An Electrochemical Impedance Spectroscopy Based Method to Reveal the Potential Interactions Between Fizzy Drinks and Their Packaging Materials

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Differential testing of food content represented in the past one of the usual methods employed to highlight the possible migration of ions or molecules from food contact materials into food. However, some of the methods developed recently offer the possibility to investigate the levigation of packaging compounds through different organic coatings into foods. The aim of this paper is to present a novel method for testing the inside coating layers, namely electrochemical impedance spectroscopy (EIS), in order to reveal the interactions that may occur between foods, food additives and the packaging materials. The experiments were conducted on two different samples, evaluated within six month time interval. From the Nyquist plots, applying a circular regression procedure, one was able to determine the values of the charge transfer resistance (R_2), a characteristic element for the structural and compositional consistency of packaging materials. One has gone further by calculating an equivalent interaction distance (eid) and a medium equivalent interaction distance (meid) and by doing these one has now succeeded to evaluate not only qualitatively but also a quantitative index for quantifying the above said interactions.

Keywords: Electrochemical impedance spectroscopy, charge transfer resistance, polymer coatings, food cans, equivalent interaction distance

A qualitative food product represents the result of a synergy between a well-balanced composition both in terms of nutrition and substances added to improve sensory and aesthetic properties of food, and choosing the right package that does not allow interactions between the food content and the packaging material. In this respect different types of packaging were created, from the controlled atmosphere ones to the varnished cans, using different lacquers acting as a protective barrier which prevent direct contact between metal and food, avoiding thereby the possible levigation from food wrapping to food content or the migration of various compounds from food toward the packaging material [1-3].

The increased demands of consumers for providing healthier, safer food products require a thorough investigation of food composition, especially regarding the additives used to improve the shelf life of food products. Researchers' attention has also focused on the interactions that may occur between food and / or food additives with the packaging materials due to the effects that the above said interactions might have on human health. The goal of the present work is not to establish the toxicity of these interactions, neither their impact on human health, but to identify the presence or the absence of these interactions [4].

In case of canned food, the structural changes made in order to fulfill the numerous requirements related to food safety, to hygienic, technological and marketing demands began many years ago. In order to obtain qualitative foods and to preserve its properties as unaltered as possible throughout the entire shelf life of the products, food and beverage cans have undergone rapid changes, evolving from plain cans to organic coatings deposits on the inner side of the packaging materials. This organic coatings covering the interior of the packaging materials aim to control and limit the degradation processes of food cans acting as an active barrier between the packaging material and food product and it also intends to make the container – food content interface more complex, as they offer good barrier properties and retard the diffusion of chemical species to and from the metal surface due to their high resistance to ionic conductivity. Nevertheless, the behavior of the organic coatings used to protect food packaging materials against deterioration depend on: the adhesion of the coating layer to the substrate, ion penetration of the protective layer, environment conditions, the presence of different food additives, the dielectric properties of the coating, etc. [5,6].

In theory, the ideal packaging material has a perfect chemical inertia which allows the food to maintain the initial characteristics. In reality, interactions occur between food and the packaging material mostly due to the deterioration of the package, but also due to the intrinsic nature of the preserved food.

When food is preserved in metallic cans the stability of the system food product / packaging material is influenced by numerous factors, the most important being the migration of different compounds from the packaging into the food content or *vice versa* [7].

The scope of this paper is to illustrate that using electrochemical impedance spectroscopy (EIS) one may reveal if any relevant and measurable interactions occur between food and / or food additives and the packaging materials, namely with the organic / polymer coatings.

This method joins other methods used to test the interactions between foods and packaging materials [8].

Experimental part

Electrochemical impedance spectroscopy is an accurate method as it offers precise quantitative data

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regarding the behavior of the polymer coatings and represents a rapid, non-destructive and convenient technique that allows the evaluation of the performance of organic coatings used to varnish the interior of food and beverage cans [9]. Through this procedure one is able to distinguish some effects that other tests are not able to reveal. EIS has also some limitations as it cannot distinguish between the multiple coatings applied on the substrate [5, 10-12].

