During the harvest season, three annual samples were carried out, for two consecutive years, 2016-2017 (Table 1).

Fruits from the central market of Corrientes were randomly selected. Each sample was composed of 15 fruits and five repetitions for each citrus species: Lemon Eureka, Valencia orange and Nova mandarin and Murcott mandarin.

**Table 1**. Sampling dates considering the different species

| Samples | Jan | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| N. Valencia | | | | | | | x | | x | | x | |
| M. Murcott | | | | | | x | | x | | x | | |
| M. Vova | | | | x | x | x | | | | | | |
| L. Eureka | | | x | | | x | | | | x | | |

For the analysis of agrochemicals, the gas chromatography technique was used, with two detectors. For the detection of chlorinated and pyrethroid agrochemicals, the Electron Capture Detector (ECD) was used and for phosphorus analysis and, in this case, for the specific carbamate under study (carbofuran), the Nitrogen-Phosphorus detector (NPD) [(17)].

We worked with pesticide standards of purity greater than 95 %. Stock solutions were prepared in concentrations close to 500 µg $mL^{-1}$ in acetonitrile or methanol and stored in amber bottles at -20 °C. The pesticide mixture is prepared in methanol, taking different volumes of each of the stock solutions until a concentration range between 0.64 and 9.95 µg $mL^{-1}$ is obtained. This solution is stored in an amber bottle at -20 °C. The solvents used in this study will be PAI ACS HPLC grade. For extraction tests, QuEChERS Restek Q-Sep ™ salts were used and Restek dSPE Q-SepTM adsorbents were used for cleaning the extracts. Triphenyl phosphate (TPP) was used as an internal standard for the phosphorus nitrogen detector (tris-(1,3-dichloro-propropyl) phosphate for the electron capture detector.

For the determination of the residues in the various citrus matrices, the previous treatment of the samples was carried out taking into account the nature of the analyte (s) to be evaluated and the chromatographic system to be adopted. The QuEChERS method was used (English acronym for Quick, Easy, Cheap, Effective, Rugged and Safe [fast, easy, economical, effective, solid and safe]), in which the samples were previously treated with NaCl and $MgSO_4$ and acetonitrile, then the elimination of interference.

For the citrus fruit samples, the extractive process applied: modified QuEChERS extractive method for fruit samples and subsequent determination of the analytes by GC are detailed below. In a 50 mL centrifuge tube, the fruit juice is exactly mass, approximately 10 g, 5 g of $Na_2SO_4$, 1 g of NaCl and 10 mL of acetonitrile are added. Stir vigorously for 1 minute and then centrifuge 10 minutes at 4000 rpm. The samples are taken to the freezer until freezing of the aqueous phase and the supernatant organic phase is extracted. The different extracts are mixed and filtered with $Na_2SO_4$ through Whatman No. 90 filter paper, to a final sample volume of 25 mL. From it, a 10 mL aliquot was taken and a mixture of primary-secondary amine (PSA), plus graphite carbon for the removal of pigments, was added, then the extracts were injected into the gas chromatograph.

The quality of citrus fruits was determined according to their physical parameters, such as the fresh mass in g, the equatorial diameter of the fruit in mm and crust thickness in mm. The juice was then preceded, free of fibrous materials and the following physicochemical evaluations were performed: volume of juice in mL; sugar content (total soluble solids, SST) expressed in ºBrix, acidity (expressed as citric acid mainly) and maturity index or ratios, which is the ratio between the total soluble solids content and total acidity (SST/AT).

Fresh dough was evaluated, using a digital scale with a sensitivity of $10^{-3}$ g; the equatorial diameter and thickness of the fruit's crust, using a digital caliber with $10^{-2}$ mm sensitivity. The juice was extracted with a Philips Model HR 1820 processor, filtered with a 1 mm diameter filter mesh. Then it was determined: volume of juice obtained per sample measured with 10 mL test tube, SST by refractometry (ATAGO digital refractometer model $Pal^{-1}$), acidity by acid base titration with 0.1N sodium hydroxide, expressing the result as g of anhydrous citric acid/100 mL of solution. The IM (ratio) was estimated using the °Brix/Acidity calculation.

