

Study of the effect of common infusions on glass ionomers using the PIXE and RBS techniques



María Gisela Verón^{a,*}, Pablo Daniel Pérez^a, Sergio Gabriel Suárez^a, Miguel Oscar Prado^{a,b}

^a Consejo Nacional de Investigaciones Científicas y Técnicas de Argentina

^b Centro Atómico Bariloche – Comisión Nacional de Energía Atómica, Av. E. Bustillo km 9.5, 8400 San Carlos de Bariloche, Argentina

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ABSTRACT

The effect of four commonly consumed beverages as mineral water, coffee, tea and mate tea on the elemental composition of a commercial glass ionomer was studied using Particle Induced X-ray Emission (PIXE) and Rutherford backscattering (RBS) techniques.

We found that after immersion in acidic media, some elements as Al, Si and Na are lost from the glass-ionomer whereas others heavier, as K, Ca and La, increase their concentration at the surface. Although the concentration profiles of Al and Si are different in different media, in all of them the Al:Si ratio was close to unity and remained constant for different periods of immersion in all media. The incorporation of K, Mg and Fe to the surface is found for common infusions while for mineral water the glass-ionomer mainly loses F and Na. The RBS technique showed that immersion in different media produced a modification of the density of the glass ionomer surface layer due to the increment of the concentration of heavier elements at the surface. The thickness of the modified surface layer extends up to 3 μm when the immersion time is seven days and more than 6 μm after 33 days of immersion.

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1. Introduction

Glass-ionomer dental cements (GICs) have proven to be useful in several areas of dentistry, mainly for restorative dentistry. The original cement was developed by Wilson and Kent in 1969 [1], and has undergone continuous development, improvement and diversification [2–5]. Glass-ionomers are water-based cements known as polyalkenoate cements. They are formed by the reaction of an acidic polymer and a basic glass in the presence of water [2–11]. The resulting cement is an aqueous, inorganic/organic network that is translucent and adheres to tooth structure [2–5,9,10,12–14]. Among its most important properties are highlighted the good biocompatibility, good chemical or specific adhesion to dental structures by an ion exchange process, [12–14] and fluoride release in vivo and in vitro [15,16]. This release of F from glass ionomers can have a cariostatic effect since its presence improves the microhardness of the enamel and reduces its solubility in an acid medium [17,18], and increases the F concentration in the adjacent tissues by inhibiting the growth of Streptococcus mutans bacteria, which delays the onset of carious lesions [19–22]. These properties are major advantages over the compos-

ite resin and amalgams. However, despite the development in the composition and characteristics of these restorative materials, one factor which influences the clinical performance of dental restorations is their resistance to damage. In the oral cavity these materials are subjected to a number of conditions that may cause changes in the physical, mechanical, chemical and aesthetic properties. One of the factors that may affect the quality of the restorations is the consumption of certain foods and beverages such as coffee, tea, soft drinks, alcoholic beverages and even fluorinated water [23,24]. The effect of these beverages on color and microhardness of composite resin materials varies depending on the intrinsic features of the composite, such as their chemical composition [23,25]. In addition, it has been found that a slow chemical alteration of dental restorations may be accompanied by release of elements from the material, and these may be related to certain biological effects [26,27]. Also, small gaps between the restorative and the tooth structure can lead to colonization by bacteria and development of secondary caries. Secondary caries is one of the leading causes of restoration failure. On the other hand, in the corrosive environment of the mouth, chemical reactions and multi-element transfer can take place at the interfaces of a tooth filling.

In general, surface damage, loss of load particles, release and uptake of inorganic ions, and bacterial action alter the properties of glass ionomers and limit the durability of a dental restoration. These processes involve several phenomena, and that require

* Corresponding author at: Av. Bustillo 9500, Centro Atómico Bariloche, R8402 AGP- S. C. de Bariloche, Río Negro, Argentina.

E-mail address: maria.gisela.veron@cab.cnea.gov.ar (M.G. Verón).

surface analysis methods [26–28]. In this sense, ion beam techniques such as Particle-Induced X-ray Emission (PIXE) and Rutherford Backscattering (RBS) Spectrometry are suited to approach this type of studies, and today are widely used in the area of dentistry. PIXE is a non-destructive method that allows to simultaneously determining all constituents of the sample with an excellent sensitivity in the order of ppm through a wide range of atomic numbers [26–30]. Rutherford Backscattering (RBS) Spectrometry is also a non-destructive technique, sensitive to elements heavier than those detected by PIXE and allows the determination of the depth distribution of the elements [31].

In this work the effect of commonly consumed beverage in elemental composition of a commercial ionomer using the PIXE and RBS techniques is studied. We analyzed the changes in the composition of the glass ionomer due to immersion in different beverages and the incorporation of new elements by the action of such liquids.

2. Materials and methods

Commercial Ketac Molar Easymix glass ionomer was selected for this study. For the preparation of specimens 4.5 parts of powder (a measuring spoon provided with the product full of powder flush) and 1 part of liquid (1 drop, approximately 0.05 ml) were mixed at room temperature for 30 s, following the instructions of manufacturers. After mixing, the material was filled into lubricated cylindrical metal molds of 5 mm diameter and 2.5 mm height. Once inside the mold, each sample was pressed with a plunger to remove air bubbles. They were covered with glass slides and took culture heater oven at 36 °C for two hours. In addition commercial coffee, tea and *mate* tea were compressed to form solid tablets of the same dimensions as the ionomer samples, in order to know the elemental composition of the infusions used as storage medium. The mineral water composition was provided by the manufacturer.

