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Abstract

Electrical characterization of products is gaining increasing interest in the food industry for quality monitoring and control. In particular, this is the case in the ice-cream industry, where machines dedicated to store ice-cream mixes are programmed "ad hoc" for different groups of products. To this purpose, the present work shows that essential product classification (discrimination between milk based and fruit based ice-cream mixes) can be done by means of a technique based on the measurements of non-linear response in the electrical behavior of the electrode-electrolyte interface. The addition of pH measurements allows to further reach the three parts classification occasionally required for advanced applications. The proposed idea is validated by means of measurements on 21 ice-cream mixes, different for producers and composition.

Keywords: food quality control; ice-cream mix; industrial sensors; electrical impedance spectroscopy; electrode-electrolyte interface.

1. Introduction

While in the early stage of the food industry the competition was mainly focused on costs, today product quality and safety are a primary concern. Consequently, products are routinely screened for important organoleptic characteristics (such as smell, aroma, color,…) as well as to guarantee that microbial content is below the maximum allowed threshold concentration.

In the past, all tests were performed off-line, i.e. a limited number of product samples were sent to a laboratory to be tested and the results became available with long delays. Today, automated production methods with integrated monitoring systems allow much faster response and the possibility to screen all the products with non destructive measurements.

In this context, food characterization by means of electrical measurements easily implementable in automatic form plays a crucial role and a number of significant examples can be mentioned: detection of water and lipid content in meat [1], dilution factor in apple puree [2], determination of pH, acidity and hardness in yogurt [3], quality control of vegetable oils [4]. In particular, as far as dairy products are considered, techniques have been proposed for the characterization of milk content [5][6][7], detection of mastitis in raw milk samples [8][9], measurement of microbial concentration in milk [10] and ice-cream [11][12][13].

A different, though related, application is automatic product recognition to optimize machine setting when dealing with different versions of the same basic product needing specific processing parameters. This is in particular the case for the ice-cream mixes, that are normally stored in dedicated machines maintaining the product at the target conservation temperature (normally in the range 2 – 6 °C), while pasteurization cycles are carried out at regular intervals (one or few days) to lower the microbial concentration below the legally allowed threshold. Different types of mixes, however, require different machine parameters setting and, to this purpose, in practice a distinction is made between milk and fruit based ice-creams, requiring different conservation temperatures and frequency of pasteurization cycles. Within the milk based products a further, less decisive discrimination is that between creamy and frozen yogurt products.

At present, specific machine parameters for these three ice-cream groups (but often differences are considered only among milk and fruit based mixes) are set manually: hence an operator is needed every time the stored ice-cream mix type is changed. Instead, if the product type could be discriminated by means of an electronic system embedded in the machine, such an intervention would be no longer necessary, with significant advantages in terms of costs, time and error reduction.

Electrical Impedance Spectroscopy (EIS) is often used for electrical characterization of food products. In EIS the sample under test is placed in direct contact with electrodes and stimulated with a sinusoidal test voltage $V_{in}(t) = V_M sen(\omega t) = V_M sen(2\pi f t)$ with fixed amplitude V_M in a definite range of frequencies. The current $I_{in}(t)$ through the electrodes due to the test signal is measured and, if the system electrode-electrolyte can be considered linear (i.e. if $V_{in}(t)$ is the weighted sum of several signals, then $I_{in}(t)$ is the weighted sum of the system response to each of the signals), the complex impedance Z can be calculated as $Z = |Z| e^{jArg(Z)} = V_{in}(j\omega) / I_{in}(j\omega)$, where $V_{in}(j\omega)$, $I_{in}(j\omega)$ are the Steinmetz phasors of the sinusoidal signals $V_{in}(t)$ and $I_{in}(t)$ respectively, |Z| is the impedance modulus and Arg(Z) the impedance phase. The acquired spectra can be represented with different graph types, such as Bode plots, where |Z| and Arg(Z) are plotted as function of the test signal frequency, or Nyquist plots where the impedance imaginary component Im(Z)=|Z|sen(Arg(Z)) is plotted vs. the real component Re(Z)=|Z|cos(Arg(Z)) for different frequencies.

EIS data for a set of samples, featuring different values of the parameter under study, are analyzed in order to extract a relation between the measured electrical parameters and the product parameter.

The electrochemical system composed of sample under test and electrodes is, however, a non-linear system [14]. To effectively apply EIS, the test signal must feature small amplitude V_M so to confine the system in a pseudo-linear region.

Nevertheless, study of the electrical response in the non-linear region (using larger amplitude excitation potentials) can extend the knowledge and provide additional data on the product.

In this paper ice-cream mixes, different for composition and producers, are tested both with EIS and in the non-linear region to achieve the products discrimination needed for practical purpose.

2. Experimental approach

The objective of the study is to discriminate a set of ice-cream mixes, different for composition and producers, in two different groups (milk based and fruit based mixes) with eventually a second level discrimination of the milk based products in creamy mixes and frozen yogurts. To this purpose, the whole set of ice-cream mixes has been subjected to the following tests:

1) EIS measurements with a sinusoidal test signal of amplitude 100 mV in the frequency range 20 Hz to 10 KHz. The acquired spectra have been analyzed to validate the electrical model and the model parameters estimated with “ad hoc” developed LabVIEW (National Instruments, Austin, USA) programs using least squares error method.