The parameters that describe the physical characteristics of the fruits and physicochemicals of the juice were treated through descriptive indicators such as the mean, the standard deviation, the coefficient of variation and the maximum and minimum values. The data obtained were subjected to normality tests by goodness of fit test with the modified Shapiro-Wilks statistic ($p \leq 0.05$) and analyzed statistically by ANOVA and Duncan test ($p \leq 0.05$) using the software Infostat [(18)]. Through the analysis of main components (ACP), the behavior of the samples of the different varieties with respect to the studied variables was analyzed, considering the varieties as classification variables. Artificial axes were constructed that allowed Biplot graphics to be obtained with optimal properties to interpret and identify associations between observations (varieties) and variables in the same space [(19)].

# RESULTS AND DISCUSSION

Table 2 shows the results obtained in the different samples, which analyzed different types of agrochemicals (cypermethrin, alpha-cypermethrin, deltamethrin, lambdacihalotrin) carbamates (aldicarb, carbofuran) and organochlorines (endosulfan), in fruit juices Fresh citrus The detection limit for the extraction technique used was calculated from each of them.

**Table 2**. Residual detection limits expressed in mg $kg^{-1}$

| Agrochemical | Detection Limit mg $kg^{-1}$ |
|---|---|
| Cipermetrina | 0.10 |
| Alfa-Cipermetrina | 0.10 |
| Deltamentrina | 0.10 |
| Lambdacihalotrina | 0.10 |
| Aldicarb | 0.20 |
| Carbofuran | 0.50 |
| Endosulfan | 0.01 |

However, in other studies carbamates residues were found, mainly in sweet chili (29.2 %) and orange (19.9 %) and organophosphorus residues were detected in all samples of the 25 foods analyzed in Brazil [14].

Of the analyzed fruits, no agrochemical residues were detected for the detection limits established for each agrochemical.

Table 3 details the results of the residue evaluation for fresh orange, tangerine and lemon fruit juices of the two years evaluated.

**Table 3**. Results of the evaluation of pesticide residues in citrus juices

| Analysis Group | Year | Samples analyzed | n | Without residues (%) | With residues (%) |
|---|---|---|---|---|---|
| Carbamatos (aldicarb, carbofuran) | 1 | Limón | 30 | 100 | 0 |
| | 1 | Naranja | 30 | | |
| | 1 | Mandarina | 30 | | |
| Organoclorados (endosulfan) | 1 | Limón | 30 | 100 | 0 |
| | 1 | Naranja | 30 | | |
| | 1 | Mandarina | 30 | | |
| Piretroides (cipermetrina, deltametrina, alfacipermetrina, lamdacialotrina) | 1 | Limón | 30 | 100 | 0 |
| | 1 | Naranja | 30 | | |
| | 1 | Mandarina | 30 | | |
| carbamatos (aldicarb, carbofuran) | 2 | Limón | 30 | 100 | 0 |
| | 2 | Naranja | 30 | | |
| | 2 | Mandarina | 30 | | |
| Organoclorados (endosulfan) | 2 | Limón | 30 | 100 | 0 |
| | 2 | Naranja | 30 | | |
| | 2 | Mandarina | 30 | | |
| Piretroides (cipermetrina, deltametrina, alfacipermetrina, lamdacialotrina) | 2 | Limón | 30 | 100 | 0 |
| | 2 | Naranja | 30 | | |
| | 2 | Mandarina | 30 | | |

By not presenting pesticide residues, it implies that through the implementation of good agricultural practices, an integrated management of pests and diseases and a good use and management of pesticides, the quality established in the markets is guaranteed, as consumers expect a constant supply of clean, high quality, healthy and safe food [13,14].