2.1. Treatment of specimens

The specimens were removed from the molds and immediately immersed in 50 ml of habitual consumption infusions or beverages: black tea, coffee, *mate* tea, and mineral water. Five specimens were stored in each medium for 0.9; 3; 7; 20 and 33 days at 36 °C. A set of virgin glass ionomer samples was reserved for use as reference.

The beverages were prepared according to the manufacturer's instructions using mineral water. They were allowed to cool to 36 °C and their pH was determined with an Altronix Ezdo-PC pH meter (Table 1). These beverages were periodically renewed to prevent their decomposition and maintain the pH constant.

Ertas et al. reported that among coffee drinkers, the average amount of consumption is 3.2 cups per day, and that the average drinking time for each cup (300 ml) is 15 min [32]. Therefore, a storage time of 20 h simulates approximately 25 days of coffee consumption. If we consider the same average amount of tea and *mate* infusions in one day, the equivalent consumption time of the three infusions in this experiment would be in the range of

25 days to 33 months (Table 2). Although mineral water is a drink consumed in less time and in greater quantity per day, in this work we will consider it as a reference, and in the same proportion as the infusions, since it was the medium used to prepare such infusions.

2.2. PIXE and RBS measurements

PIXE and RBS measurements were performed with 2.0 MeV H⁺ and 2 MeV ⁴He⁺⁺ particles beam respectively, in a 1.7 MV tandem accelerator 5SDH Pelletron NEC located at the Centro Atómico Bariloche, Argentina.

After the storage time of the samples in different infusions, they were removed, washed with distilled water and allowed to dry.

For PIXE measurements, five samples of each species were fixed on aluminum holder and kept in vacuum for 24 h. Protons with energy of 2 MeV impacted perpendicularly on the surface of the samples, losing their kinetic energy until they were finally stopped or backscattered out of the sample. Part of its kinetic energy is used to ionize sample atoms, generating electrons in higher energy excited states. When electrons go back to its lower energy level they emit photons which are characteristic of each atomic species present in the sample. The analysis of these X-ray spectra allows to calculate the sample surface composition. In this work the PIXE spectral analyses were performed using GUPIX software [33]. For RBS measurements, samples of each species were fixed on an aluminum holder and kept in vacuum during 24 h. Samples were bombarded by a 2 MeV⁴He – beam. It is considered that these particles collide elastically with the target atoms, being dispersed elastically with an energy characteristic of the mass of the dispersing center. In addition, they lose energy as they travel within the material, both in the entrance way and the exit. The dispersed particles are detected in a backward directions, corresponding to scattering angles greater than 90° (backscatter), with a silicon barrier detectors. In our setup we fixed the detection angle at 165 degrees. The energy spectrum of the detected particles contains information on the composition of the target and on the distribution in depth of the constituent elements. The SIMNRA computer code was used to analyze the spectra generated by RBS [34].

3. Results and discussion

3.1. Elemental composition of the commercial glass ionomer and ingredients used for the preparation of beverages

Fig. 1 shows a PIXE spectrum obtained for the commercial reference glass ionomer. The amplitude of the peaks is qualitatively related to the elemental concentration of the samples. The detected elements mainly include C, O, F, Na, Al, Si, P, Ca and La, and their respective concentrations are presented in Table 3.

The elemental composition of the ingredients used for the preparation of beverages (coffee, tea and *mate* tea) is depicted in Fig. 2. A group of elements which is present in the preparation ingredients is not found in the virgin ionomer, such as N, S, Cl, K, Ti and Mn (see Fig. 2 and Table 4).

Table 1
pH of storage beverages.

Beverage	pH
coffee	5.5
black tea	5.76
<i>mate</i> tea	5.91
mineral water	8.13

Table 2
Equivalent consumption time between 0.9 and 33 days.

Storage time		Equivalent time of consumption [days]
[days]	[hours]	
0.9	21	26
7	168	210
20	480	600
33	792	990

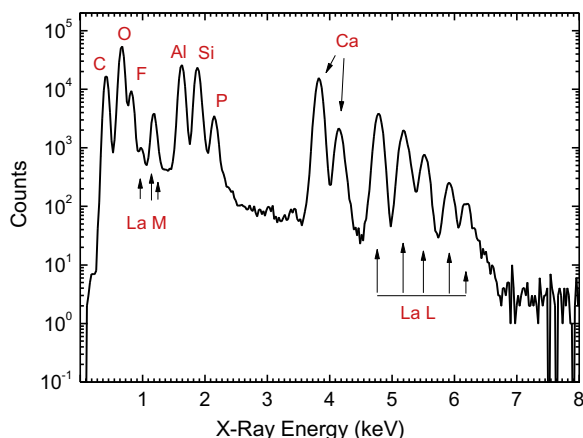


Fig. 1. PIXE spectrum of the commercial reference glass ionomer.

Table 3
Elemental composition of the commercial glass ionomer detected by PIXE.