2) The electrical response in the non-linear region has been studied by stimulating the sample with a sinusoidal test signal of frequency 20 Hz and amplitude in the range 10 mV to 2 V. The measured data has been fitted to a non-linear empirical model (described in section 5) and the model parameters calculated by Levenberg-Marquardt algorithm (LMA). LMA is an iterative technique that locates the minimum of a multivariate function that is expressed as the sum of squares of non-linear real valued functions. The algorithm needs initial guess for the function parameters to be used as starting values for the iterative procedure. It has been implemented using built-in project libraries from LabVIEW.

3) pH measurements have been performed by means of a Crison micropH 2000 (Crison Instruments, South Africa). The instrument has been calibrated before each measure using standard buffer solutions featuring pH 4 and 7 respectively.

Statistical analysis has been carried out with PHStat (Prentice Hall statistical add-on for Microsoft EXCEL). Student t-test assuming unequal variances and non-parametric Mann Whitney test have been performed to find significant differences in the measured mean values of measured parameters (confidence level of 95 %). Multiple regression analysis has been carried out using the Best-Subset procedure to investigate the correlation between pH values and measured electrical parameters.

3. Measurement setup

All the measurements of this work are made with Lab instruments.

The setup used for the experiments is illustrated in Fig. 1 (a): the product samples are incubated in a thermal chamber WTC Binder providing the target temperature with an uncertainty of 0.1 °C. Measures have been carried out at two different temperatures (4 °C and 35 °C). The two temperatures have been chosen according to the following rules: 4 °C is the standard temperature the ice-cream mixes are stored while 35 °C is the temperature used in a microbial biosensor system recently developed by the authors [13]. Thus, the choice has been made with the idea of a future implementation in industrial environment as a sensor integrated in the tank of the storing machine (4 °C) or in a separate chamber controlled with the embedded biosensor system (35 °C). However, the measures at 4 °C resulted in poor repeatability (see Supplementary Material for more information). This can be related to the fact that at 4 °C the ice-cream mixes are in a semi-viscous frozen state and also small temperature variations can produce relatively large changes in the product structure. Thus, in the following, only measures at 35 °C are discussed. Electrical characteristics of the sample (|Z| and Arg(Z)) are measured with an LCR meter Agilent E4980A, controlled via USB interface by a PC system that is also used to acquire measured data and further data processing. The sample under test is placed in a 10 ml container with cap shaped stainless steel electrodes. Two types of sensors are used: sensor A (Fig. 1 (b)) consists of two electrodes while sensor B (Fig. 1 (c)) has four electrodes that are shorted together in couples as shown in the figure. The difference between the two sensors is related to the generated electric field. Both sensor geometries have been simulated using the software Comsol Multiphysics v4 (Comsol Inc, Palo Alto, USA). The electric field distribution is also shown in Fig. 1 (b) and (c). Sensor B is characterized by more homogeneous electric field with higher values than sensor A for both the field and its gradient. All the ice-cream mixes have been tested with both types of sensors.

4. Ice-cream mixes

Measurements have been performed on a set of 21 ice-cream mixes, different for ingredients and producers, which can be classified in two main categories: fruit and milk based. The latter category can be further divided in creamy and frozen yogurt products. The ice-cream mixes as well as the measured pH values are listed in Table 1: those from 1 to 14 are milk based ("creamy" ones from 1 to 10 and frozen yogurt mixes from 11 to 14), while those from 15 to 21 are fruit based. The composition of the 21 ice-cream mixes is reported in the Supplementary Material.

The ice-cream mixes production has been carried out using a Carpigiani Pastomaster RTL machine to prepare, pasteurize and age ice-cream mixes. The basic steps in the manufacturing are as follows:

- Mixing of ingredients (i.e. mixing powder with water in the tank of the pasteurizer).
- Pasteurization.
- Cooling to 4°C.
- Aging at 4°C for 10 hours.

5. Electrical circuit model

EIS has been carried out with a sinusoidal test signal of amplitude (V_M) 100 mV on the frequency range 20 Hz to 10 KHz (logarithmically spaced). Preliminary measurements were performed with the LCR meter full frequency range (20 Hz to 2 MHz). However, since the high frequency response resulted in higher noise-to-signal ratio and lower repeatability (see the Supplementary Material for more details) only the frequency range 20 Hz to 10 KHz is discussed. Fig. 2 (a) shows the Nyquist plot for three different samples measured with sensor A: the samples are two milk based mixes (#3 and #9 in Table 1) characterized by different fats content and a fruit based mix (#19 in Table 1). As can be seen a linear relation exists between Im(Z) and Re(Z).

The electrical model used to fit the data in the investigated frequency range is shown in Fig. 2 (b): it is composed of a resistance R_m (accounting for the resistance of both the sample and the interface) and a constant phase element CPE (resulting from the essentially capacitive component due to the interface electrode–medium) in series. Since the ice-cream is an unstructured material no distinct dispersion exists within the radiofrequency range up to several MHz. The sample impedance is thus purely resistive while the reactive component is essentially due to the electrode interface. The impedance of CPE is described by two parameters (Q and α) where Q represents the double layer capacitance, while α accounts for the non ideal electrode-medium interface (the case α=1 refers to an ideal capacitance). The reason for using a CPE instead of a linear capacitor is the non ideal behavior of electrode interface [15]. Moreover, the calculated impedance using a linear capacitor results in Re(Z) to be independent of frequency, contrary to the Nyquist plot of Fig. 2 (a).