Internal maturation is determined by the Maturity Index (relationship between the concentration of total soluble solids and acidity), so that it must reach the minimum required to start harvesting. The values found for the parameters evaluated correspond to the rules of commercialization of the internal market, according to resolution N° 145 of the regulation of quality of citrus fruits for internal market and export of the Ministry of Agriculture and Livestock of the Nation [(20)], where a minimum SST-Acidity 7 to 1 ratio is required for mandarins, while oranges must have an SST-Acidity 6 to 1 ratio.

In lemons, the level of acidity is especially important and has standards between 5 and 7 %, compared with about 1 % in oranges and tangerines. The results were around these standard values, except for Eureka lemon and Murcott mandarin, which were below the standards, 4.11 and 0.70 % acidity, respectively.

The Valencia orange and Nova mandarin samples were found within the standard values (Table 4). According to other research [(2)], organic acids contribute significantly to the total acidity of the juice, with citric acid being the predominant organic acid (70-80 % of the total). Organic acids are considered an important source of acidic taste in the fruit and a source of energy in the plant cell.

Acids generally decrease during maturation, since they can be used as respiratory substrates or converted into sugars, although they are also used for the formation of aromatic and flavor compounds. In the ripening phase, free acids progressively decrease, as a consequence, fundamentally, of a dilution process, which happens as the fruit increases in size and juice content. It is important to note that total acidity is commonly used as a component to calculate the maturity index, rather than as an independent parameter.

**Table 4**. Physical parameters of the fruit and physicochemicals of citrus juice in the domestic market in the province of Corrientes

| Citrus variety | Variable | Media | [1]DE | Minimum | Maximum | Median |
|---|---|---|---|---|---|---|
| Limón Eureka | Masa | 2019.04 | 392.72 | 1473.50 | 2605 | 2114.50 |
| | DE | 69.95 | 3.59 | 64.79 | 75.90 | 71.70 |
| | EP | 6.92 | 1.09 | 5.25 | 8.43 | 7.10 |
| | mL Jugo | 684.7 | 60.94 | 570 | 830 | 670 |
| | % Jugo | 34.96 | 6.48 | 25.90 | 47.50 | 34.10 |
| | ºBrix | 8.02 | 1.95 | 5 | 10.8 | 7.9 |
| | Acidez | 4.11 | 2.02 | 1.48 | 6.8 | 4.57 |
| | Ratio | 3.12 | 2.66 | 0.8 | 6.92 | 1.7 |
| Mandarina Nova | Masa | 1847.7 | 452.3 | 1016.5 | 2542.5 | 2037.5 |
| | DE | 67.78 | 3.31 | 62.05 | 73.48 | 67.35 |
| | EP | 2.63 | 0.44 | 1.9 | 3.2 | 2.65 |
| | mL Jugo | 850.48 | 241.3 | 470 | 1160 | 965 |
| | % Jugo | 45.62 | 3.76 | 36.4 | 49.63 | 45.9 |
| | ºBrix | 13.23 | 1.55 | 11 | 15.2 | 13.5 |
| | Acidez | 1.03 | 0.08 | 0.9 | 1.2 | 1 |
| | Ratio | 12.81 | 1.66 | 10.8 | 15.15 | 12.99 |
| Mandarina Murcot | Masa | 1779 | 51.28 | 1750 | 1870 | 1760 |
| | DE | 76.16 | 1.52 | 73.5 | 77.2 | 76.9 |
| | EP | 3.2 | 0.67 | 2.6 | 4.2 | 3.1 |
| | mL Jugo | 658 | 39.78 | 610 | 705 | 655 |
| | % Jugo | 36.96 | 1.78 | 34.5 | 39.2 | 37.4 |
| | ºBrix | 8.4 | 0.55 | 8 | 9 | 8 |
| | Acidez | 0.7 | 0 | 0.7 | 0.7 | 0.7 |
| | Ratio | 12.15 | 0.68 | 11.47 | 12.9 | 12.15 |
| Naranja Valencia | Masa | 2321.2 | 134.7 | 2085.8 | 2585 | 2305.25 |
| | DE | 71.33 | 6.29 | 64.51 | 78.3 | 70.82 |
| | EP | 2.83 | 0.56 | 1.93 | 3.48 | 3.04 |
| | mL Jugo | 1169.63 | 139.25 | 1037 | 1510 | 1122.5 |
| | % Jugo | 50.33 | 4.26 | 45.57 | 58.41 | 48.91 |
| | ºBrix | 10.99 | 0.58 | 10 | 11.6 | 11 |
| | Acidez | 1.01 | 0.12 | 0.86 | 1.2 | 1 |
| | Ratio | 11.08 | 1.56 | 8.97 | 13.34 | 11.27 |