Elements	Concentration [% p/p]	Error [%]
C	22.1	0.5
O	35.0	0.2
F	5.7	1.2
Na	1.4	1.2
Mg	0.04	27.1
Al	8.1	1.3
Si	7.7	0.3
P	1.2	1.1
Ca	6.6	1.0
Fe	0.01	44.9
La	12.1	0.7

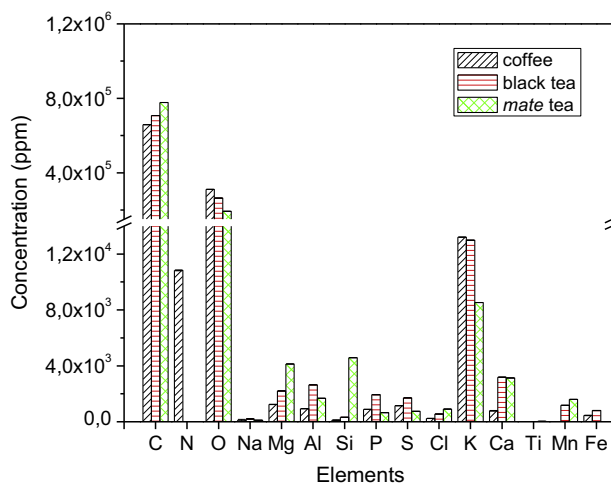


Fig. 2. Elemental composition of samples of pure coffee, black tea and *mate* tea obtained by PIXE analysis.

3.2. Variation of the concentration of main elements of the commercial glass ionomer by the action of infusions

After storage of the samples in the infusions, a notable difference was observed in the elemental composition of the starting glass ionomer. As it was expected, this difference was greater in acid beverages than in mineral water.

Fig. 3 shows the variation of the elemental concentration of the glass ionomer stored in mineral water.

A loss of Na was observed throughout the experiment, accompanied by a decrease in the concentration of F. Both elements have

a similar concentration profile. This effect was observed by Wilson et al. who studied the release of fluoride and other chemical species from a glass ionomer cement in distilled water [35]. They concluded that fluoride release is controlled by releasing sodium in order to preserve the electroneutrality of the system, and that fluoride associated with different cations of sodium appears to be unavailable for release.

On the other hand, a slight increase in the concentration of Al, Ca, P and La was observed in the first 20 h of storage, this increase being approximately 15% for calcium and 5% for the rest of the elements. Thereafter, P and La remained approximately constant until the end of storage. Calcium presented increases and decreases in the different study times, reaching a gain of 22% at 20 days of immersion, which declined to its initial value at the end of the experiment. In this instance, Si and Al showed, in turn, an increase in concentration (12% and 23% respectively). These results differ from what would be expected for these elements, since other authors have reported that aluminum, silicon and phosphorus are released from the material in any situation, regardless of pH, this effect being more marked in acid media [36–38]. This demonstrates the effect of the ions present in the mineral water, which on the one hand decrease the rate of exit of the ions from the ionomer to the surrounding medium, and on the other, the possible formation of insoluble deposits on the surface of the material over time they could precipitate. The increase of the calcium concentration at twenty days and subsequent decrease could be due to this effect.

3.3. Variation of the elemental composition of the glass ionomer in acidic beverages

In the acidic media the variation of the elemental composition is complex. The storage of samples in black tea (Fig. 4) and *mate* tea (Fig. 5) determined two groups of elements: Na, Al and Si (Group I), and La, F and Ca (Group II).

An inflection point was observed at seven days of storage, from which each group presented a different behavior.

In the first group, a continuous decrease in concentration was observed as a function of storage time, whereas in the second group the concentrations showed an increase. This increase was prominent between 7 and 20 days, from there a slight decrease or increase in the concentration of F, Ca and La was observed until the end of the experiment. Phosphorus showed a different behavior, remained practically constant from the seven days of storage in black tea, while followed the concentration pattern that F, Ca and La until the 20 days of storage in *mate* tea, decreasing when arriving at 33 days.

On the other hand, the storage of the ionomer in coffee did not allow the separation of groups of elements, but the inflection points were the same. The most noticeable changes were observed in the concentration of Al, Si and F after seven days of storage. Unlike the behavior of the samples stationed in tea and *mate* tea, Al and Si increased their concentration by 60% with respect to their initial value (Fig. 6).

According to the PIXE analysis of the reference samples, the coffee has a lower concentration of Al and Si, compared to the samples of black tea and *mate* tea (Fig. 2 and Table 4), so it can be inferred that the higher concentration of these elements in the surface do not come from the interaction of such elements with the surrounding ions, but from the greater release of Al and Si from inside the glass ionomer, which initially accumulate at the surface, and then dissolve with the storage time. From this behavior we can infer that coffee has greater penetration power than other beverages, favoring the selective exit of some elements. This effect was predominant in the case of Fluoride, a great variation in its concentration was observed, with a loss of 100% after seven days of storage in this beverage. However, the samples stored in the three

Table 4
Elemental composition of samples of pure coffee, black tea and *mate* tea obtained by PIXE analysis.

Elements	coffee		black tea		<i>mate</i> tea	
	Concentration [ppm]	Error [%]	Concentration [ppm]	Error [%]	Concentration [ppm]	Error [%]
C	658565.3	0.2	707176.8	0.24	777674.0	0.1
N	10828.6	36.1	–	–	–	–
O	311017.8	0.4	264144.8	0.4	193433.4	0.2
Na	105.4	71.5	204.6	31.4	102.6	25.9
Mg	1235.5	5.1	2210.4	3.0	4127.3	0.8
Al	936.4	5.1	2644.3	2.2	1680.9	1.4
Si	115.8	28.0	319.2	10.2	4588.8	0.6
P	887.5	3.9	1935.8	2.2	657.8	2.1
S	1153.6	3.0	1712.4	2.2	746.6	1.7
Cl	238.4	10.1	555.7	4.8	908.5	1.5
K	13200.8	0.8	12986.9	0.8	8529.4	0.5
Ca	784.7	21.1	3192.2	6.5	3131.3	2.7
Ti	–	–	–	–	30.5	21.4
Mn	–	–	1174.1	7.2	1605.3	2.7
Fe	451.3	21.1	800.8	11.6	239.8	13.4