With the model of Fig. 2 (b) it is:

$$Z = R_m + Z_{CPE} = R_m + \frac{1}{Q(j\omega)^\alpha} = R_m + \frac{e^{-j\frac{\pi}{2}\alpha}}{Q\omega^\alpha} = R_m + \frac{\cos(\frac{\alpha\pi}{2})}{Q\omega^\alpha} - j\frac{\sin(\frac{\alpha\pi}{2})}{Q\omega^\alpha} \qquad (1)$$

Thus:

$$\mathrm{Re}(Z) = R_m - ctg(\frac{\alpha\pi}{2}) \times \mathrm{Im}(Z) \qquad (2)$$

The parameters R_m, Q and α are determined by best fitting the experimental data with the proposed electrical model for all ice-cream mixes and both sensors. The determination coefficient R^2 between experimental and fitted data is found to be never lower than 0.998, thus validating the electrical model. The parameter α is found to be almost independent on the measured samples with values in the range 0.73-0.79 for both sensors. Fig. 3 shows the experimental data (|Z| and Arg(Z)) as well as the curves fitting the model in the case of the vanilla flavored Angelito mix (# 9 in Table 1) and sensor A.

The electrical characterization in the non-linear region for the electrode-medium system is investigated measuring |Z| with a sinusoidal voltage signal of fixed frequency and V_M in the range 10 mV to 2 V (with logarithmic spacing). Fig. 4 shows $|Z|_{10mV}$-|Z| vs. V_M (logarithmic scale) for different frequencies in the case of the Angelito mix (# 9 in Table 1) and sensor A. The value of |Z| is almost constant for small signal amplitude (i.e. $V_M \ll V_{MT}$, with V_{MT} never lower than 200 mV), while for higher values of V_M, it decreases linearly with $Log_{10}(V_M)$, thus producing an increase of

$|Z|_{10mV}$-$|Z|$. The results clearly indicate that increasing the test signal frequency results in an increase of the cut-off amplitude V_{MT} and a decrease of the slope in the non-linear region.

In order to characterize the electrical response in the non-linear region for the tested products, the curves have been fitted with the empirical model $|Z| = |Z|_{10mV} + \beta_1 \cdot Log_{10}(1 + (V_M / V_{MT})^{\beta_2})$, where $|Z|_{10mV}$ is the value of $|Z|$ for small signal amplitude (i.e. linear response region), V_{MT} the cut-off amplitude (separating the linear from non-linear region) while β_1 and β_2 are empiric parameters used to fit the curve. Fitting procedure has been carried out by LMA. The iterative algorithm has been run with the following initial guess for parameters $|Z|_{10mV}$=300 β_1=0.6 V_{MT}=600 β_2=11 for all ice-cream mixes and both sensors. Fitting procedure resulted in high determination coefficient (R^2 > 0.99), thus validating the empirical model. The slope λ in the non-linear region has been estimated with the following procedure: when $V_M >> V_{MT}$ the empirical model function can be simplified as $|Z| \approx |Z|_{10mV} + \beta_1 \cdot Log_{10}(V_M / V_{MT})^{\beta_2} = |Z|_{10mV} + \beta_1 \cdot \beta_2 \cdot Log_{10}(V_M / V_{MT})$, thus:

$$\lambda = \frac{\partial |Z|}{\partial Log_{10}\left(V_M / V_{MT} \right)} \approx \beta_1 \cdot \beta_2 \qquad (3)$$

The model parameters are estimated by LMA for f = 20 Hz, since, as shown in Fig. 4, non-linear response is stronger (higher values of λ) at lower frequencies. However, only values of λ are reported in section 6, since the other parameters exhibit lower correlation with the ice-cream mixes groups.

6. Results and discussion

6.1. Electrical impedance spectroscopy

The ice-cream mixes have been tested following the procedures described in section 2 and section 5. The experimental results are illustrated in Fig. 5. Statistical analysis of the presented data indicates that significant differences exist between fruit based and both creamy and frozen yogurt mixes in the case of R_m. Fruit based mixes are generally characterized by higher values of R_m than milk based mixes. In particular, mean values of R_m for fruit based mixes are 838.9 Ω and 276.2 Ω for sensor A and sensor B, respectively. Instead, the corresponding values for creamy mixes are 328.7 Ω and 95.3 Ω, while for frozen yogurt products these values are 406.9 Ω and 74.1 Ω. However, a small number of fruit based mixes (banana and kibana based mixes, # 17 and 20, respectively) exhibit values of R_m comparable with those of the milk based group, due to the presence of potassium salts that greatly enhances conductivity.