This work provides the results obtained during the experiments performed on two different types of energy drink cans (S_1 and S_2) covered on the inside with polymer films. Sample S_1 was cut from a carbonated energy drink dose with a capacity of 250 mL, containing: water, sugar, acidity regulators (citric acid and sodium citrate), carbon dioxide, taurine (0.4%), inositol, caffeine aroma (0.03%), colorants (sulphite ammonia caramel, riboflavin), vitamins (pantothenic acid, B_6, B_{12}). The second sample (S_2) was cut from a carbonated energy drink dose with a capacity of 250 mL, containing: water, sucrose, glucose, acidity regulator (sodium citrate, magnesium carbonate, citric acid), taurine (0.4%) caffeine (0.03%), inositol, vitamins (niacin, pantothenic acid, vitamin B_6, vitamin B_{12}), flavours, colorants (caramel, riboflavin).

A batch of three tests were conducted initially and repeated after six months for each considered sample. Electrochemical impedance spectroscopy may supply valuable information with respect to the organic/polymer layers deposited on a metallic substrate.

The experimental data were obtained using a Voltalab 40 PGZ301 system. The procedure settings consisted in scanning the frequency of the signal from 100 kHz to 100 mHz using a 10 mV perturbation.

The electrochemical cell used to perform the experiments was filled with sodium chloride solution (NaCl 3.5%, 50 mL) and maintained at 25°C, while two platinum electrodes were used, one as auxiliary electrode while the other was connected through a capacitor with the Ag/AgCl reference electrode in order to reduce the phase shift at high frequencies. The working electrode was built so that the samples fit inside it and only the inside part of the can (the polymer film) could came into direct contact with the sodium chloride solution (NaCl 3.5%).

The Nyquist plots resulting from the electrochemical impedance spectroscopy tests were processed by applying a circular regression procedure which provided useful information regarding the charge transfer resistance (R_2), the ionic resistance, the ionic conductivity, etc. In this particular case, the charge transfer resistance represents the parameter one was interested in, as its variation gives useful information regarding the presence or the absence of any interactions between food and/or food additives and the packaging materials.

Theoretically, the value of the charge transfer resistance (R_2) represents the most appropriate parameter for monitoring the protective properties of the coatings as it is a characteristic element for compositional and structural consistency of the packaging [10].

Results and discussions

The experiments were focused on highlighting the use of electrochemical impedance spectroscopy to evaluate whether or not interactions took place between food and / or food additives and the food contact material.

Figure 1 illustrates a Nyquist plot after applying the circular regression procedure corresponding to one of the experiments conducted during the first batch of experiments performed on the first energy drink can (S_1), while the figure 2 illustrates the Nyquist plot corresponding

