DETERMINATION OF MINERAL COMPOSITION OF ORGANIC AND CONVENTIONAL BEVERAGES BY DISPERSIVE ENERGY X-RAY FLUORESCENCE SPECTROMETRY

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ABSTRACT

Fruits are natural sources of minerals whose ingestion is recommended in a balanced diet. The increasing consumption of fruit-based beverages demands the development of rapid methods to evaluate their quality parameters. X-ray fluorescence spectrometry is an analytical-nuclear technique that is gaining space in the environmental and geological fields, and has been explored modestly in the food field. The main objective of this work was to develop a methodology to determine the mineral content of fruit-based beverages by applying this technique. Beverages manufactured from organic and conventional fruit varieties were evaluated, aiming to compare their nutritional value. The research was divided into three steps: in the first step, a direct measurement of the samples was made, that is, without prior preparation; in the second, standard curves were prepared with the elements of calcium and potassium, based on the category of ‘fine samples’. Lastly, these curves were used to determine concentrations of calcium and potassium in the samples of juices and pulps prepared as ‘fine samples’. The fine sample measurements showed results more exact compared to that obtained from the direct measurements. From the data evaluated, it was not possible to attribute better nutritional quality to either the organic or conventional samples.

Keywords: X-ray fluorescence; minerals; food analysis

RESUMO

As frutas são fontes naturais de minerais cuja ingestão é recomendada em uma dieta equilibrada. O aumento no consumo de bebidas à base de fruta exige o desenvolvimento de métodos rápidos para avaliar os seus parâmetros de qualidade. Espectrometria de fluorescência de raios-X é uma técnica analítica nuclear que está ganhando espaço nas áreas ambientais e geológicas, e tem sido explorado modestamente na área de alimentos. O principal objetivo deste trabalho foi desenvolver uma metodologia para determinar o conteúdo mineral de bebidas à base de frutas, aplicando essa técnica. Bebidas processadas a partir de variedades de frutas orgânicas e convencionais foram avaliadas, com o objetivo de comparar o seu valor nutricional. A investigação foi dividida em três etapas: na primeira etapa, uma medição direta das amostras foi realizada, isto é, sem preparação prévia. Na segunda etapa, as curvas padrão foram preparadas com os elementos de cálcio e de potássio, com base na categoria de “amostras finas”. Por último, estas curvas foram utilizadas para determinar as concentrações de cálcio e potássio nas amostras de sucos e polpas preparadas

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como "amostras finas”. Os resultados das “amostras finas” mostraram-se mais eficiente quando comparado com o obtido a partir de medições diretas. A partir dos dados avaliados, não foi possível atribuir uma melhor qualidade nutricional para qualquer uma das amostras orgânicas ou convencionais.

Palavras-chave: Fluorescência de Raios X, minerais, análise de alimentos.

INTRODUCTION

In recent years alerts directed at the risks of diseases, such as high blood pressure, diabetes and other heart diseases, most of which connected to obesity, has created a favorable environment for an increase in the consumption of healthier foods, containing natural ingredients. In 2008 a survey carried out by the Mintel agency showed that the term ‘natural food’ was the most popular one in the launching of foods and beverages throughout the world. Terms such as “absence of additives and preservatives”; “organic and/or whole foods” were also considered as “natural foods” (Halliday, 2009). Organic foods are products of vegetable or animal origin, free of agricultural pesticides or any other type of chemical product, since these are substituted by cultural practices in order to establish an ecological balance in the agricultural system. This fact contributed to the association of these foods with health benefits (Brasil, 2007). The increasing production of these foods has promoted a market for the so-called organic beverages.

Juices represent an important source of minerals such as potassium and calcium, whose daily recommended ingestion according to the FDA (Food & Drug Administration, USA) is 1000 mg (Altman, 1998), apart from minor elements, such as iron, copper, zinc and manganese, although in some cases these metals are the result of contamination during elaboration of the product (Varnam & Sutherland, 1997).

Considering the importance of minerals to human health, and the accelerated production rhythm of the fruit juice and pulp industries, there is a clear need for the development of quick methodologies to quantify the mineral nutrients in foods.