Conductivity for the dairy products is mainly related to fats and salt content: higher concentration of milk fats results in higher values of R_m, while the increase in salt concentration leads to resistance decrease, as can be clearly seen comparing the values of R_m for mixes 1 and 2. However, comparison between mixes 2 and 3 clearly indicates that pasteurization temperature also plays a role in the measured electrical characteristics, since the same mix subjected to high temperature pasteurization cycle (85 °C) results in a higher value for R_m than that of the mix pasteurized at lower temperature (65 °C). On the other hand, it is known that differences in pasteurization temperature can significantly alter some organoleptic characteristics of the product: for instance, [16] showed that ice-cream mixes pasteurized with high thermal cycle (between 75 °C and 82 °C) exhibit lower fat clumping, viscosity and freezing time, and higher protein stability. To investigate if repeated pasteurization cycles can effectively alter the product electrical characteristics, mix 2 has been subjected to low temperature pasteurization cycles (65 °C) at time intervals of 1 day and the electrical parameters have been measured after each cycle : no correlation was observed between the electrical parameters and the number of pasteurization cycles, thus showing that only thermal cycling with high temperature significantly affects the product characteristics, while repeated cycling at lower temperature produces no detectable change.

As far as values of Q are considered (expressed as $10^6 s^\alpha/\Omega$), fruit based and frozen yogurt mixes exhibit values significantly higher than those of creamy mixes: mean values of 66.6 and 64.6 for sensor A and 121.9 and 114.7 for sensor B as compared to 51.5 and 93.5 for creamy mixes. Once again, overlapping values of Q exist among different groups and no significant difference between frozen yogurt and fruit based mixes is detected.

On the whole, the results shown in Fig. 5 indicate that EIS does not allow to reliably discriminate milk and fruit based ice-creams.

6.2. Electrical response in the non-linear region

As already anticipated, searching for a method to reliably discriminate the different products groups, the electrical response in the non-linear region has been investigated.

Fig. 6 shows the values of λ in the non-linear region for all mixes and both sensors. As can be seen fruit based mixes are all characterized by values of λ lower than the other groups: this is particularly evident for sensor B, that is able to reliably discriminate fruit based mixes, while with sensor A the gap between values of λ for the different groups is smaller, thus leading to less accurate detection and possible misclassification of ice-cream mixes with high milk fat content. In the case of frozen yogurt, the values of λ are not significantly different from those of creamy mixes: thus the two groups cannot be discriminated with this parameter.

These results clearly indicate that measurements of λ provides a reliable method to automatically discriminate milk based from fruit based ice-creams, as required for automatic machine setting (with sensor B resulting in larger differences for the values of λ of the two groups and thus more reliable discrimination). The distinction between creamy and frozen yogurt mixes cannot be performed by analyzing values of λ (as can be seen in Fig. 6).

If required, reliable discrimination between creamy and frozen yogurt products can be achieved by measuring the mix pH. As can be seen in Table 1, creamy mixes are almost neutral (pH > 6) while frozen yogurt mixes exhibit pH values in the range 4.5 to 5. Fruit based products, instead, have pH values in the range 2 to 5, with few exceptions, such as # 16 in Table 1, featuring pH = 6, due to a content of organic acid much lower than other fruit based mixes [17].

Since all the three product groups of interest can be discriminated by means of combined measurements of pH and electrical parameters, correlation between electrical parameters and pH has been studied.

6.3. Correlation between electrical and pH measures

The correlation between measured electrical parameters R_m, Q and λ for both types of sensors and pH has been investigated, and the results are presented in Supplementary Material, where the values of pH are plotted versus the corresponding electrical parameter for all ice-cream mixes and both sensors. The results indicate poor correlation between pH and the corresponding electrical parameter, especially R_m, where a determination coefficient as low as 0.216 and 0.17 (for sensor A and B respectively) is found.

Better results are obtained for the correlation of pH with λ (0.444 and 0.489) and Q (0.533 and 0.492). However, the determination coefficient never higher than 0.533 is not satisfactory, preventing a reliable estimate of pH with electrical measures. Multiple regression analysis has been carried out to test if expressing pH as linear function of more than a single electrical parameter significantly increases the correlation. The best results are obtained (for both sensors) by using Q and λ as independent variables, namely: $pH = b_0 + b_1*Q + b_2*\lambda$, where b_0, b_1 and b_2 are numerical parameters. In this way, however, the determination coefficient R^2 (corrected for the use of multiple variables) increases only slightly in the case of the data obtained with sensor A (0.621) while no improvement is found in the case of sensor B.

Thus, pH can not be reliably inferred by electrical parameters R_m, Q and λ.

The overall results from the study are presented in Table 2. Regarding the primary discrimination between milk based and fruit based mixes, although the resistive component of the impedance R_m is characterized by statistical significantly different values for the two groups, the discrimination is not reliable due to few fruit based mixes characterized by higher conductivity. On the contrary, the parameter λ measured in the non-linear region can provide reliable discrimination between the two groups (in particular using sensor B). The second level discrimination of milk based mixes in creamy mixes and frozen yogurts can be reliably achieved by pH measure, while electrical parameter Q (although characterized by significantly different values for the two subgroups) doesn't provide a reliable solution due to overlapping values between the two subgroups.

7. Conclusions

In this paper the possibility to discriminate different groups of ice-cream mixes by means of electrical measurements, so as to allow automatic setting of product storing machines has been studied. To this purpose, a distinction between milk and fruit based products is essential, and sufficient for most practical purposes. Furthermore, within the first category it is sometimes required to discriminate frozen yogurt products from the remaining (creamy) ice-creams.

To reach the goal, this work has investigated the possibility to use Electrical Impedance Spectroscopy (performed by stimulating the sample with a sinusoidal test signal of amplitude 100 mV and frequency in the range 20 Hz to 10 KHz) showing that it does not provide a reliable solution.