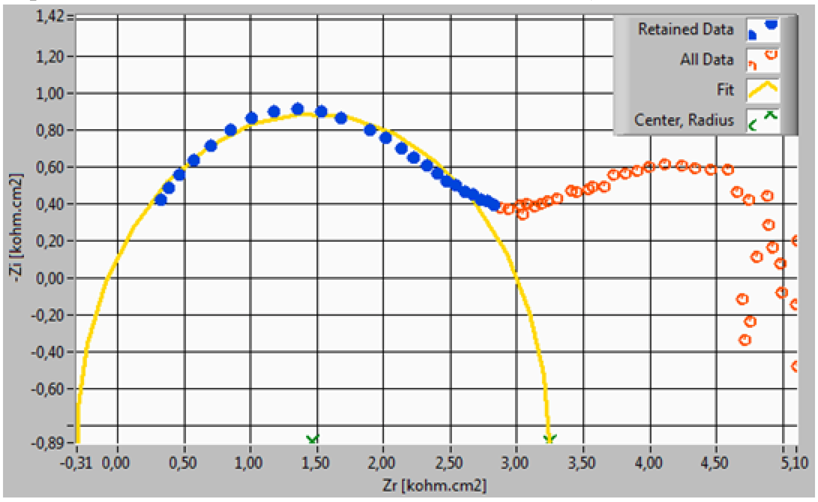

Fig. 1. Nyquist plot for S_1 – measured initially

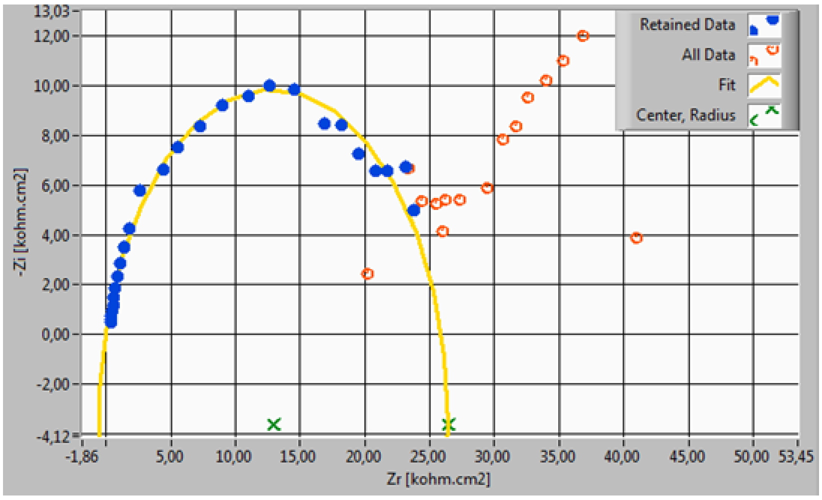

Fig. 2. Nyquist plot for S_1 – measured after six months

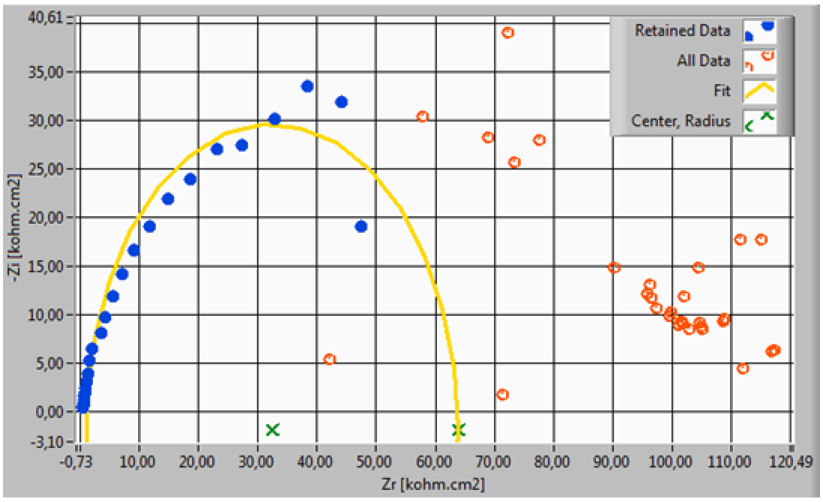

Fig. 3. Nyquist plot for S_2 - measured initially

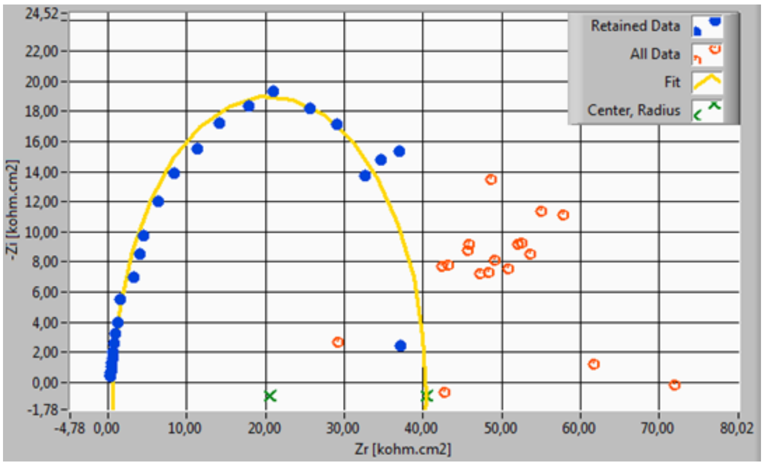

Fig. 4. Nyquist plot for S_2 - measured after six month

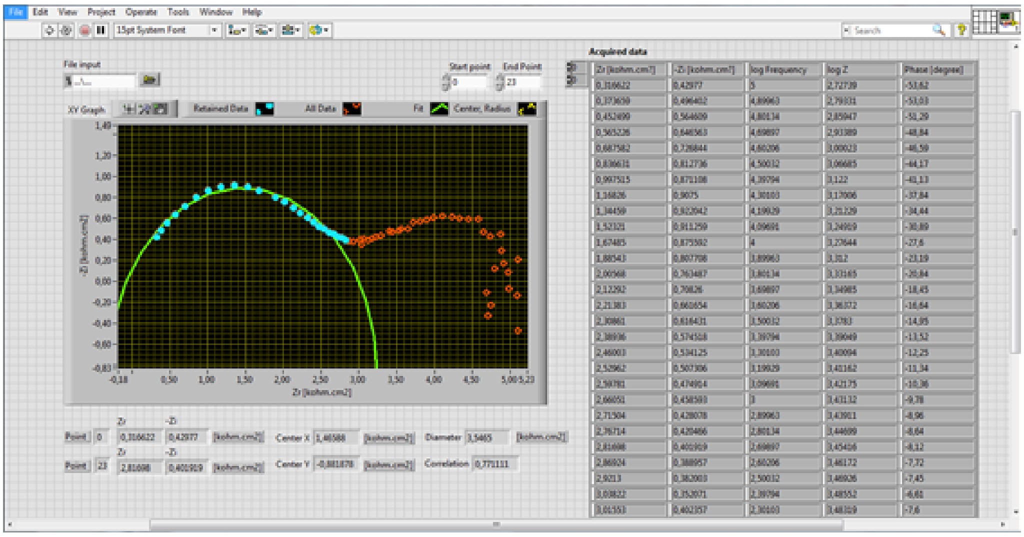

Fig. 5. The graphical interface of visualization module created using graphical programming language National Instruments - Labview

to the second batch of experiments conducted after six months.

Figure 3 illustrates a Nyquist plot after applying the circular regression procedure corresponding to one of the experiments conducted during the first batch of experiments performed on the second energy drink can (S_2), while the figure 4 illustrates a Nyquist plot corresponding to the second batch of experiments, repeated after six months.

One has created a visualization module (fig. 5) which allows the representation of the acquired data as Nyquist diagrams using graphical programming language National Instruments - Labview (fig. 6).