Various instrumental analytical techniques have been employed to determine the mineral composition of beverages. According to Grindlay et al. (2011), there are many criteria that should be considered in defining an appropriate technique for a determined analysis. Some of the main criteria are: (i) the analyte concentration; (ii) the number of elements to be determined; and (iii) possible interferants of the analysis. In a literature review carried out by the same authors, they found that in a study of the mineral composition of wines, atomic spectrometry techniques were widely used, being divided between: mass spectrometry coupled to induced plasma (ICP-MS) (40% of the total); atomic emission spectrometry coupled to induced plasma (ICP-AES) (18%); atomic absorption spectrometry (16%); flame atomic absorption spectrometry (15%); total reflection X-ray fluorescence spectrometry (TXRF) (7%); and others used on a smaller scale, together accounting for 4% of the total.

In a project developed by Reto et al. (2007), to evaluate the chemical composition of infusions of green tea samples commercialized in Portugal, the diversity of techniques available for the instrumental analysis of beverages was apparent. According to the element or compound to be determined, they opted for the most adequate technique. Thus to determine fluorine, they used a digital pH meter with an electrode selective for this element. Atomic absorption spectrometry was used to determine the aluminum, chromium, selenium, iron and manganese contents, and flame atomic absorption spectrometry to quantify sodium and potassium. Finally, high performance liquid chromatography (HPLC) was used to analyze the organic compounds (caffeine and catequins).

The multi-element analysis by X-ray fluorescence is a quali-quantitative method based on the measurement of the intensities of the characteristic X-rays emitted by the chemical elements components of a sample, when duly excited (Nascimento Filho, 1999). This technique has been used for the quali-quantitative evaluation of the chemical composition of various types of sample of agricultural, agroindustrial, geological and environmental interest. Since it is a non-destructive, instrumental technique, allowing for the quick, low cost and simultaneous analysis of various elements, it has considerable potential for application in various areas, where there is a need to correlate the essential elements with the toxic ones (Nascimento Filho, 1999). The conventional instruments provide a rapid measurement, but require a long digestion time of the solid samples (Moraes, 2004).

Currently one of the main applications of X-ray fluorescence in the environmental area is in the evaluation of the mineral composition as a means to analyze the contamination of waters and soils. The studies of Moraes (2004) and Gregório (2001) are examples of this type of application.

Although still in a modest way, X-ray fluorescence has been already applied in food analyses.

Golob et al. (2005) determined the concentration of trace elements in different types of honey in Slovenia as from total reflection X-ray fluorescence spectrometry (TXRF).

The samples were measured directly, just diluted with doubly distilled water. The authors concluded that the analysis by TXRF was adequate to determine the botanical origin of the honey, since they showed that each type of honey evaluated presented its own characteristics in terms of mineral composition. The method had some advantages, such as a short analysis time, which, as a consequence, made it adequate for cases where large numbers of samples are evaluated, and also because no chemical pre-treatment of the samples was necessary, reducing the risks of contamination.

Wave dispersion X-ray fluorescence spectrometry (WDXRF) was applied by Jastrzebska et al. (2003) in the analysis of phosphorus-rich foods, such as soybean products (transgenic and non-transgenic) and dairy products. The samples were first dried and then treated in different ways: the soybean products were ground and the dairy products were ashed before being analyzed in the equipment. To validate the method, the results were compared to those obtained by standard methodology. The WDXRF analysis was quicker and its sample preparation simpler. The methodology can be applied in this way as an adequate technique for food inspection and laboratory quality control.

Anderson (2009) used a portable X-ray tube to evaluate the presence of toxic elements in beverage samples (cranberry juice), cocoa powder, fine films and ceramic lacquers. The equipment easily distinguished the beverage contaminated with Cr, Cu and As and the cocoa powder contaminated with Pb and As, from the non-contaminated products. In addition, it was capable of making this distinction without removing the products from their original packages, made of PEAD, PET or a 7 µm thick plastic film. In the analysis of surfaces (fine films and ceramic lacquers) the calibrated equipment made accurate measurements of Pb. The focus of the methodology was qualitative analysis, but it was shown that simple calibration provided accurate results for Pb in surfaces. In comparison to isotopic X-ray fluorescence spectrometry, the portable equipment showed greater sensitivity, and the analysis times were shorter.

X-ray fluorescence spectrometry was cited by Yuan et al. (2011) as a potential technique for the determination of heavy metals in phytotherapeutic medications.

Other studies involved the application of X-ray fluorescence spectrometry in the analysis of lobsters (Barrento *et al*., 2008); potato starch (Noda et al., 2006); and heavy metals in wild mushrooms (Carvalho et al., 2005).

Most of the studies involving food samples use total reflection X-ray fluorescence spectrometry (TXRF) or wave dispersion X-ray fluorescence spectrometry (WXRF). Studies concerning the use of dispersive energy X-ray fluorescence spectrometry (DEXRF), the methodology employed in the present work, are a little scarce. This highlights the pioneering spirit of this work in the food and beverage sector.