Instead, electrical characterization in the non-linear region (obtained with a sinusoidal test signal of frequency 20 Hz and amplitude in the range 10 mV to 2 V) is shown to do the work as far as the basic distinction between milk and fruit based products is concerned.

As the second level distinction within the first category, it can be done measuring the pH values of the products, which is lower for frozen yogurt than for the creamy mixes.

Although the experiments of this work have been carried out with Lab instruments, measurements of electrical response in the non-linear region can be implemented in the form of a low-cost electronic board, and this holds also for pH determination. Thus, the present work provides the fundamentals for a possible future development of an embedded system that can open the road for fully automatic industrial ice-cream machines.

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#	Ice-cream mix	pH

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1	*Soft serve mix (low fat content – pasteurization at 65 °C)*	6,2
2	*Soft serve mix (high fat content – pasteurization at 65 °C)*	6,3
3	*Soft serve mix (high fat content – pasteurization at 85 °C)*	6,2
4	*Egg based ice-cream mix*	6,6
5	*Fiordilatte ice-cream mix*	6,6
6	*Chocolate ice-cream mix*	7
7	*Fabbri soft serve Chocolate mix*	6,8
8	*Pregel soft serve Chocolate mix*	6,7
9	*Angelito Vanilla Flavour Dairy Ice Cream Mix*	6,4
10	*Mondi ice-cream mix*	6,9
11	*Pregel Yogursprint mix*	4,6
12	*Pregel Yogursprint mix + fresh yogurt*	4,4
13	*Yogurt mix*	5,1
14	*Yogurt soft serve mix*	5,2
15	*Orange based ice-cream mix*	3,5
16	*Prickly pear based ice-cream mix*	6,2
17	*Banana based ice-cream mix*	4,8
18	*Strawberry based ice-cream mix*	3,6
19	*Pear based ice-cream mix*	4,5
20	*Kibana based ice-cream mix*	3,8
21	*Lemon based ice-cream mix*	2,7

Table 1 Ice-cream mixes tested in this work as well as measured values of pH.

	SENSOR A			SENSOR B			
	R_m	**Q**	**λ**	**R_m**	**Q**	**λ**	**pH**
Milk based mixes/Fruit based mixes	*		X	*		X	*
Creamy mixes/Frozen Yogurt mixes		*			*		X

Table 2 Feasibility of ice-cream mixes discrimination based on the measures of electrical parameters and pH. X indicates that the corresponding parameter is suitable for the discrimination of the corresponding groups. * indicates significantly different values between the two groups but non reliable discrimination due to overlapping values.

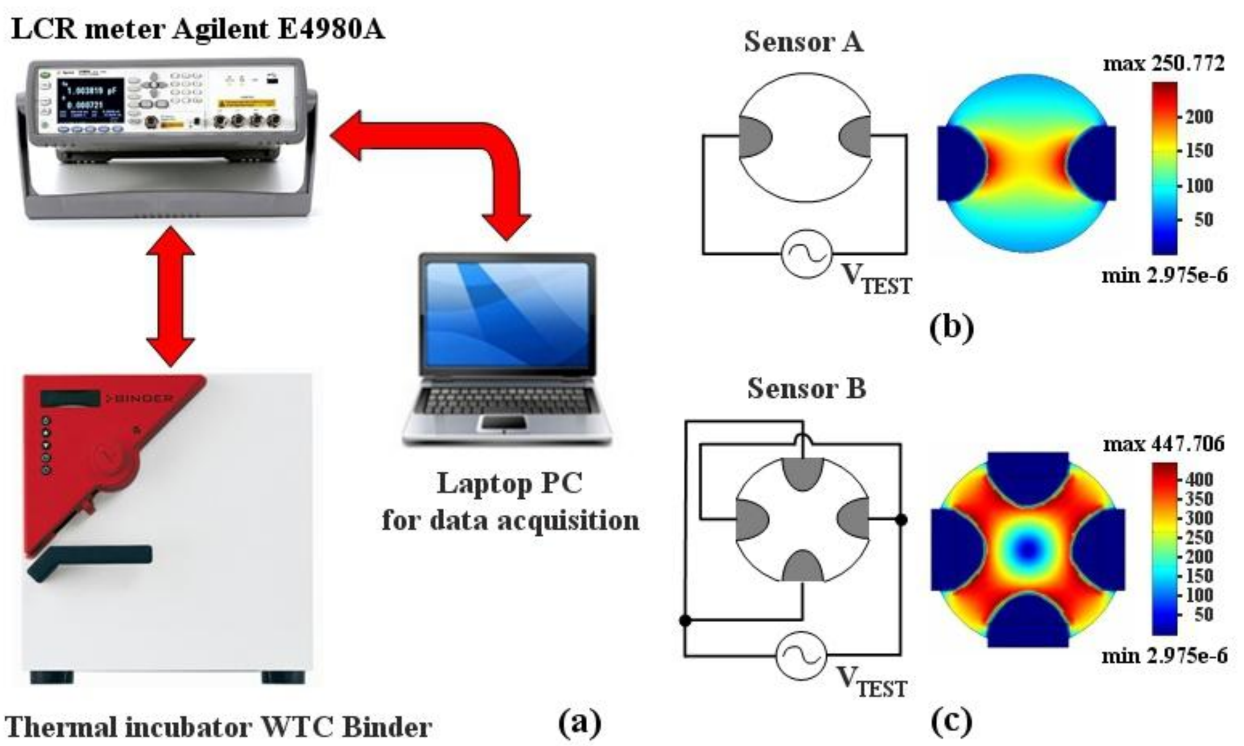

Fig. 1 Measurement setup used in the electrical characterization of ice-cream mixes (a). Geometries and simulations of the generated electric field for sensor A (b) and sensor B (c).

