Elemental concentration of tomato paste and respective packages through particle-induced X-ray emission

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ABSTRACT

The elemental concentrations of three brands of Brazilian tomato paste packed in cans and Tetra Pak® cardboard boxes were determined through the Particle-Induced X-ray Emission (PIXE) technique. The elements Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Br and Rb were identified in the tomato pastes. The metallic cannisters are characterized primarily by the presence of Fe and Sn, while several elements including Al, Cl, Ti, Fe and Zn showed up in Tetra Pak® boxes. The elemental concentrations of tomato paste varied significantly among different brands and packages. The major elements present in tomato paste are Na, Cl and K with concentrations ranging from 1700 mg/kg up to 7500 mg/kg, while trace elements like Br and Rb had average concentrations around 2 mg/kg. Tomato paste from different brands and packages stored for long periods of time were evaluated as well. Canned tomato paste showed distinct rising and decreasing trends of Fe and Al concentrations as a function of the storage time respectively. Possible transfer mechanisms are discussed.

1. Introduction

In the rank of the most important vegetables in the world from either the economical or the nutritional point of view, tomatoes stand second right after potatoes. The per capita world consumption during the 2012/13 cycle was equivalent to 5.3 kg of tomatoes in the form of processed products such as tomato paste and ketchup among others. The global production of tomatoes for the industry reached almost 40 million tons in 2016, while the Brazilian production of about 1.2 million tons placed Brazil as the 8th tomato producer globally (Dorais et al., 2008; Treichel, 2017).

According to the Brazilian legislation, tomato paste should be obtained from ripe tomatoes pulp (*Solanum lycoperaicum*) that contains no less than 6% of natural tomato soluble solids together with salt (maximum of 5% of NaCl) and sugar (maximum of 1%) (ANVISA, 2005, 1978). The final product is stored in cans, cardboard boxes (Tetra Pak®) or glassware and it is usually safe for consumption during the next 18 months. Once the packing material is assumed to be inert, the final elemental composition of the tomato paste should correspond basically to that of the tomatoes, additives and other products used during the industrial processing.

Regarding composition, factors such as soil and use of pesticides and fertilizers can influence the final elemental content of the tomatoes. Thus, the comparison of tomato products stemming from tomatoes grown in different farms and regions may result in substantial differences of the elemental composition (Belitz et al., 2009). Although the container material of processed foodstuff is tested for durability and has the sole purpose of preserving and keeping the food inside it safe for human consumption, changes in the food products have been reported due to the interaction between the container itself and the foodstuff inside it (Al-Thagafi et al., 2014; Boufleur et al., 2013; Türker and Yüksel, 1997).

The study of elemental composition of foodstuff may be used as a mean to control quality and origin of the products. The determination of

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elemental composition of tomatoes and tomato products has been carried out using techniques such as Inductively Coupled Plasma - Atomic Emission Spectrometer (ICP-AES) (Al-Thagafi et al., 2014), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Lo Feudo et al., 2010), Atomic Absorption Spectroscopy (AAS) (Dallatu et al., 2013; David et al., 2008; Iwegbue et al., 2012; Türker and Yüksel, 1997) and Particle-Induced X-ray Emission (PIXE) (Romero-Dávila and Miranda, 2004). The influence of packages on foodstuff has been reported e.g. for tomato paste (Al-Thagafi et al., 2014; Türker and Yüksel, 1997), for canned tuna fish (Boufleur et al., 2013; Dantas et al., 2008), for beer (Vela et al., 1998) and for soft drinks (Zucchi et al., 2005).

Among several techniques available for elemental analysis, ion-based techniques have gained impetus in the past years due to their reliability and most importantly to their broad analytical power. Indeed, a single ion beam technique like PIXE can be employed for the analysis of quite different materials like metals, liquids and organic tissues in general, thus increasing the confidence level of the results. Therefore, PIXE is quite suitable for studies involving different materials like, for instance, foodstuff and their respective packages. Moreover, PIXE (Johansson et al., 1995) offers advantages like multielemental capability, relatively fast analysis and simplicity as far as sample handling is concerned. This technique is based on the production of characteristic X-rays through charged particle bombardment of the samples under study. PIXE has good sensitivity (of the order of parts per million) and is non-destructive, allowing several measurements of a single sample if required.