In this context, the objective of this study was the development of a methodology to determine minerals in fruit juices and pulps using dispersive energy X-ray fluorescence spectrometry (DEXRF), observing any differences between organic and conventional products.

Material and Methods

Samples of grape, passion fruit, mango and guava juices were used in the development of a method to determine the mineral composition of beverages using dispersive energy X-ray spectrometry. In addition to the juices, the mineral concentrations were evaluated in strawberry and West Indian cherry pulps. For each organic sample, a conventional sample with the same flavor was also were analyzed.

All the samples, except the organic West Indian cherry pulp, were acquired from local shops in Campinas (SP, Brazil). The organic samples all possessed certification stamps from the Biodynamic Institute (IBD) or from ECOCERT, Brazil.

The West Indian cherry pulp was extracted from fruits acquired from an organic producer certified by the IBD, using an inclined pulper with brushes.

The samples used in the metal analyses were submitted to two preparation methods. A direct measurement of the pulp and juice samples was first made to verify the capacity of the response of the equipment with respect to the metals present and of interest in the initial study.

Subsequently, standard multi-element solutions were prepared with the objective of constructing standard curves for each metal under analysis. Both the standard solutions and the samples were prepared using the category of analysis of ‘fine samples’, which will be described in more detail in the coming items. Finally the existence of statistically significant differences at 5% between the mineral composition of the conventional and organic products was evaluated.

The research was carried out according to the steps described in the following topics.

Part I: Direct measurement of the juice and pulp samples

This type of analysis represents a non-destructive method. The juices and pulps were not submitted to any treatment before being inserted into the X-ray fluorescence spectrometer.

The juices and pulps were analyzed in the category of ‘liquid solutions’ of the X-ray fluorescence spectrometer (SHIMADZU, model 900 HS, Japan). In this category, the equipment carries out a qualitative and quantitative analysis of the solution. Thus, the result provided by the equipment showed the presence of some metals not focused on this study.

A 5 mL of each sample was placed in the cylindrical polyethylene cell with an external diameter of 32 mm, and the base composed of the film Mylar® (polyterephthalate) with a thickness of 6 µm.

The irradiation conditions were the same for the determination of all the metals, as described in Table 1.

Table 1. Irradiation parameters for liquid samples.

Metal	Irradiation time (s)	Dead Time (%)	Voltage (kV)	Eletric Current (µA)	Recorded Spectra (keV)	Colimator (mm)	Atmosphere
Not specified	200	14	50	1000	0 up to 40	10	Air

Part II: Construction of standard curves using a dispersive energy X-ray fluorescence spectrometer

The analytical procedure started with a collectanea of data about the mineral composition of the fruit components of each sample, using the Brazilian Food Composition Tables (TACO, 2006) as reference, as presented in Table 2. The choice of the metals was based on their concentrations and presence in all the fruits. In this way, there were chosen three metals for analysis: potassium, which has a high concentration in all samples; calcium, that has an intermediate concentration, and iron, which has a very low concentration that could be considered as a ‘trace element’ in the samples here studied.

Table 2. Data from Brazilian Food Composition Tables for mineral and ash concentration in brazilian fruits.

Fruit	Ash (g/100g)	Calcium (mg/100g)	Magnesium (mg/100g)	Iron (mg/100g)	Potassium (mg/100g)	Sodium (mg/100g)
Raw West Indian Cherry	0.4	13	13	0.2	165	Tr
West Indian Cherry (frozen pulp)	0.3	8	9	0.2	112	1
Red guava	0.5	*	7	0.2	198	Tr
Raw Haden Mango	0.4	12	8	0.1	148	1
Mango (frozen pulp)	0.4	7	9	0.1	131	7
Raw Tommy Atkins Mango	0.3	8	7	0.1	138	Tr
Raw Passion fruit	0.8	5	28	0.6	338	2
Passion fruit (frozen pulp)	0.5	5	10	0.3	228	8
Passion fruit (bottled	0.5	4	4	0.3	201	22

concentrated juice)						
Raw Strawberry	0.5	11	10	0.3	184	Tr
Raw Italy Grape	0.6	7	5	0.1	162	Tr
Raw Ruby Grape	0.5	8	6	0.2	159	8

Source: TACO, 2006.