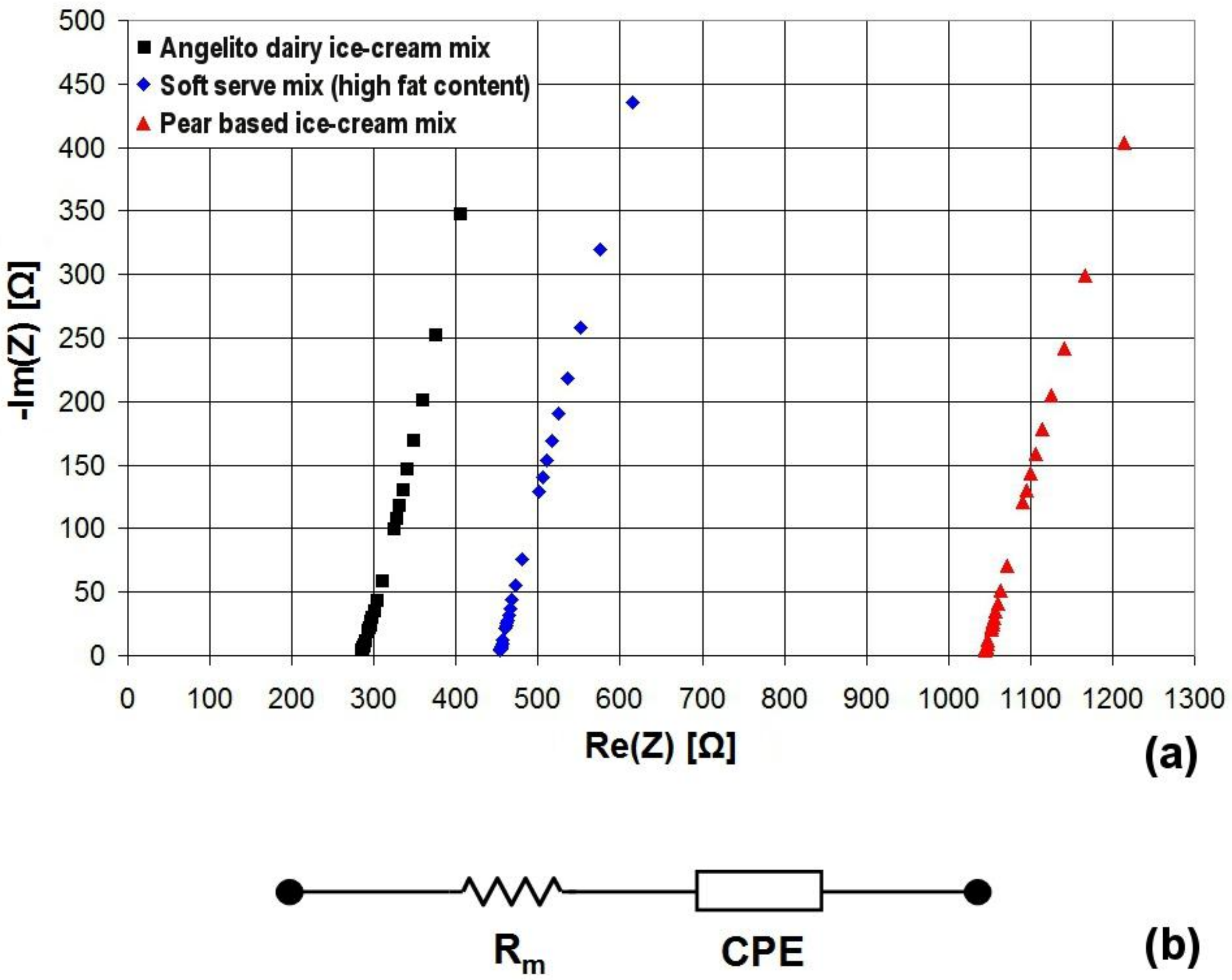

Fig. 2 Nyquist plot for three different ice-cream mixes (a) and electrical circuit used to model the sensors electrical response (b).