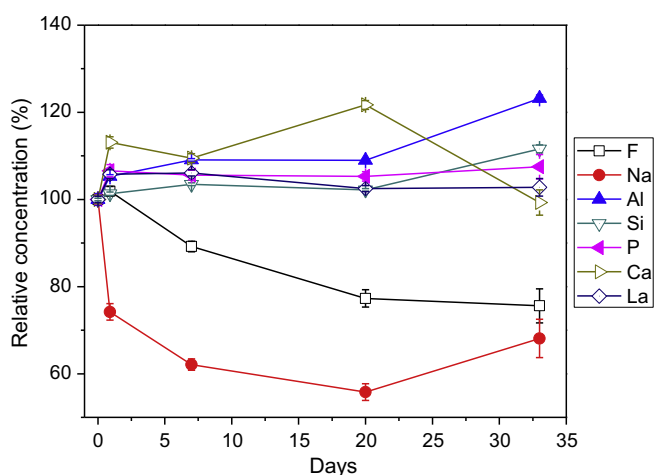


Fig. 3. Relative concentration of the chemical elements of the glass ionomer stored in mineral water.

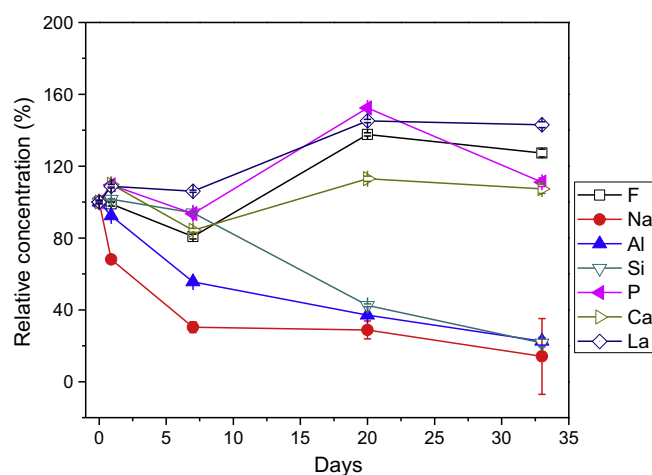


Fig. 5. Relative concentration of the chemical elements of the surface of the glass ionomer stored in *mate* tea.

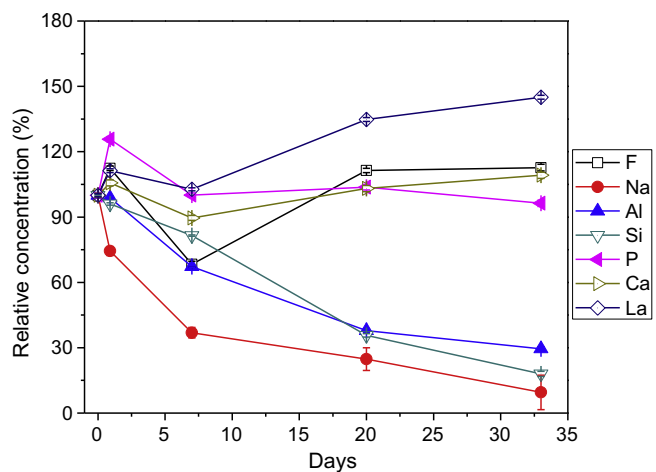


Fig. 4. Relative concentration of the chemical elements of the surface of the glass ionomer stored in black tea.

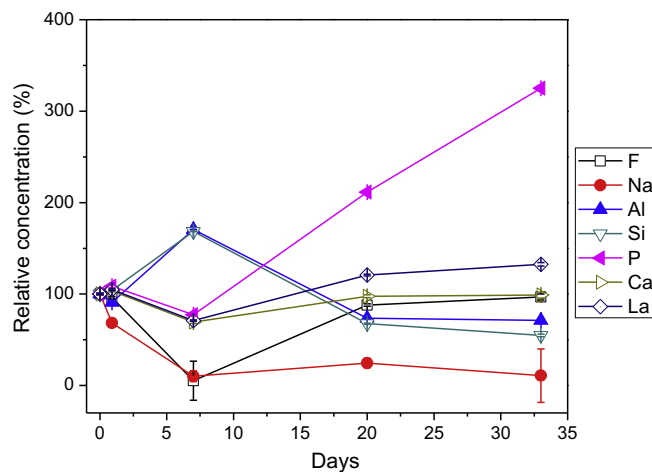


Fig. 6. Relative concentration of the chemical elements of the surface of the glass ionomer stored in coffee.

beverages: coffee, tea and *mate* tea, showed similarity in the concentration profile of F, Ca and La (Figs. 4–6). This suggests that storage in acid medium favors the release of fluorine to form calcium and lanthanum compounds.

On the other hand, although the concentration profile of Al and Si was different in the storage beverages, in all of them the relation Al:Si was close to unity throughout the experiment, this suggests that within the first four weeks there may have been a consistent

set of chemical compounds formed from these elements, and these are the compounds that dissolve in solution.

3.4. Adsorption of elements from infusions

In addition to the variation of the concentration of the major constituent elements of the commercial ionomer due to storage in beverages, the presence of new elements such as K and Mn was detected, and the increase in the concentration of Mg and Fe, which had only been detected as traces at the beginning of the experiment.