***Abbreviations**: Tr: traces. The term “trace” was adopted in the following situations: a) nutrition values rounded for numbers between 0 and 0,5; b)nutrition values rounded for numbers between 0 and 0,05; c) nutrition values rounded for numbers between 0 and 0,005 and; d)nutrition values below the limits of quantification.

Based on the concentrations of these minerals in each fruit, the concentrations used to prepare the multi-element standard solutions were determined (Table 3).

Table 3. Concentration of multi-element solutions (mg/100mL)

Solution	Potassium	Calcium	Iron
1	400.0000	25.0000	1.0000
2	300.0000	12.5000	0.5000
3	180.0000	5.0000	0.2000
4	90.0000	2.5000	0.1000
5	45.0000	1.0000	0.0100

The glassware used to prepare the solutions was washed with deionized Millipore® water, maintained in a 0.1N nitric acid solution for 24 hours, and then rinsed again in deionized water after each period, to avoid the possibility of contamination.

The salts used in the preparation of these solutions were potassium sulfate (K_2SO_4), calcium sulfate dihydrate ($CaSO_4.2H_2O$) and ferrous sulfate septahydrate ($FeSO_4.7H_2O$). Deionized Millipore® water was used to dilute the salts.

The equipment used in the analyses was a model 900 HS Shimadzu dispersive energy X-ray fluorescence spectrometer (DEXRF).

One of the categories for analysis presented by the X-ray fluorescence spectrometer is that of ‘fine samples’ and an example of this type of analysis can be found in Moraes (2004). The author analyzed sediments from river bottoms, carrying out drying and subsequent pressing, so as to concentrate the sample into a lozenge. In the present work, the sugary consistence of the concentrated juices and pulps avoided pressing, so to overcome this problem small amounts of the sample were added to quantitative filter paper to allow for an analysis in the category of ‘fine samples’.

The procedure used quantitative filter paper with a grammage of 85 g/m^2 and thickness of 2.0 µm. The original diameter of the filter paper was reduced from 125 mm to 30 mm, since this was the diameter recommended by the manufacturer in the equipment manual (SHIMADZU). A 50 µL aliquot of each of the multi-element solutions was pipetted into each filter using an automatic pipette. The filters were placed in desiccators with silica, and vacuum applied manually using a syringe for a period of 24 hours, recording the initial and final weights of each.

Knowing the concentration of each of the solutions, the volume added to each filter (50 µL) and the mass of each filter, the mass of each metal present in the filters and its corresponding % mass could be calculated. More details about the calculations will be given in section 2.3.

A standard curve was constructed for each of the three metals, based on the % mass of the respective metal calculated in the filter. The function of the standard curves was to correlate the concentration of metal in the filter (in % mass) with the intensity of the X-ray characteristic of that metal, as measured by the equipment detector. This allows one to determine the concentration of the metal in samples in which the concentration is unknown.

Part III: Thin samples – use of quantitative filter paper to dry the juices and pulps

As in section 2.2., a quantity of 50 µL of each sample was pipetted into a quantitative filter paper with a diameter of 30 mm. The filters were placed in desiccators with silica for 24 hours, with manual application of vacuum using a syringe, recording the initial and final weights for each sample.

The analysis was carried out as from the standard curves constructed in section 2.2. Thus, when the equipment detected an intensity of an X-ray characteristic of each metal present in the sample, the software correlated this value with the concentration (in % mass) predicted for this metal by the standard curve.

The irradiation conditions varied according to the metal analyzed, and are summarized in Table 4.

Table 4. Parameters for thin samples analysis.

Metal	Irradiation time (s)	Dead time (%)	Voltage (kV)	Eletric Current (µA)	Recorded Spectra (keV)	Collimator (mm)	Atmosphere
Potassium	80	0	15	1000	0 up to 20	10	Air
Calcium	80	0	15	1000	0 up to 20	10	Air
Iron	80	1	50	1000	0 up to 40	10	Air

The results calculated by the software of the spectrometer were subsequently submitted to other calculations, considering that the equipment determined the concentration in the dry filter and not in the juice. Thus the amount of metal in the samples was determined according to the following procedures:

The concentration calculated by the equipment [C] was equivalent to the % mass represented by a given metal. This concentration was represented by:

C = [(mass of the metal in 50µL)/(mass of the filter)]*100

Since the masses of the dry filters are known:

Mass of metal in 50µL = (C/100)*mass filter

The proportion for the amount of metal that would be present in 100 mL can then be determined:

For example: calculating the potassium content of an organic grape juice, as follows:

C = 0.425%

Mass of filter = 73.9 mg

Thus the mass of potassium in 50µL = 0.314075 mg

Therefore for 100 mL juice: 628.15 mg of potassium.