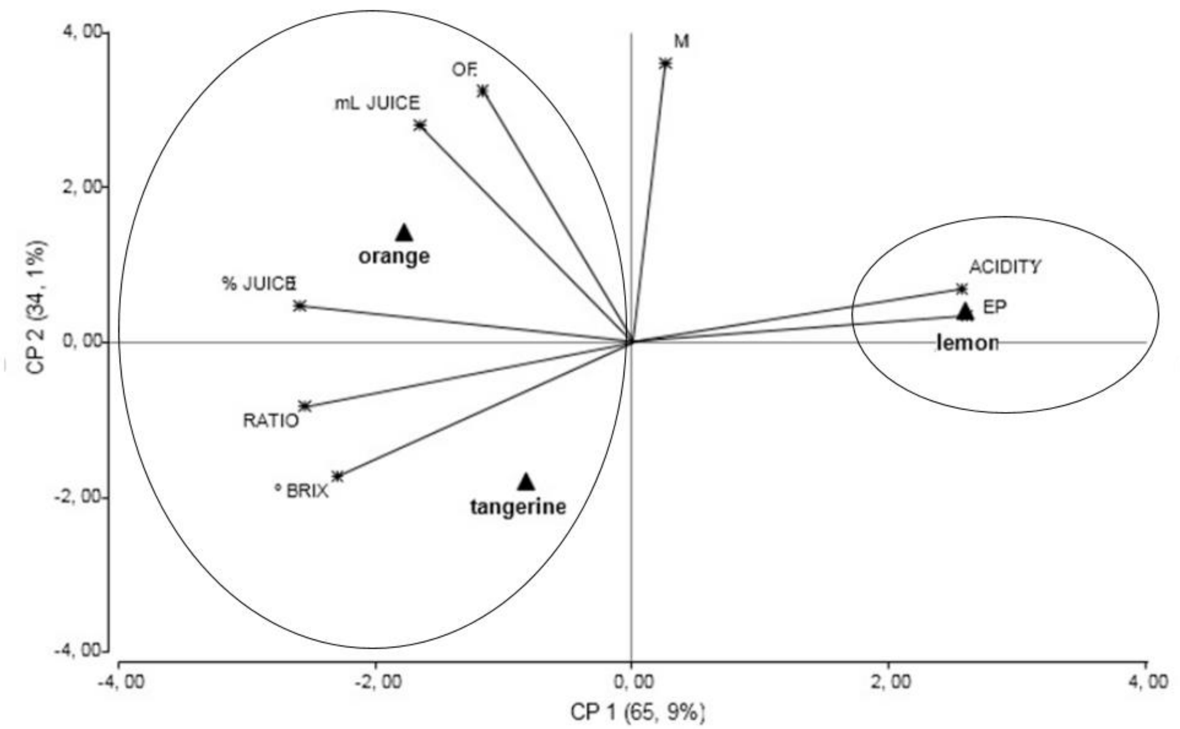
The lower acid values in lemons and Murcott mandarin, could be related to fertilization. Fertilization management, either by the type of fertilizer or by the dose used, causes changes in the internal and external quality parameters of the fruit. According to other studies, the use of urea (6 g plant$^{-1}$, weekly, throughout the growth cycle) produced an increase in the fruit load per plant [21], which resulted in a lower weight and individual diameter of the fruits. In addition, it modified the internal quality, mainly, through lower levels of ° Brix, SST, lower acidity and higher Ratio, compared to organic fertilization (chicken bed: it was supplied during the month of September at a dose of 17 kg plant$^{-1}$) and Witness (without fertilization). The varieties where this effect was mostly expressed were Washington navel, Valencia late and Clemenules.