One has also calculated the average of the values obtained for the charge transfer resistance during the first batch of experiments and compared them with the average of R_2 obtained during the tests performed after six months.

As one may see, table 1 contains information related to: the values of the charge transfer resistance obtained initially, the ones obtained after six months, the value of the equivalent interaction distance (*eid*) and the medium equivalent interaction distance (*meid*) calculated in order to quantify the magnitude of the above described interactions. This descriptor (*meid*), equivalent to the corrosion penetration index, shows the structural changes of packaging and should not be regarded as a physical size, but rather as a change of the electrical resistance of the package after the interactions above described take place.

The equivalent interaction distance (*eid*) was calculated using the equation:

$$eid = \frac{Rf - Ri}{Ri} * d \text{ , µm} \quad (1)$$

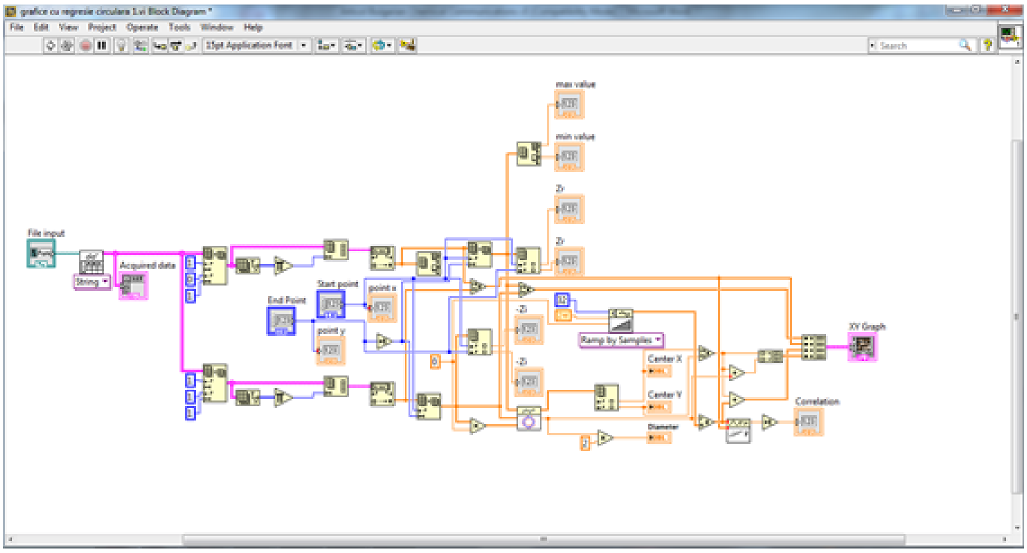

Fig. 6. The block diagram for visualization module created using graphical programming language National Instruments - Labview

where R_i represents the charge transfer resistance obtained during the first batch of experiments, R_f is the charge transfer resistance obtained after six months and *d* represents the coating thickness.