The results were evaluated using an analysis of variance (ANOVA) and Tukey's means test (5%) through the software SAS® (SAS Software 9.1 TS1 for Windows).

Results and Discussion

Part I: Direct measurement of the juice and pulp samples

Table 5 shows the results obtained for the concentrations of the metals evaluated and application of Tukey's means test (5%) for the samples of juice and pulp, comparing the same flavors.

Table 5. Metal concentration in samples analysed by direct measurement and its Tukey's means test (5%):

Sample	**Calcium** (mg/100g)	**Potassium** (mg/100g)	**Iron** (mg/100g)
Organic passion fruit juice	0.0000^a	11.0000^a	2.0000^b
Conventional passion fruit juice	0.0000^a	30.0000^a	3.0000^a
Organic mango juice	0.0000^a	32.0000^b	2.5000^a
Conventional mango juice	0.0000^a	60.0000^a	2.5000^a
Organic guava juice	0.0000^a	27.5000^a	2.5000^a
Conventional guava juice	0.0000^a	19.5000^a	1.5000^a
Organic grape juice	0.0000^a	315.0000^a	3.0000^a
Conventional grape juice	0.0000^a	68.5000^b	3.0000^a
Organic West Indian cherry pulp	0.0000^a	77.0000^a	2.5000^a
Conventional West Indian cherry pulp	0.0000^a	42.0000^a	1.0000^a
Organic strawberries pulp	0.0000^a	43.5000^a	1.5000^a
Conventional strawberries pulp	3.5000^a	93.5000^a	2.5000^a

a: samples did not show statistically significant difference at 5 %.
b: samples showed statistically significant difference at 5 %.

According to Table 5, calcium was only detected in the pulp of conventional strawberries.

Comparing the results obtained with those presented in Table 2, in general the values obtained for calcium and potassium were below the expected values, except for the potassium content in the organic grapes, which showed a value above that reported by TACO (2006). With respect to iron content, the concentrations of this mineral were about 10 times higher than those verified in Table 2.

Comparing organic and conventional samples, statistically significant differences at 5% were only observed in the potassium content of mango and grape juices, while for iron concentration, only passion fruit juices showed statistically significant differences at the same level.

However, the difference in the metal concentration found between some samples could not be entirely associated with the fact of the sample being organic or not, since there are many cultivation factors, such as the fruit variety used and also the process technology used to manufacture the juices or extract the pulps.

Since metals are highly diluted in samples of fruit juices and pulps without prior preparation, this could represent a difficulty in their detection by this equipment. In addition, the organic matrix in which the metals are diluted (sugars, fibers, lipids) represents another factor which interfering in the quality of the results, since it influences the background noise in the analyses. These factors could explain the fact that the majority of the concentrations detected by the equipment were below the values described in the literature.

In order to determine iron, copper and zinc in seven samples of sugarcane liqueur commercialized in the southeast of Brazil, Cunha and Silva *et al*. (2004) incinerated the samples in a muffler at 500ºC, followed by digestion with nitric acid (30% v/v) to minimize the background noise caused by the sucrose present in the samples. They used a total reflection X-ray fluorescence spectrometer (TXRF). The relative sensitivities of each element were adjusted in the equipment using standard multi-element solutions. The results showed that the methodology employed for the multi-element analysis of the samples was applicable, the only disadvantage being the time taken in digesting the samples.

In the present work, in the analysis of liquid samples, sample digestion could be an alternative to be employed to make it possible to obtain more exact results. However, this would represent an increase in the time demanded for the analysis.

According to the results evaluated, the direct measurement of the samples did not allow one to obtain reliable results when compared to the references consulted.

Part II: Construction of standard curves using a dispersive energy X-ray fluorescence spectrometer

In the analysis by X-ray fluorescence, the construction of a standard curve signifies establishing a correlation between the concentration of the element under analysis with the measurement of the intensity of the characteristic X-ray emitted by the atoms of this element, after the sample has passed through a process of excitation (Nascimento Filho, 1999).

Excitation is the step in which a sample receives an amount of energy sufficient to eject electrons from an atom, leaving it in an unstable state necessary to start the process which allows for the emission of a characteristic X-ray, which is well defined for each element (Gregorio, 2001).