In research conducted, results were found between 1.2 and 1.3 % acidity in Valencia orange and Murcott mandarin [22] and the same author in 2015 [23] found values between 1.46 and 1.54 % acidity in orange Valencia.

The fruits processed in this evaluation showed values between 25.9 % to 47.5 % of juice in lemons, 45.57 to 58.41 % in oranges, 36.40 to 49.63 % of juice in mandarin Nova and 34, 50 % to 39.20 % in Murcott tangerine (Table 4), results that are above the minimum values required for each variety [20] (the minimum standard juice content is 30 % for lemons, oranges and mandarins intended to internal consumption).

The fruits must also reach the minimum size (gauge) indicated in the Quality Standard in order to be marketed [20]. These are set between 50-85 mm for lemons, 55-90 mm for oranges and tangerines. The average calibers found were all values between the standard ranges (Table 4). Similar results were found in 'Valencia late' orange fruits and 'Murcott' tangor in Santa Rosa, Corrientes [22].

Figure 1 shows the graphic representation of the Principal Component Analysis (ACP) of the fruit quality and citrus juice variables. The Eureka lemon samples showed a greater association with the acidity of the juice, mass and the thickness of the fruit's crust, variables that presented significantly higher values in the Eureka lemon samples (Table 5); the orange and tangerine samples were associated with the variables mL and percentage of juice and with the equatorial diameter of the fruit, maturity index or ratio and with ºBrix.




M: fresh mass in g, EP: average crust thickness in mm, SD: equatorial diameter of the fruit in mm, % of juice, mL of juice, ºBrix: soluble solids content, acidity, and Ratio or maturity index in Mandarin, orange and lemon fruits.

**Figure 1**. Biplot resulting from Principal Component Analysis (ACP) of the variables

**Table 5**. Physical parameters of the fruit and physicochemicals of citrus juice in the domestic market in the Province of Corrientes

| Citrus variety | [1]M (g) | [2]DE | [3]EP | mL Juice | % Juice | º Brix | Acidity | Ratio |
|---|---|---|---|---|---|---|---|---|
| N. Valencia | 2321 c | 71.33 a | 2.83 a | 1169.6 c | 50.33 b | 10.99 b | 1.01 a | 11.08 b |
| M. Murcott | 1779 ab | 76.16 b | 3.20 ab | 658 a | 36.96 a | 8.40 a | 0.70 a | 12.15 b |
| M. Nova | 1847 ab | 67.78 a | 2.63 a | 850 b | 45.62 b | 13.23 c | 1.03 a | 12.81 b |
| L. Eureka | 2019 bc | 69.95 a | 6.92 c | 684.7 a | 34.96 a | 8.02 a | 4.11 b | 3.12 a |

These results indicate that depending on the physicochemical condition of the citrus fruits evaluated, they have an optimum maturity condition, with good fruit size. The Valencia orange fruits, despite having a significantly smaller fruit size, compared to lemon, managed to obtain significantly higher juice content (mL and % juice), the mandarin Nova presented intermediate values and lemon and Murcott mandarin the significantly lower values of these two variables.

The higher Ratio values were found in orange and tangerine, of interest both for fresh consumption and for the concentrated juice industry and manufactured products such as jams and jellies, while the lemon samples showed a particularly important level of acidity, very close to standard values.

# CONCLUSIONS

- The fruits do not have residues of carbamates, organochlorines or pyrethroids and, therefore, ensures product quality and safety for the market and the final consumer.
- The quality parameters of the citrus fruits of Valencia orange, Nova and Murcott mandarin and Eureka lemon presented adequate fruit size, high amount of juice (mL and % of juice) and an average concentration of total soluble solids that exceed standard levels.
- The highest values of juice and the ratio in orange and tangerine are of interest, both for the consumption of fresh fruit, and for the industry and make the variety of Valencia orange and mandarins Nova and Murcott, more attractive for the consumer as fresh fruit.

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