Since most PIXE systems are capable of detecting element with $Z > 10$, another technique is required for the detection of light elements like carbon, oxygen and nitrogen. Usually, these elements are the predominant ones in organic samples like the tomato paste and therefore their concentrations are important for corrections of the X-ray spectra used for trace element analysis by PIXE. In this case, we employed another ion beam analytical technique, namely Rutherford Backscattering Spectrometry (RBS) (Chu, Mayer & Nicolet, 1978). This technique is based on the detection of He ions after backscattering events with the nucleus of target atoms.

The aim of this work was to characterize the Brazilian tomato paste through the PIXE technique. Different brands of tomato paste were purchased in the retail market for analysis in order to investigate their elemental composition and possible correlations regarding parameters such as brands, packages and storage time. Finally, statistical analysis was carried out in order to check the variability among different brands and packages.

2. Materials and methods

2.1. Samples

Three popular Brazilian brands of tomato paste were purchased in the local market. The tomato pastes were packed either in cannisters or in cardboard boxes (Tetra Pak®). The brands were Elefante (13 cans), Quero (4 Tetra Pak® boxes and 5 cans) and Arisco (5 Tetra Pak® boxes and 5 cans). The net weight of the tomato pastes ranged from 100 g to 600 g.

Several Elefante cans and Quero Tetra Pak® boxes were stored from 6 to 81 months in order to evaluate any possible changes in the elemental concentrations of the tomato paste as a function of time. Before opening, the packages were thoroughly washed and cleaned with a neutral detergent (phosphate-free) and carefully rinsed with water. A visual inspection of all packages was carried out in order to check their integrity and no problems were found in any of them. In particular, cans were checked for fractures, corrosion and enamel failure which could lead to the contamination of the tomato paste (Kontominas et al., 2006).

As the PIXE system requires the use of solid samples, the contents of each package had to be dried up. To that end, samples were weighed and put in a beaker inside an oven at temperatures ranging from 100 to 140 °C. The drying process took from 2 h up to 10 h depending on the sample. Once dried, the samples were homogenized and pressed into 2 mm thick pellets with a diameter and mass of 25 mm and 1.5 g respectively. For each package, 6 samples were prepared.

For the analysis of the inner parts of the packages, pieces of cans and cardboard boxes were cut in 25 mm diameter disks after the contents were removed from them. These disks were cleaned, washed and dried under ambient conditions.

2.2. Instrumentation and techniques

The experiments were carried out at the Ion Implantation Laboratory (Institute of Physics, Federal University of Rio Grande do Sul). A 3 MV Tandetron accelerator provided a 2 MeV proton beam to for the PIXE experiments. The samples were accommodated in a holder inside the reaction chamber kept at a pressure of about 10^{-6} mbar. The positioning of the samples on the beam was carried out through an electromechanical system coupled to a CCD camera. The X-rays induced in the samples by proton were detected by a Si(Li) detector (Sirius 80 e2V, Scientific Instruments) and by a HPGe detector (EG&G, Ortec) placed at -135° and +135° with respect to the beam direction respectively. The energy resolution of the Si(Li) and the HPGe detectors were around 150 eV and 170 eV at 5.9 keV respectively. The tomato paste samples were irradiated during 500 s each with an average current of 2.5 nA, while the cardboard boxes samples were irradiated during 200 s with similar currents. Finally, the cans were irradiated with a much reduced proton beam (about 0.15 nA) during 200 s in order to avoid problems related to the dead time of the acquisition system.

The RBS measurements were performed in order to obtain the relative mass of light (matrix) elements such as carbon, nitrogen and oxygen present in the tomato paste. A 1.2 MeV He^+ beam with an average current between 10 and 20 nA was employed. The RBS chamber was kept at a pressure of about 10^{-6} mbar. The backscattered He ions were detected by a silicon surface barrier detector (EG&G Ortec) placed at -165° with respect to the beam direction. The energy resolution of the detector was 20 keV for alpha particles.