Fig. 7 shows the variation of the K concentration. After storage for seven days in *mate* tea and tea the concentration were 5547 and 5534 ppm respectively, and remained approximately constant for different storage times. In samples stored the same time in coffee, a slightly lower concentration (4957 ppm) was detected, but unlike the previous ones, it increased until the end of the experiment, reaching a value of approximately 15300 ppm. Hadley et al. [39] reported that potassium could be absorbed by a glass ionomer cement after being immersed in KF solutions, and that this absorption is a function of erosion of the matrix of the compound. As mentioned above, this beverage showed a greater penetration power in the material than the rest of the drinks being this effect accentuated with the time of storage, accordingly, a higher concentration of K was detected after 33 days of immersion. In mineral water only traces were detected at seven days (76 ppm).

The presence of Mn was observed in samples stored in *mate* tea and tea but not in the samples removed from coffee (Fig. 8), in agreement with the PIXE results of the ingredients from which the infusions were prepared.

In the samples stored in *mate* tea there was a continuous increase of the concentration of Mn, reaching a value of 6000 ppm. In the samples stored in tea a similar increase was observed at seven days, but from that there was a lower gain in the concentration. This result is consistent with the higher concentration of this element in the pure *mate* samples (Fig. 2, Table 4).

On the other hand, Fe and Mg that were in the starting ionomer as trace elements, underwent changes after storage in the beverages. In the case of iron, a significant increase in Fe concentration was observed after 7 days of storage of the ionomer in coffee, reaching a concentration 15 times higher than the initial value (Fig. 9). In the rest of the infusions the increase was less important than in coffee.

The PIXE analysis of the pure samples of black tea, *mate* tea and coffee did not present significant differences in the concentration

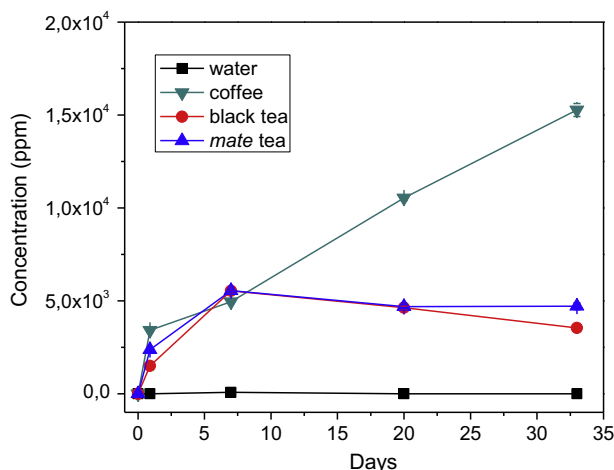


Fig. 7. Concentration of K on the glass ionomer surface stored in all media.

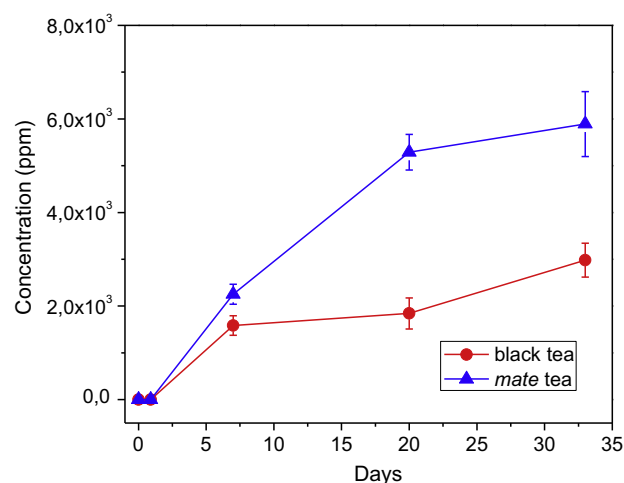


Fig. 8. Concentration of Mn on the glass ionomer surface stored in tea and *mate* tea.

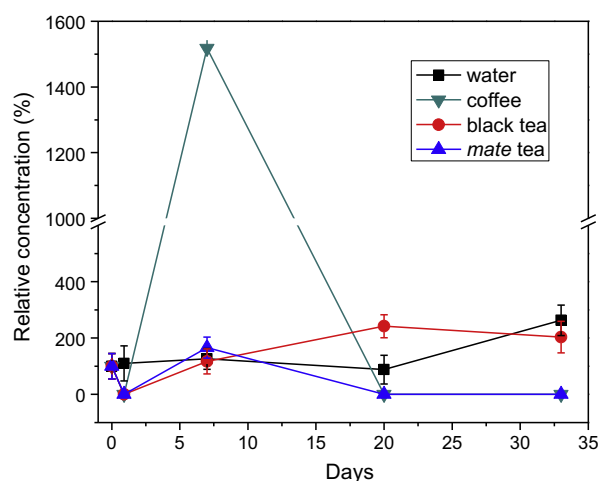


Fig. 9. Relative concentration of Fe on the glass ionomer surface stored in all media.

of this element (Table 4). Therefore, this result can be attributed, as in previous cases, to the greater penetration power of this beverage, facilitating the exit of this element from deeper areas of the material, and subsequent accumulation thereof on the surface of the material. However, this argument does not justify the change in the concentration of Mg.

The samples removed from the *mate* tea and tea showed an increase in concentration of this element higher than that observed in samples stored in coffee (Fig. 10). In this case, the PIXE analysis of reference samples of tea, *mate* tea and coffee presented a difference in concentration of magnesium, being higher in *mate* tea (*mate* tea > tea > coffee). This suggests that the absorption of this element from the surrounding liquid predominates over the erosion effect of the material. In general, the absorption of cations of valence other than one has been scarcely reported.