In the construction of the standard curve of a determined element as from samples of known concentrations, the equipment records the intensity of the X-ray emitted for each concentration and establishes a correlation between the values. Thus when a good coefficient of correlation is reached (normally R^2 greater than 0.95) the curve can be applied such that the content of this element is determined in a sample of unknown concentration.

The standard curves for the elements calcium and potassium were constructed as from the units of quantitative filter paper to which the multi-element solutions were added as described in section 2.2.

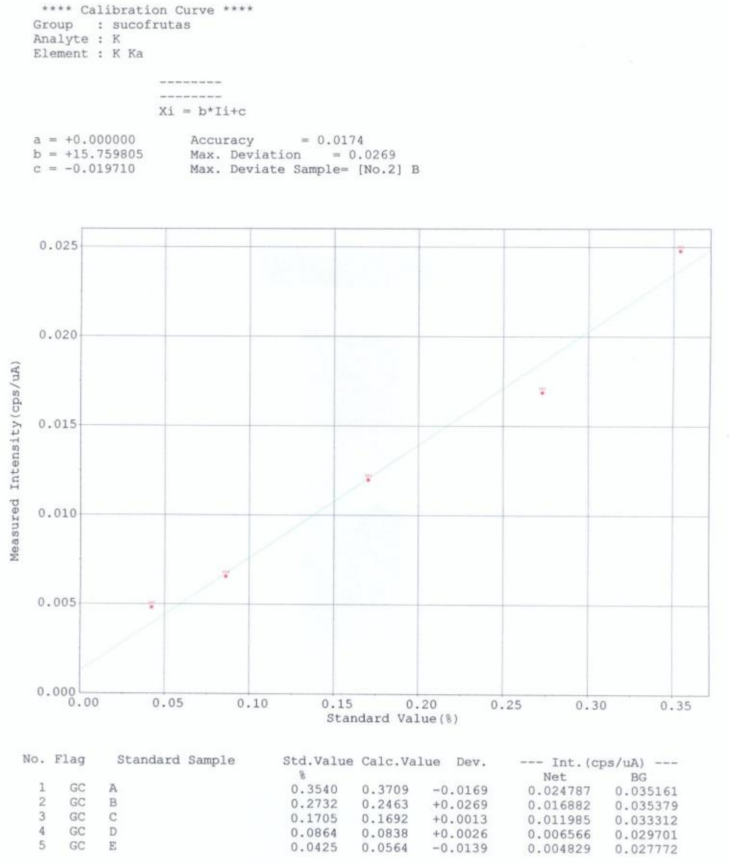
In the case of the element iron, the curve showed a distinctly non-linear nature and was not applied in the detection of this element.

Table 6 shows the values used for the construction of the standard curve expressed as percent mass. The respective values in mg/100 mL are shown in Table 3.

Table 6. Concentration of multi-element solutions in quantitative filter paper. Values are expressed in mass percentage.

Multi-element Solution	Calcium	Iron	Potassium
1	0.02212	0.00088	0.35398
2	0.01138	0.00046	0.27322
3	0.00473	0.00019	0.17045
4	0.00240	0.00010	0.08637
5	0.00095	0.00001	0.04253

Figure 1 shows the standard curve for potassium, shown as an example.



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 **** Calibration Curve ****
Group   : sucofrutas
Analyte : K
Element : K Ka

                  --------
                  --------
                  Xi = b*Ii+c

a = +0.000000        Accuracy       = 0.0174
b = +15.759805       Max. Deviation     = 0.0269
c = -0.019710        Max. Deviate Sample= [No.2] B
```