2.3. Data analysis

The PIXE spectra were analyzed using GUPIXWIN software (Campbell et al., 2000) developed at the University of Guelph (Canada). In short, this software takes into account all experimental parameters and makes use of an extensive database including ionization cross sections and proton energy loss among others. Through a proper calibration of the system, a simultaneous fitting of all X-ray peaks converts elemental peak areas into concentrations.

The RBS analysis was carried out with SIMNRA code (Mayer, 1999). This software performs a simulation of RBS spectra using Rutherford and non-Rutherford cross sections. Different aspects of the experimental setup can be included in the simulations. In particular, this software handles non-structured samples like those studied in the present work.

For calibration purposes, PIXE and RBS experiments were carried out with tomato leaves standard (NIST Standard Reference Material 1573a) under the same experimental conditions as those used for the analysis of tomato paste samples.

The PIXE results were compared with the statistical tests T test and ANOVA One-way, followed by Tukey's post hoc test (5% level of significance). The comparison was performed between samples from different brands.

Finally, all results discussed in the present work refer to wet weight unless otherwise stated.

2.4. Uncertainties

Concerning the uncertainties, they were calculated directly from the variance of the data. It is important to note that these uncertainties are much larger than those stemming from the least-square fitting procedures of the spectra. Therefore, the final values and uncertainties quoted in the present work are represented by the mean and the respective standard deviation.

3. Results and discussion

3.1. Recovery values

Table 1 shows the certified and recovery values obtained for the analysis of tomato leaves standard (NIST Standard Reference Material 1573a) used for the calibration of the PIXE experimental setup. The recovery values vary from 0.6 % for Al to 2.5 % for Cu, thus attesting the reliability of the system setup.

3.2. Packages

The metallic cans are essentially made of Fe and Sn. It is important to bear in mind that the inner walls of the cans are coated with a thin layer (few micrometers thick) of a special enamel or varnish to serve as a sealant of the metal layers. The same holds true for cardboard boxes where the sealant is replaced by thin sheets of polyethylene. The Tetra Pak® boxes are characterized by Al, P, S, Cl, K, Ti, Cr, Fe, Zn and Ga. The statistical analysis of cans and cardboard boxes reveals that no significant differences were observed among the same type of packages from different brands. Conversely, previous studies carried out on canned tuna fish (Boufleur et al., 2013) indicate that different brands of canned tuna fish used different cans in terms of elemental concentrations. Moreover, tuna cans are characterized by large amounts of Al and Fe with smaller contributions of Ti and Cr (Boufleur et al., 2013). Finally, the tomato paste cans studied in the present work are quite similar to those of table cream (Ferrari et al., 2020).

Fig. 1 shows the relative elemental concentrations of the internal walls from all cans and cardboard boxes studied in this work. The Fe concentration in the cans (~ 94 %) is much higher than that found in the Tetra Pak® package. The main element found in Tetra Pak® boxes is Al with a relative concentration of about 95 %.

3.3. Tomato paste

According to the RBS analysis, the organic composition of tomato paste normalized to 100 % consists of 72.4 % carbon, 12.4 % nitrogen and 15.2 % oxygen.

The average X-ray spectra of all tomato paste brands are shown in Fig. 2. The following elements were detected in all tomato paste samples through the PIXE technique: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, Br and Rb. Concentrations of Cr, Ni and Sr were found above the limit of detection (LOD) only in some of the samples. In this case, the concentrations of Cr, Ni and Sr ranged from 0.2 mg/kg to 1.5 mg/kg, 0.4 mg/kg to 3.1 mg/kg and 0.3 mg/kg to 4.1 mg/kg respectively. Despite Sn was present in the cans, it was not observed in any of the canned tomato paste samples. The tomato pastes evaluated in this section were good for consumption, i.e. they were opened and analyzed within less than 18 months after the production date.

Table 1
Elemental concentrations (mg/kg dry weight) of tomato leaves standard (NIST Standard Reference Material 1573a) and respective experimental recoveries obtained for the PIXE technique. Values marked with an asterisk refer to data measured but not certified by the supplier.