3.5. RBS measurements

In this section we show the experimental results obtained with RBS spectrometry with 2 MeV He particles colliding with the same samples analyzed by PIXE after 7 and 33 days immersed in coffee, tea, *mate* tea and mineral water.

We observe first that 2 MeV alpha particles penetrate a maximum depth of 9–10 μm , the range of the projectile in the Glass

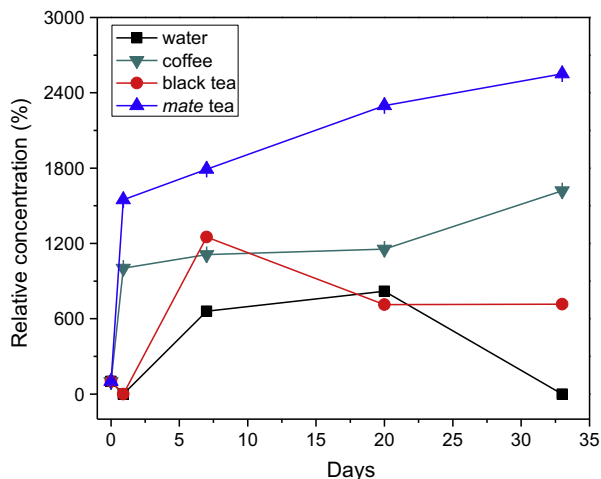


Fig. 10. Relative concentration of Mg on the glass ionomer surface stored in all media.

Ionomer (GI) according to simulations from SRIM code [40]. To obtain such a result we have taken the elemental composition from our previous PIXE analysis and used it to simulate the target to be irradiated by alpha particles in the SRIM calculation. A typical RBS spectrum is the counting of projectiles collected, as a standard way adopted by most researchers in the literature, at a fixed backscattered angle ($\theta = 165^\circ$ in our case) as a function of their energies [31]. Impinging projectiles, after having a hard and elastic collision with target nucleus, can be scattered backward towards the detector bringing information about atoms distribution in the sample. In this way, a RBS spectrum shows a maximum energy due to those projectiles that were scattered at the surface by the heaviest nuclei. However, as the projectile can penetrate and travel inside the target interacting with electrons before a hard collision with a target nucleus, there is an effective energy loss which increases in the way-out to the detector. In this manner, a RBS spectrum from a multielemental sample, such as a GI, contains information about the sample atoms composition and distribution. The final energy of the projectile can be used therefore to have a measure of the mass of the target nucleus, and depths of location of target species.

In Fig. 11 we show, as an example, the RBS spectra obtained by bombarding the glass ionomer samples surface after being immersed 7 days in mineral water and *mate* tea, respectively. As we have found no important differences between our virgin

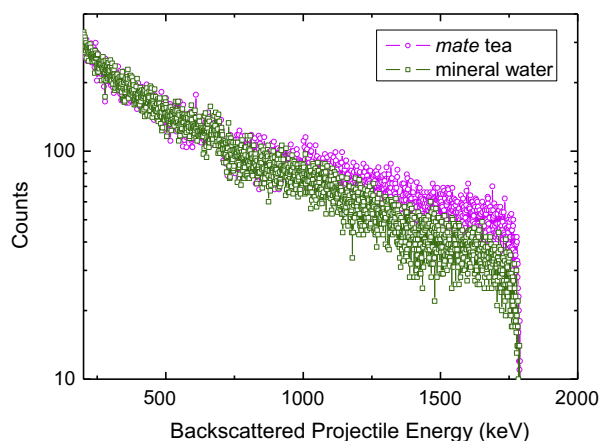


Fig. 11. RBS spectra taken with glass ionomer immersed during 7 days in mineral water (open square) and *mate* tea (open circle).

ionomer and those immersed in mineral water, we compare our results obtained after immersion in different infusions to that registered for mineral water. In order to quantify the effect on surface of the immersed ionomers, we obtained the ratios between spectra corresponding to an immersed glass ionomer in a given infusion (coffee, tea, mate tea, and mineral water) to that obtained with the pure or virgin glass ionomer.

We can observe that from the lowest energy up to 1000 keV approximately, there are no main differences between both spectra shown in Fig. 11. Both spectra show a different behavior for energies larger to 1000 keV and differences are larger near the maximum energy. To see more clearly such differences, we show in Fig. 12 the ratio between spectra for glass ionomer stored 7 days in mate tea and mineral water, which correspond to those shown in Fig. 11.

As stated, the ratio mineral water/pure ionomer is nearly unity, indicating that both spectra are nearly equal, and that mineral water do not affect appreciably the virgin ionomer. Furthermore, the ratio depicted in Fig. 12 comparing the effect of *mate* tea infusion to mineral water is approximately unity for energies lower than 1000 keV. Most energetic projectiles interacted with atoms at different distances from the surface, and were backscattered towards the detector providing information on target changes. We suppose that major changes were produced when backscattered energies were larger than 1000 keV.

A rapid sight on the quotients allows observing an important surface change in the glass ionomers that evidently is produced by the chemical action and ionic contribution of infusions.

To estimate the value of the depth where changes begin to be appreciable, we use the following arguments and procedure.