```
No. Flag    Standard Sample      Std.Value Calc.Value  Dev.     --- Int.(cps/uA) ---
                                    %                              Net       BG
 1   GC   A                       0.3540   0.3709   -0.0169    0.024787  0.035161
 2   GC   B                       0.2732   0.2463   +0.0269    0.016882  0.035379
 3   GC   C                       0.1705   0.1692   +0.0013    0.011985  0.033312
 4   GC   D                       0.0864   0.0838   +0.0026    0.006566  0.029701
 5   GC   E                       0.0425   0.0564   -0.0139    0.004829  0.027772
```

Figure 1. Standard curve for potassium.

The abscissa axis represents the concentration in percent mass for a determined element, whereas the ordinate axis gives the intensity of the characteristic X-ray (in cps/ µA) detected for each concentration for this same element. The intensity detected by the equipment is proportional to the concentration of the element represented on the standard curve. Thus the higher the concentration of a determined metal the greater the intensity detected by the equipment.

The coefficient of correlation calculated for potassium was 0.9818, which is considered to be a satisfactory value.

For the standard curve of calcium, the coefficient of correlation calculated was 0.8886, a value inferior to that calculated for the standard curve of potassium. Since the concentrations of calcium in the multi-element solutions were lower, this could show that the sensitivity of the equipment to detect metals reduces as the concentration decreases.

For the standard curve of iron, whose solutions showed concentrations to the order of up to 10^3 lower than those of potassium, a correlation could not be established between the concentrations and the intensities of the characteristic X-rays. This result also indicated a reduction in sensitivity of the equipment to detect low concentrations of metals.

Therefore, the use of dispersive energy X-ray fluorescence spectrometry in foods may not be effective in the determination of traces of heavy metals or contaminants, when this method of sample preparation is used.

Part III: Thin samples – use of quantitative filter paper to dry the juices and pulps

Table 7 shows the results obtained for calcium and potassium in the samples evaluated. Since it was not possible to elaborate a standard curve for the iron as previously discussed this element was not detected.

Table 7. Calcium and Potassium contents for juices and pulps in quantitative filters.

Sample	Calcium (mg/100g)	Potassium (mg/100g)
Organic passion fruit juice	8.8400[a]	152.0000[a]
Conventional passion fruit juice	4.1280[a]	202.2720[a]
Organic mango juice	14.4200[a]	345.3500[b]
Conventional mango juice	56.9700[b]	678.5760[a]
Organic guava juice	34.3500[a]	355.8660[a]
Conventional guava juice	5.2560[b]	427.0500[b]
Organic grape juice	25.1260[b]	628.1500[a]
Conventional grape juice	25.9540[a]	430.2900[b]
Organic West Indian cherry pulp	111.5520[a]	1352.0640[a]
Conventional West Indian cherry pulp	87.1680[b]	848.5260[b]
Organic strawberries pulp	206.9760[a]	1549.6320[a]
Conventional strawberries pulp	80.1040[b]	1109.8280[b]

a: samples did not show statistically significant difference at 5 %.
b: samples showed statistically significant difference at 5 %.

In general, the results in Table 7 showed higher values in comparison to the data presented in Table 2, especially for potassium content. This behavior could be related to both intrinsic aspects of the composition of the samples analyzed and also to the methodology applied. An analysis of the same samples using a standard methodology, such as atomic absorption spectrometry, could be an alternative in order to have a standard value for comparative purposes.

West Indian cherry and strawberry pulps presented statistically significant differences at 5 % between the organic and conventional varieties for calcium and potassium contents. Furthermore, in these samples, the organic varieties showed higher concentrations for both minerals.

On the other hand, the conventional mango juices showed higher potassium and calcium concentration, in comparison to the organic variety, this difference being statistically significant at 5%.

No statistically significant differences at 5 % were found out between the organic and conventional samples of passion fruit juice.

For the samples of guava and grape juices, although significant differences were verified between the organic and conventional varieties, it was not possible to conclude which of them presented the richer mineral composition.

CONCLUSIONS

X-ray fluorescence spectrometry showed possibilities for application in evaluating the mineral composition of juices and pulps.

The sensitivity of the equipment in detecting metals was lower at lower metal concentrations, showing that this might not be adequate methodology for the detection of trace metals.