Element	Tomato Leaves	
	Certified value (mg/kg)	Recovery value (mg/kg)
Mg	12000*	11918
Al	598 ± 12	594 ± 10
P	2160 ± 40	2142 ± 39
S	9600*	9559
Cl	6600*	6540
K	27000 ± 500	26650 ± 493
Ca	50500 ± 900	49628 ± 889
Mn	246 ± 8	240 ± 8
Fe	368 ± 7	359 ± 7
Cu	4.7 ± 0.1	4.6 ± 0.1
Zn	31 ± 1	30 ± 1
Br	1300*	1267
Sr	85*	83

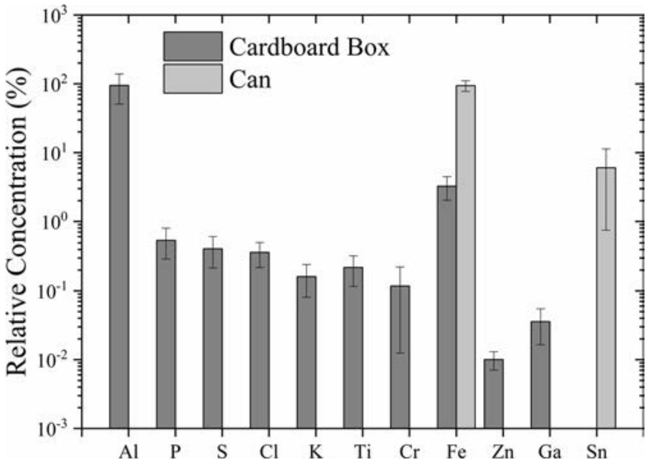

Fig. 1. Relative concentrations of the elements present in cardboard boxes and in metal cans. The uncertainties correspond to the respective standard deviations. All results for each type of container were normalized to unity.

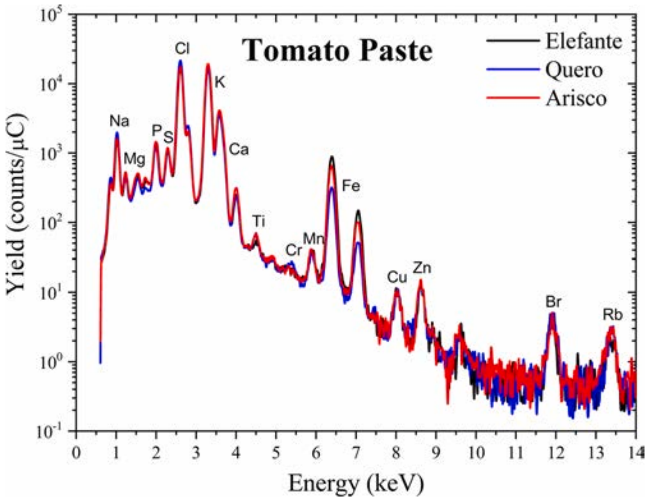

Fig. 2. X-ray spectra of tomato paste as a function of the X-ray energy. The yield of all spectra were normalized by the charge accumulated during the experiments. Each spectrum represents the average over several measurements. Black line: Elefante brand; blue line: Quero brand; red line: Arisco brand. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 2 presents the average elemental concentrations of tomato paste together with individual results per brand. The differences among brands are indicated by different subscript letter (a–c) within each row while equal letters represent equal concentrations from the statistical point of view with the observed level of significance of 5 %. In general, Cl, K and Na are the major elements found in tomato paste with mean concentrations ranging from ~3500 mg/kg (Na) up to ~5500 mg/kg (Cl). In addition, Mg, P and S have a substantial contribution in terms of concentration, while elements like Ti, Zn and Rb are trace elements with concentrations around 2 mg/kg. Despite Cl and Na are present in the tomato fruits with concentrations around 400 mg/kg and 63 mg/kg

Table 2
Elemental concentrations of tomato pastes studied in this work. The overall tomato paste corresponds to the average of $N = 18$ samples obtained from the analysis of Elefante, Quero and Arisco tomato paste brands. All results are represented by the mean and the respective standard deviation and are given in units of mg/kg (wet weight). Equal subscript letters (a-c) within each row represent equal concentrations from the statistical point of view ($p < 0.05$). CAN stands for canned tomato paste while TP stands for Tetra Pak® tomato paste boxes.