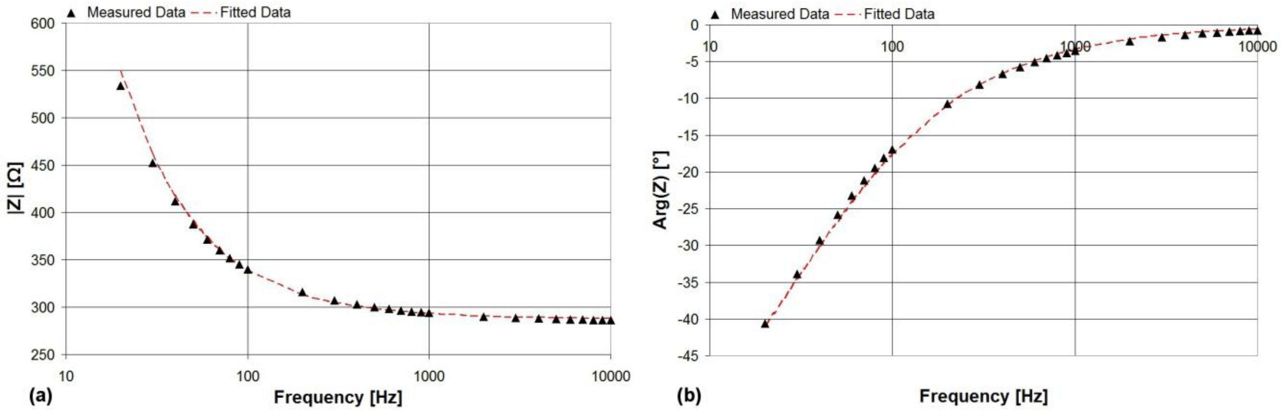

Fig. 3 |Z| (a) and Arg(Z) (b) vs. frequency of the applied test signal for the Angelito mix (# 9 in Table 1) and sensor A. High correlation ($R^2 > 0.998$) is achieved for all ice-cream mixes and both sensors between measured data and the electrical model of Fig. 2 (b).

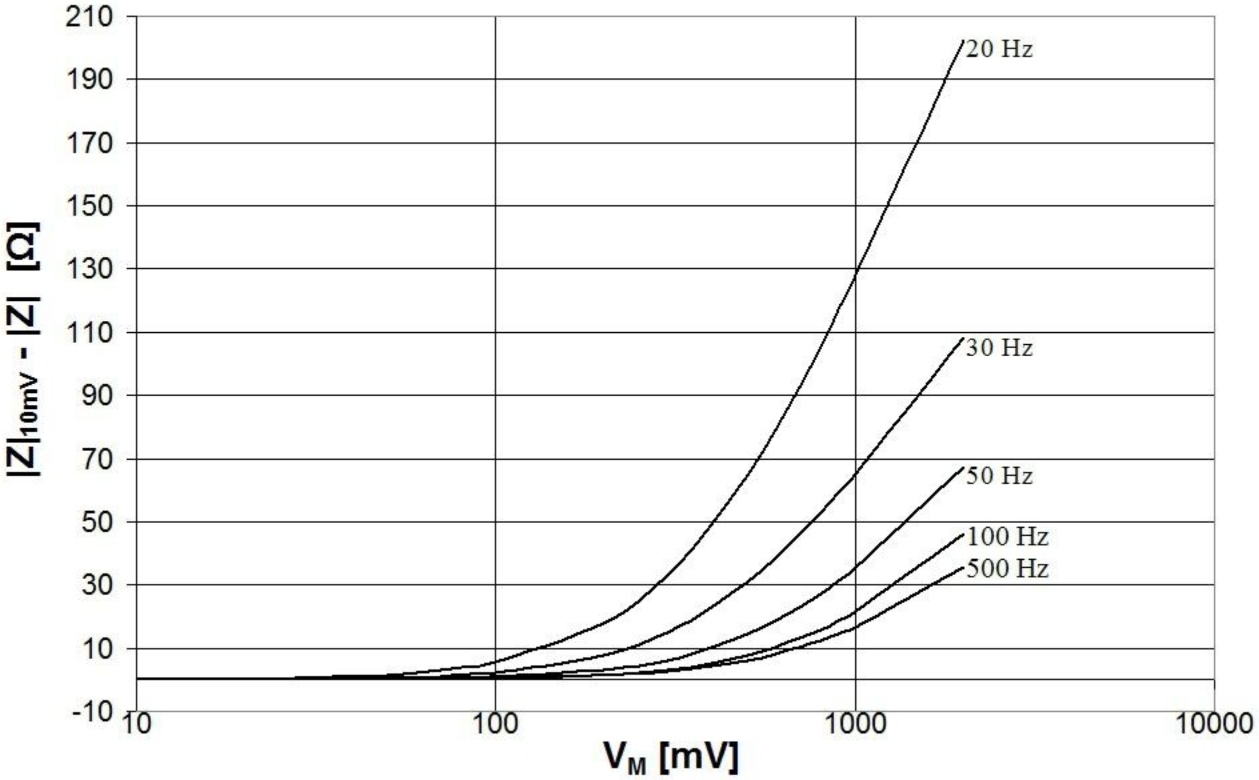

Fig. 4 $|Z|_{10mV}$ - $|Z|$ vs. the amplitude V_M of the applied test signal for different frequencies in the case of the Angelito mix (# 9 in Table 1) and sensor A. Non-linear response is stronger at low frequencies.