The medium equivalent interaction distance (*meid*) was calculated using the equation:

$$meid = \frac{Rf-Ri}{Ri} * \frac{d}{t}, \ \mu m/month \quad (2)$$

where R_i represents the charge transfer resistance obtained during the first batch of experiments, R_f is the charge transfer resistance after six months, *d* represents the coating thickness, while *t* represents the time expressed in months.

Using a coating thickness gauge tester one has gone further by measuring the thickness of the coating layers for the studied samples, in this particular case two different types of energy drink cans, as the organic polymer coatings represent the predominant protective layers that have been used for a long time and will also be used in the future, as they offer a remarkable protection despite their thickness (for example for the studied samples the thickness of the coating layers was around 11-15 µm - these values were obtained after the average was calculated as a result of a series of repeated measurements performed on the same sample). The average, the standard deviation along with the relative standard deviation can be seen in table 1 where one has gathered all these information for each considered sample.

As one may see from table 2, the value obtained for the equivalent interaction distance (*eid*) corresponding to the first type of energy drink can (S_1) was 100.75µm, the one for the medium equivalent interaction distance (*meid*) was $2.015 \cdot 10^{-1}$ mm/year ,while the thickness of the coating layer was 13.38µm. Even if initially, these values seem to be too high related to the thickness of the polymer coating, as already mentioned, these (*eid* and *meid*) should not be regarded as a physical size, but rather as a change of the electrical resistance, which can be explained as a change of the conductivity. Therefore, the increased value of the charge transfer resistance along with those related to the equivalent interaction distance and the medium equivalent interaction distance can be associated with processes related to deposit formation, oxidation, accumulation of food traces, etc.

One has done the same for the second energy drink can (S_2), but in this particular case the value obtained for the equivalent interaction distance (*eid*) was -3.771µm, the value of the medium equivalent interaction distance (*meid*) was $-7.542 \cdot 10^{-3}$ mm/year, while the thickness of the coating layer was 11.15µm. In this situation, due to the fact that the values obtained are negative, it is obvious that some interactions took place between the polymer coating protecting the inside walls of the cylindrical can and the energy drink content; this may be explained taking into account the structural modifications and/or deteriorations (dissolutions, cracks, levigations) of the protective layers.

Table 1
THE AVERAGE, THE SD AND THE RSD OF THE THICKNESS OF THE COATING LAYERS FOR BOTH STUDIED SAMPLES

Sample	Thickness average [µm]	Standard deviation [µm]	Relative standard deviation [%]
S_1	13.38	1.69	12.62
S_2	11.15	0.85	7.65

Table 2
CENTRALIZED DATA RESULTED FROM PROCESSING THE NYQUIST PLOTS CORRESPONDING TO THE EXPERIMENTS CONDUCTED FOR EACH STUDIED SAMPLE INITIALLY AND AFTER SIX MONTHS AND THE VALUES OBTAINED FOR THE EQUIVALENT INTERACTION DISTANCE (*EID*) AND THE MEDIUM EQUIVALENT INTERACTION DISTANCE (*MEID*).

Sample	Mean value of the charge transfer resistance [kohm·cm^2] initially	Mean value of the charge transfer resistance [kohm·cm^2] after 6 months	Equivalent interaction distance [µm]	Medium equivalent interaction distance [mm/year]
S_1	3.177	27.097	100.75	$2.015 \cdot 10^{-1}$
S_2	59.547	39.407	-3.771	$-7.542 \cdot 10^{-3}$

It should also worth to be mentioned that one should also take into account the compositions of the studied samples, as these might influence the interactions between the beverage and the packaging material.

Conclusions

The electrochemical impedance spectroscopy may be successfully used to evaluate whether or not interactions occur between the packaging and the food content, offering the possibility to perform not only a qualitative but also a quantitative evaluation of the above said interactions. The experiments conducted on both types of energy drink cans can showed that the thickness of the coating layers is also of a paramount importance, influencing the safety and defining the shelf life of the metallic coated food packaging, as the thickness of the coating layers of S_1 was greater than the one measured for S_2 and the values of *eid* and *meid* demonstrated that sample S_1 performed much better than S_2.

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