Elements	Average Tomato Paste		Elefante (CAN)	Quero (TP)	Arisco (TP)
	Concentration (mg/kg)	min – max (mg/kg)	Concentration (mg/kg)	Concentration (mg/kg)	Concentration (mg/kg)
Na	3574 ± 1277	1753 – 5026	4632 ± 243 $_{a}$	4230 ± 284 $_{b}$	1858 ± 101 $_{c}$
Mg	288 ± 100	172 – 448	416 ± 24 $_{a}$	265 ± 14 $_{b}$	184 ± 8 $_{c}$
Al	47 ± 13	23.7 – 69.8	54 ± 12 $_{a}$	43 ± 16 $_{a}$	44 ± 9 $_{a}$
Si	43 ± 17	26.4 – 104	57 ± 24 $_{a}$	36 ± 5 $_{a}$	37 ± 11 $_{a}$
P	348 ± 127	193 – 519	507 ± 9 $_{a}$	330 ± 21 $_{b}$	208 ± 12 $_{c}$
S	375 ± 109	223 – 513	493 ± 14 $_{a}$	394 ± 21 $_{b}$	239 ± 12 $_{c}$
Cl	5522 ± 2000	2701 – 7547	7113 ± 275 $_{a}$	6625 ± 537 $_{a}$	2827 ± 128 $_{b}$
K	3960 ± 1335	2341 – 5812	5591 ± 155 $_{a}$	3852 ± 168 $_{b}$	2435 ± 82 $_{c}$
Ca	131 ± 35	84 – 197	172 ± 15 $_{a}$	127 ± 7 $_{b}$	94 ± 8 $_{c}$
Ti	2.2 ± 1.7	0.8 – 6.7	2.2 ± 0.3 $_{a}$	2.8 ± 2.7 $_{a}$	1.5 ± 0.5 $_{a}$
Mn	1.1 ± 0.4	0.6 – 1.8	1.3 ± 0.5 $_{a}$	1.1 ± 0.4 $_{a}$	0.8 ± 0.1 $_{a}$
Fe	42 ± 28	18.5 – 83.7	79 ± 3 $_{a}$	22 ± 3 $_{b}$	24 ± 5 $_{b}$
Cu	0.9 ± 0.4	0.4 – 1.7	1.2 ± 0.5 $_{a}$	1.0 ± 0.1 $_{a}$	0.5 ± 0.1 $_{b}$
Zn	1.5 ± 0.6	0.7 – 2.6	2.2 ± 0.3 $_{a}$	1.7 ± 0.3 $_{b}$	1.0 ± 0.2 $_{c}$
Br	2.3 ± 1.0	1.0 – 4.4	3.1 ± 1.0 $_{a}$	2.5 ± 0.4 $_{a}$	1.2 ± 0.2 $_{b}$
Rb	2.0 ± 0.8	0.9 – 3.5	1.8 ± 0.6 $_{ab}$	2.7 ± 0.8 $_{a}$	1.4 ± 0.4 $_{b}$

respectively (Belitz et al., 2009), these values are much lower than those found in this work for tomato paste. The relatively high concentrations of these elements found in this work can be attributed to the addition of NaCl to the tomato paste according the limit of 5% of tomato mass established by the Brazilian sanitary authority (ANVISA, 1978).

Our results for Na, S, Ca, Ti, Mn and Cu are within the range of concentrations found by Romero-Dávila and Miranda. Romero-Dávila and Miranda have determined major and trace elements present in tomato paste and fresh tomatoes from Mexico, USA, Japan, Colombia and Chile using the PIXE technique (Romero-Dávila and Miranda, 2004). However, their concentrations of some elements are much smaller than those observed in the present study. For instance, while the concentration of Fe measured in this work varied from 18 mg/kg up to 84 mg/kg, the overall Fe concentration measured by these authors ranged from 0.1 mg/kg up to 2.4 mg/kg (Romero-Dávila and Miranda, 2004). On the other hand, the concentrations of Fe, Cu and Zn found in this work were compatible with the range of values found by Iwegbue and collaborators who measured trace elements of canned tomato paste consumed in Nigeria (Iwegbue et al., 2012). In particular, Iwegbue and collaborators reported Fe concentrations in the Nigerian tomato paste in the range between 0.1 mg/kg up to 113 mg/kg. Finally, the concentrations of Fe and Al determined in the present study for canned tomato paste are compatible with those reported by Al-Thagafi and collaborators (Al-Thagafi et al., 2014).