We processed data of Fig. 12 to calculate the average depth ΔX by considering the backscattered projectile energy and the average stopping power of the ionomer, obtained by SRIM simulation [40]. As is very well known, the stopping power of a solid material is a function of the projectile energy with a maximum near 750 keV for our present case. The initial value of the stopping power is $S \sim 200 \text{ keV}/\mu\text{m}$ for the impinging energy $E_p = 2 \text{ MeV}$, being the maximum $260 \text{ keV}/\mu\text{m}$ for 750 keV. When projectiles interact with the glass ionomer, they propagate losing their energy by Coulomb interaction with electrons. Then, after travelling a distance ΔX , they could have a hard collision with a target nucleus and be backscattered towards the surface during a distance $\Delta X/\cos(\theta)$ up to the exit to the detector located at $\theta = 165^\circ$. During this process there is a net energy loss ΔE . It is clear that, in a rough approximation, we could estimate the stopping power as $S \sim \Delta E/2\Delta X$ by

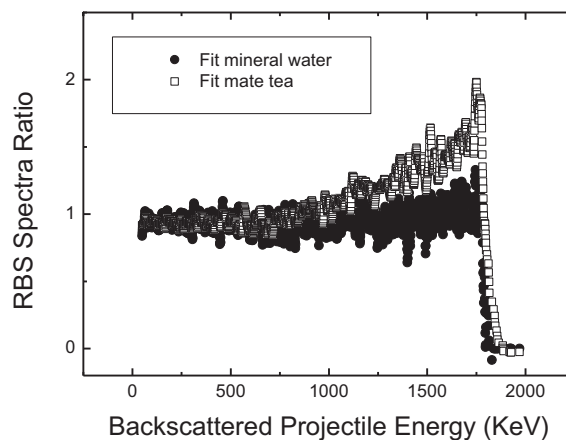


Fig. 12. RBS ratios between spectra obtained with the glass ionomer immersed 7 days in *mate* tea to that with a pure ionomer (Open squares) and that corresponding to mineral water to that with a pure ionomer (Closed circles).

supposing $\cos(\theta) \sim 1$ and that there is no momentum and energy transfer by the projectile in the hard collision. As our purpose is to get the depth where the projectile was backscattered, we obtain $\Delta X \sim \Delta E/2S$. However, we can still improve our approximation to provide a more accurate result by using the standard equation given by the expression:

$$\Delta E = \Delta X \cdot \left(K + \frac{1}{|\cos(\theta)|} \right) S \quad (1)$$

$\Delta X = 0$, is defined for the projectile elastic scattering with the heaviest surface atom of the ionomer and corresponds to the maximum backscattered energy in the RBS spectra of Fig. 11 (~1800 keV). K is the Kinematic Factor [31] that, for a particular system is the ratio between the backscattered to the incident energy. As the ionomer is composed by a number of different elements (See Table 3), the Kinematic Factor K , was set as an average. A value $K = 1$ means that there is no energy transfer to the target, i.e.: the mass of the projectile is negligible respect to that of the atom target. θ , is the detection angle, which is 165 degrees in our setup. S is the stopping power of the ionomer, obtained by SRIM code simulation, and considered constant as an average in our rough calculation.

Details related to the expression (Null) are given in Feldman [31].

The ratio of Fig. 13 gives evidences of major and significant changes at the surface of an ionomer immersed at mate tea, as a function of penetration depth of the alpha particle used as projectile. It means that the projectile acts as a probe of changes introduced within the ionomer by *mate* tea or whatever infusion of common use. The ratio is nearly unity for depths larger than 2 μm , suggesting that there are minor changes due to immersion in the selected infusion.

Though the statistical dispersion of the experimental data is large, the result shows chemical or structure modifications at the ionomer surface by the action of the infusion after a period of immersion in *mate* tea of 7 days up to a depth greater than 2 μm . The estimated uncertainty produced with this approximation is less than 0.5 μm .

This unexpected result encourages us to perform the same experiment with an ionomer immersed in a longer period of time to observe if the changes that occur depend on it or simply saturate rapidly in a few hours of immersion in the infusions studied in this work.

Fig. 14 shows RBS spectra for the glass ionomer immersed in coffee and water during 33 days. In the same way that we

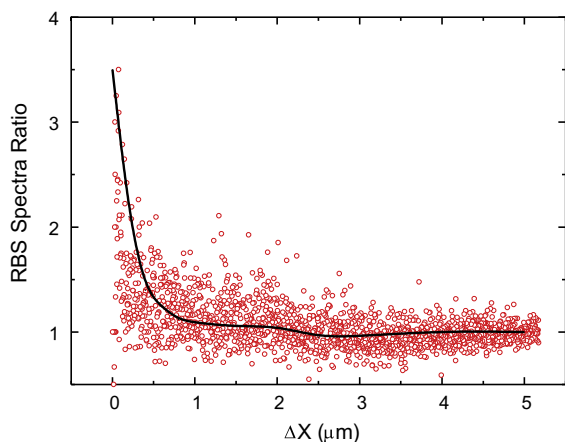


Fig. 13. The Ratio between RBS spectra as a function of average depth in the glass ionomer after 7 days immersion in mate tea. This result is similar for all common infusions studied in this work.

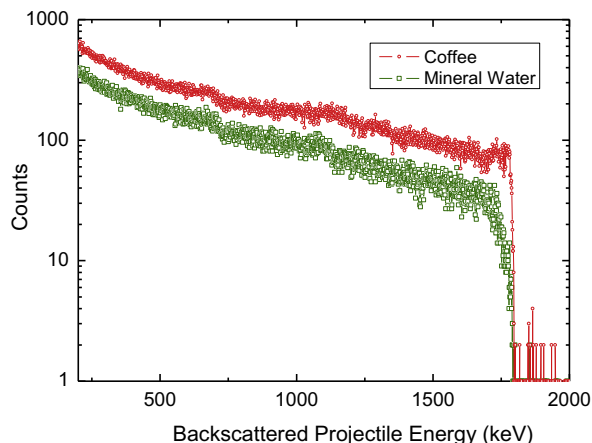


Fig. 14. RBS spectra obtained with ionomers immersed in coffee and mineral water during 33 days.

proceeded with results of 7 days of immersion, we performed the ratio of RBS spectra for the period of 33 days. Again, but this time in a more important way, the quotients show noticeable modifications due to different infusions. The most remarkable feature now is that the penetration depths are clearly larger. It means that the modification of the ionomer surface chemistry is greater for a longer period of immersion in the particular infusion.