From the results obtained it was not possible to conclude if the quality of the mineral composition was directly related to whether the sample is originated from an organic or conventional culture, even though a tendency for greater mineral content in organic samples was observed. Thus a more detailed investigation is required, with control of the agricultural and industrial processes in the production of the samples, as also the presentation of comparative results between the methodologies already used, such as atomic adsorption spectrometry, and the methodology evaluated in the present study.

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REFERENCES

ABIR. Brazilian Association of soft drinks and non-acoholic drinks. Available in: <http://www.abir.org.br/rubrique.php3?id_rubrique=141>. Accessed on: Dec.15th 2008.

ALTMAN, T.A. **FDA and USDA Nutrition Labeling Guide : Decision Diagrams, Checklists, and Regulations.** Lancaster: TECHNOMIC PUBLISHING COMPANY, 1998.

ANDERSON, D.L. Screening of foods and related products for toxic elements with a portable x-ray tube analyzer. **J. Radional. Nucl. Chem.,** v.282, p. 415-418, 2009.

BARRENTO, S.; MARQUES, A.; TEIXEIRA, B.; VAZ-PIREZ, P., CARVALHO, M.L.; NUNES, M.L. Essential elements and contaminants in edible tissues of European and American lobsters. **Food Chemistry**, 111, p.862 -867, 2008.

BRASIL. Ministry of Agriculture, Livestock and Supplies; Secretary of Agriculture Policy; Inter-American Institute for cooperation in agriculture. **Supply Chain of Organic Products - Agribusiness Series,** 1st ed, Brasilia: Quality Printing and Publishing, 2007.

CARVALHO, M.L.; PIMENTEL, A.C.; FERNANDES, B. Study of Heavy Metals in Wild Edible Mushrooms under different pollution conditions by x-ray fluorescence spectrometry. **Analytical Sciences**, v. 21, Jul. 2005.

CUNHA E SILVA, R.M.; ALMEIDA, E.; VALENCIA, E.P.E.; NASCIMENTO FILHO, V.F. Determination of Fe, Cu and Zn in sugar-cane spirits commercialized in Southeastern Brazil by TXRF. **Journal of Radioanalytical and Nuclear Chemistry,** vol 260, n. 1, p. 3 -7, 2004.

GOLOB, T.; DOBERSEK, U.; KUMP, P.; NECEMER, M. Determination of trace and minor elements in Slovenian honey by total reflection X-ray fluorescence spectroscopy. **Food Chemistry**, 91, p. 593-600, 2005.

GREGÓRIO, M.A. **Speciation and determination of arsenic and selenium in natural water samples by fluorescence X-ray energy dispersive.** Campinas, 2001, 109p. Dissertation (Master in Civil Engineering area of concentration in water), Faculty of Civil Engineering, State University of Campinas, UNICAMP.

GRINDLAY, G.; MORA, J.; GRAS, L.; LOOS-VOLLEBREGT, M.T.C. Atomic spectrometry methods for wine analysis: a critical evaluation and discussion of recent applications. **Analytica Chimica Acta**, v.691, p. 18-32, 2011.

HALLIDAY, J. Natural comes out top in new product claims in 2008. **Food Navigator**. Available in: <http://www.foodnavigator.com/Financial-Industry/Natural-comes-out-top-in-new-product-claims-2008>. Accessed on Jan. 29th 2009.

JASTRZEBSKA, A.; BRUDKA, B.; SZYMANSKI, T; SZYK, E. Determination of phosphorus in food samples by X-ray fluorescence spectrometry and standard spectrophotometric method. **Food Chemistry,** 83, p. 463–467, 2003.

MORAES, L.M.B. **Use of two variants of the x-ray fluorescence (EDXRF and TXRF) determination of Pb in water and sediment.** Piracicaba, 2004, 96p. Dissertation (Master of Science. Area of Concentration: Nuclear Energy in Agriculture), School of Agriculture Luiz de Queiroz (ESALQ), University of São Paulo (USP).

NASCIMENTO FILHO, V.F. **Nuclear Analytical Techniques Fluorescence X-ray energy dispersive (EDXRF) and total reflection (TXRF)**. Piracicaba: ESALQ, Department of Physics and Meteorology, SCENE, 1999. 32P. Available at: <http://web.cena.usp.br/apostilas/Virgilio/cen-5723/EDXRF_TXRF.doc>. Accessed on: Jan. 9th 2008.

NODA, T.; SHOGO, T.; MORI, M.; TAKIGAWA, S.; MATSUURA-ENDO, C.; KIM, S.; HASHIMOTO, N.; YAMAUCHI, H. Determination of the phosphorus content in potato starch using an energy-dispersive X-ray fluorescence method. **Food Chemistry**, 95, p.632-637, 2006.

RETO, M.; FIGUEIRA, M.E.; FILIPE, H.M.; ALMEIDA, C.M.M. Chemical composition of green tea (*Camellia sinensis*) infusions commercialized in Portugal. **Plant Foods Hum Nutr.**, v. 62, p. 139 – 144, 2007

SAS Software 9.1 TS1 for Windows. Available at: em: <http://www.sas.com/>. Accessed on Oct. 15th 2011.

TACO. Brazilian Food Composition Tables, 2006. Available at: <http://www.unicamp.br/nepa/taco/>. Accessed on: May 29th 2009.

VARNAM, A.H.; SUTHERLAND, J.P. **Bebidas: tecnología, química e microbiología.** v. 2. Zaragoza: Acribia, 1997.

YUAN, X.; CHAPMAN, R.L.; WU, Z. Analytical methods for heavy metals in herbal medicines. **Phytochemical analysis.** V. 22, Iss. 3, p. 189- 198, May/Jun 2011.