Regarding the different brands analyzed in this work, the elemental concentrations found for Elefante brand are generally higher than those found for Quero brand and about twice than those found for Arisco brand. The only exception to this rule is Rb whose concentration is highest for Quero brand. For all elements but Al, Si, Ti and Mn, there are significant differences in the concentrations between at least 2 brands. The mean concentrations of Na, Mg, P, S, K, Ca and Zn are distinct among the 3 brands. The differences among brands shown in Table 2 may be explained by several factors including field location, field practices and different industrial processing protocols. In particular, industrial protocols vary according to the amount of tomatoes and additives used to process tomato paste.

Besides tomato paste from Arisco brand, tomato sauce with parsley stored in cans from the same brand were analyzed as well. These results were compared with those obtained for tomato paste from the same brand packed in cardboard boxes. Fig. 3 reveals that most elements have concentrations compatible to each other while Na, Mg, Al, Si, Cl and Fe have distinct concentrations. Indeed, higher concentrations were found for Mg, Al, Si and Fe in tomato paste. For elements such as Na, Al, Si and Cl the concentrations differ by a factor 2 between the two kinds of products. For example, the average concentrations of Cl for tomato paste and tomato sauce are (2827 ± 128) mg/kg and (6324 ± 312) mg/kg respectively. The analysis of fresh tomatoes, canned tomatoes and canned tomato paste carried out by Al-Thagafi and co-workers (Al-Thagafi et al., 2014) found different concentrations of Al among all types of samples analyzed. Moreover, they found that the concentrations of Fe were similar for the canned tomatoes and tomato paste. The higher concentrations of these elements in the canned food was attributed to the preservatives, food processing and corrosion of the cans. In our case, the differences could be explained in terms of packing (cardboard boxes and cans) and product (tomato paste and tomato sauce seasoned with parsley).

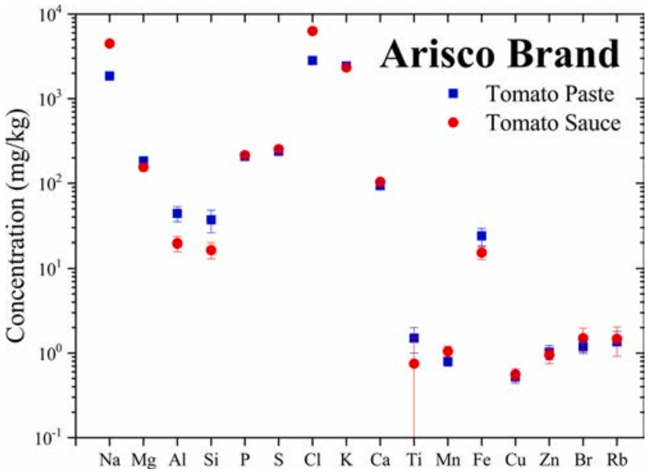

Fig. 3. Elemental concentrations (mean and standard deviation) of tomato paste (stored in cardboard boxes) and tomato sauce with parsley (stored in cans) from Arisco brand. The average concentrations are given in mg/kg (wet weight).

Since tomato pastes were packed in different kinds of containers (Elefante brand in cans while Arisco and Quero brands in Tetra Pak® boxes), the different concentrations of some elements like Fe could be related to the packages themselves (Table 2). In order to check whether there is any interaction between the packages and their respective contents, several cardboard boxes and cans of Quero and Elefante brands respectively were stored for several years. The storage time (ST) is defined as the time between the fabrication date and the opening date. The expire date of both products are 18 months after fabrication. Al and Fe were chosen for this study since they are the most abundant elements found in Tetra Pak® boxes and cans respectively according to the results shown in Fig. 1.

The concentrations of Al and Fe tomato paste stored in Tetra Pak® boxes as a function of the storage time are shown in a linear-linear plot in Fig. 4. These results reveal a quite similar decreasing behavior of the Al and Fe concentrations as a function of the storage time. It is important to note that these results are affected by relatively large uncertainties due to the small number of data points. The parameters of the linear fit are shown in Table 3. The results for Al indicate a slope compatible to zero within the uncertainties. On the other hand, the concentration of Fe decreases over time.