In Fig. 15 we show the quotient for 33 days of immersion between coffee and mineral water corresponding to the spectra shown in Fig. 14. We should note that for the lowest backscattered energies the ratio is larger than unity, giving an indication of the ionomer modification by the immersion in coffee. This result shows that chemical and structure ionomer changes are deeper with a longer period of immersion in liquid infusions. The structure and masses distribution of cations inside the ionomer could be inferred by paying attention to the steps at 700 and 1100 keV. The magnitude of infusion penetration into the ionomer is immediately evident because the ratio is larger than unity even for the lowest backscattered projectile energies.

The results depicted in Fig. 16 clearly show surface modifications of glass ionomers by immersion in a coffee infusion after 33 days.

The larger the ratio, the larger the ionomer surface depth modification. Such a result is consistent with those presented in Figs. 4, 5, 6 in the sense that concentration of heavier elements (Ca, La)

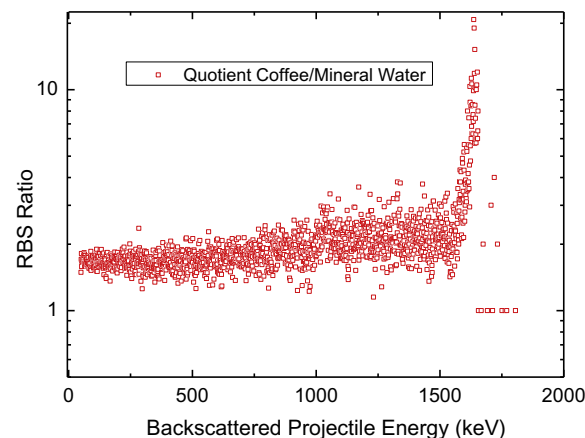


Fig. 15. RBS Ratios for 33 days of immersion between coffee and mineral water corresponding to the spectra shown in Fig. 14.

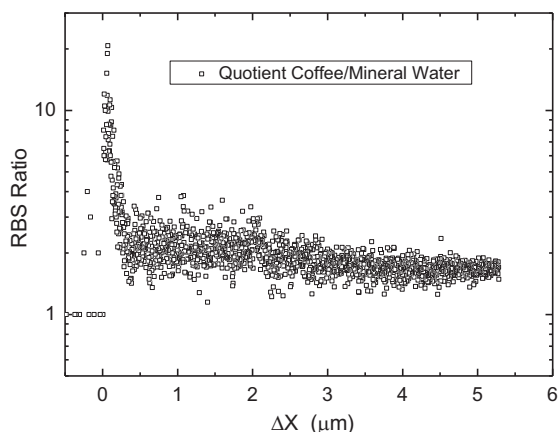


Fig. 16. The Ratio between RBS spectra as a function of average depth in the glass ionomer after 33 days immersion in common infusions.

grow at the surface after immersion. Also, results shown for K, Mn, Fe, follow this trend in that these element concentrations grow in general after increasing immersion periods in different infusions.

Heavier element masses backscattered He projectiles with higher energies giving higher counting rates. In glass ionomers immersed in infusions or beverages with higher concentration of heavier elements, the surface modifications are larger. The magnitude of surface modifications is larger for longer immersion times.

A final comment respect to the application of equation Null should be done. We used a constant value for the stopping power and an average Kinematic Factor, however the main uncertainty should stem in the range of validity of the equation, given that for the depths considered here, there are important changes in the stopping power, particularly for the largest values of ΔX . We show with a simple model that common infusions like coffee, are able to modify physical and chemical characteristics of restorative ionomers.

4. Summary and conclusions

The effect of four commonly consumed beverages as mineral water, coffee, tea and *mate* tea on the elemental composition of a commercial glass ionomer surface was studied using Particle Induced X-ray Emission (PIXE) and Rutherford backscattering (RBS) techniques.

We studied the evolution of commercial ionomer constituents after immersion in acidic media during several periods ranging from few hours up to 33 days.

We observed that, some elements as Al, Si and Na decrease in concentration for common infusions as tea, *mate* tea and coffee, whereas others as K, Ca and La, heavier than the first, increase as a function of the storage time. Such a result obtained by PIXE analysis is consistent with our RBS study, which indicates clearly that heavier elements migrate to the ionomer surface after immersion in the studied infusions.

The respective concentrations of Al and Si were measured in the studied media and we found that the Al:Si ratio was close to unity in all cases, remaining constant for different periods of immersion. We also report on the incorporation of K, Mn, Mg and Fe to the surface for common infusions during different storage periods while for mineral water, the most common beverage, the glass ionomer mainly produce the release of F and Na after long periods of consumption.

The RBS analysis showed that immersion in different media produced a localized modification of the glass ionomer density due to the increment of the concentration of heavier elements at the surface. The thickness of the modified surface layer can be esti-

mated around 3 μm when the immersion time is seven days and more than 6 μm after 33 days of immersion.

The relevance of the present results is evident in restorative dentistry, since the peremptory nature of dental restorations made with glass ionomers is evident.

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