Fig. 5 shows the log-linear plots of the elemental concentrations of Al and Fe as a function of the storage time for tomato paste stored in cans. In this case, Table 3 reveals that data from Al and Fe were fully compatible with linear fittings in log-linear plots, thus indicating an exponential behavior of the Al and Fe data as a function of the storage time. Clearly, the Fe concentration increases as a function of storage time while the Al concentration decreases. Changes of Fe concentration in canned food have already been reported for tomato paste (Türker and Yüksel, 1997) and tuna fish (Boufleur et al., 2013). During a period of one year, Türker and Yüksel found an increase in the concentration of Fe in canned tomato paste from 6.8 mg/kg to 20.6 mg/kg. Similarly, results obtained by Boufleur and co-workers indicate an increase of Fe concentration at a rate of 1.2 mg/kg/month over a period of 20 months (Boufleur et al., 2013).

Despite the large uncertainties of Al and Fe concentrations, the results shown in Figs. 4 and 5 suggest that an exchange mechanism between the tomato paste and the package could be at play. Indeed, Table 2 shows that tomato paste from Quero brand (packed in Al-rich cardboard box) has more Al than Fe. On the other hand, tomato paste from Elefante brand (packed in Fe-rich cannister) has more Fe than Al. Despite the exchange mechanism of Al between the cardboard box and the tomato paste is not conclusive (Fig. 4 and Table 3), the transfer of Fe from the cannister to the tomato paste is clearly seen in Fig. 5 and corroborated by the results shown in Table 3.

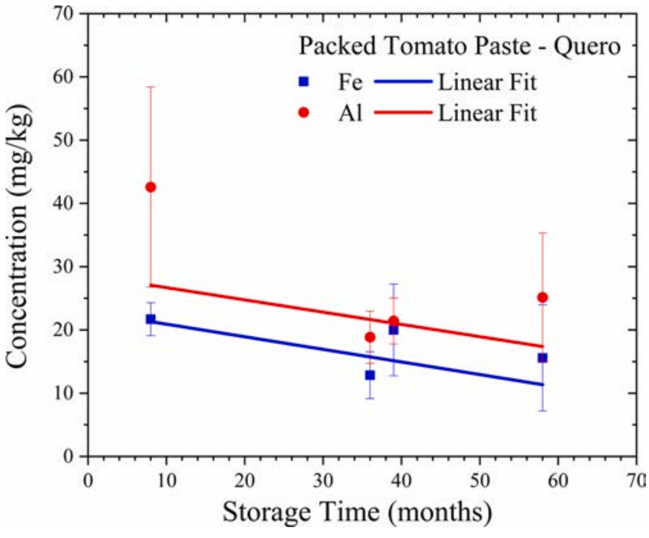

Fig. 4. Linear-linear plot of the mean concentrations of Fe (blue squares) and Al (red circles) as a function of the storage time for Quero brand tomato paste packed in Tetra Pak® boxes. Uncertainties correspond to standard deviation. The red and blue lines stand for a linear fit of the Al and Fe data respectively. The fitting parameters are shown in Table 3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 3
Parameters corresponding to a linear fit of the linear-linear plots for tomato paste stored in Tetra Pack® boxes (Fig. 4) and of the log-linear plots for tomato paste stored in cans (Fig. 5).

Element	Package	Brand	Intercept	Slope
Fe	Tetra Pak®	Quero	(22.9 ± 2.7) mg/kg	- (0.2 ± 0.1) mg/kg/month
Al	Tetra Pak®	Quero	(28.6 ± 14.0) mg/kg	- (0.2 ± 0.4) mg/kg/month
Fe	Can	Elefante	(1.8 ± 0.1) log (mg/kg)	(0.016 ± 0.002) log(mg/kg)/month
Al	Can	Elefante	(2.1 ± 0.1) log (mg/kg)	- (0.009 ± 0.002) log (mg/kg)/month

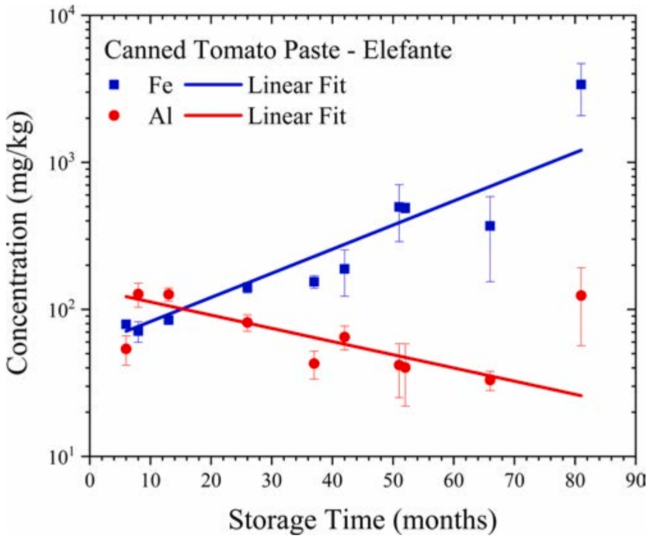

Fig. 5. Log-linear plot of the mean concentrations of Fe (blue squares) and Al (red circles) as a function of the storage time for Elefante brand canned tomato paste. Uncertainties correspond to standard deviation. The red and blue lines stand for a linear fit of the Al and Fe data respectively. The fitting parameters are shown in Table 3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Figs. 4 and 5 show a decreasing trend on the concentrations of Fe and Al respectively in tomato paste. One possible explanation for this mechanism would be a passivation of the internal surfaces of the packages. For long periods of storage time, salts, additives and organic compounds present in the tomato paste may lead to a degradation of the internal surface of the package. In this case, Fe present in the medium could passivate Al-rich surfaces while Al from the medium could passivate Fe-rich surfaces. Both cases would lead to a decrease of these elements in the tomato paste.

4. Conclusions

Brazilian tomato paste packed in cans and Tetra Pak® boxes was analyzed using a single ion beam technique, namely Particle-Induced X-ray Emission (PIXE). The packages were analyzed by PIXE as well. The elements Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, Br, Rb and Sr were found in tomato paste. Elements like Cr, Ni and Sr were detected in some of the samples only. Moreover, Al and Fe are the main constituents of Tetra Pak® and cans respectively. Despite cannisters contain substantial amounts of Sn, this element was not detected in any tomato paste sample analyzed in this work.

Among all elements, Cl has the highest concentrations in all tomato paste brands analyzed in this work with concentrations as high as 7000 mg/kg. The concentrations of trace elements like Cu, Zn, Br and Rb vary between 1 and 2 mg/kg. While tomato paste packed in Al-rich cardboard boxes contains more Al than Fe, tomato paste packed in Fe-rich canisters has more Fe than Al. Despite the concentration of Fe is higher in tomato paste packed in cans than in cardboard boxes, the concentration of Al is around 47 mg/kg regardless the type of package of the tomato paste.

Our results suggest that a transfer mechanism of Al and Fe takes place to and from the tomato paste for long periods of storage time. There is clear indication that Fe could migrate from the can to the tomato paste and, to a lesser degree, from the tomato paste to the cardboard box. Therefore, the concentration of Fe in canned tomato paste increases as a function of storage time, reaching about 3000 mg/kg after 80 months of storage. Under this circumstance, a single intake of about 67 g of this tomato paste would reach toxic levels for Fe in humans (Pais and Jones, 1997).

In the case of canned tomato paste, Al appears to be transferred from the tomato paste to the Fe-rich can. Similarly, Fe seems to be transferred from the tomato paste to the Al-rich cardboard box. One possible mechanism for this metal exchange between the tomato paste and the container walls could be the passivation of the Fe-rich surface by Al and of the Al-rich surface by Fe. However, it must be stressed that this transfer mechanism might be important for long periods of storage time only and has no substantial impact over 18 months corresponding to the expire date of the tomato pastes studied in this work.

Finally, it is important to note that the uncertainties of the elemental concentrations are relatively large, which hamper any attempt to model the transfer mechanism in a more elaborate way.

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Declaration of Competing Interest

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