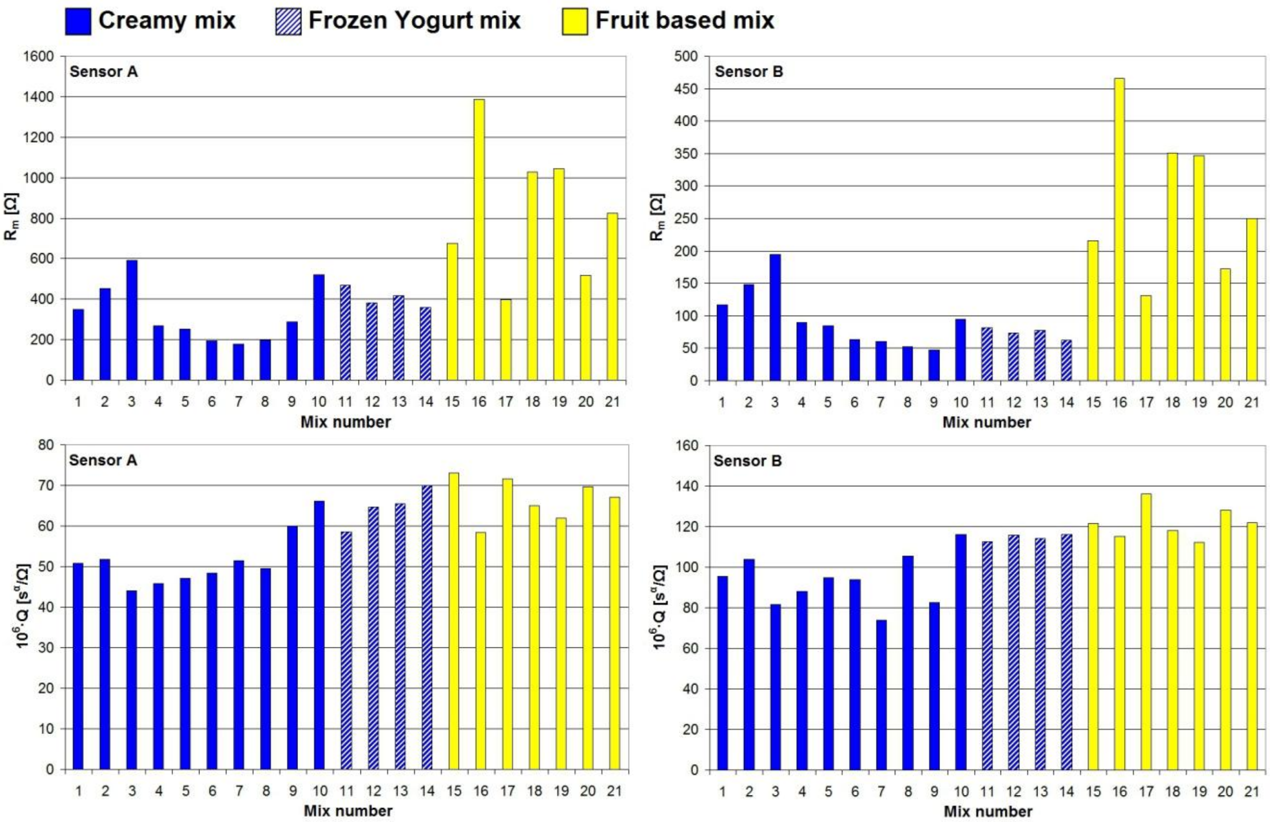

Fig. 5 Histograms of R_m and Q for all ice-cream mixes and both sensors used in this work. Creamy mixes bars are blue colored, frozen yogurt mixes are blue/white colored and fruit based ice-cream mixes are yellow colored.

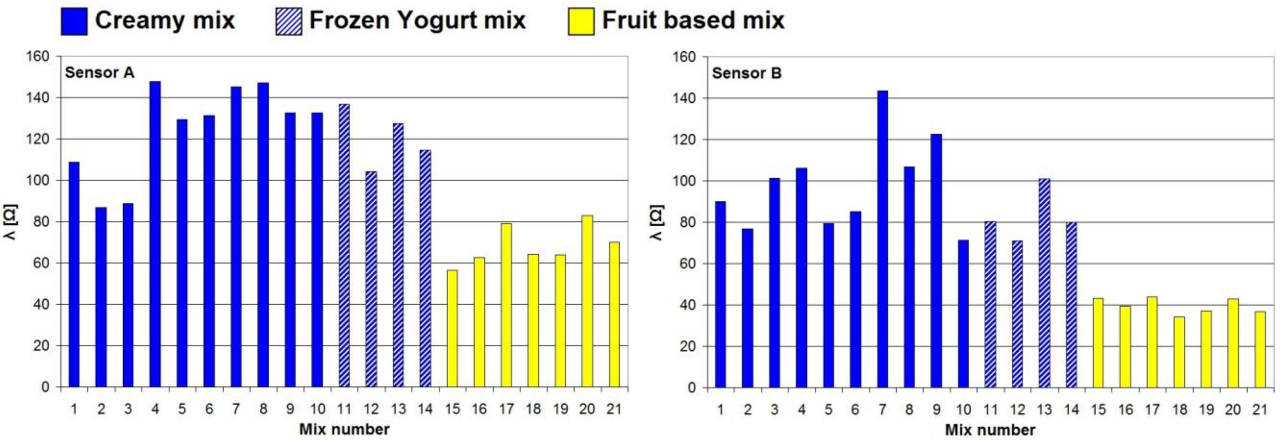

Fig. 6 Histograms of λ for all ice-cream mixes and both sensors. Creamy mixes bars are blue colored, frozen yogurt mixes are blue/white colored and fruit based ice-cream mixes are yellow colored.

Supplementary material

Automatic Ice-Cream Characterization by Impedance Measurements for Optimal Machine Setting

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1. Ice-cream mixes

Measurements have been performed on a set of 21 ice-cream mixes, different for ingredients and producers. In the following, the recipes for every mix used in the study are presented.

#	Ice-cream mix	Composition
1	*Soft serve mix (low fat content – pasteurization at 65 °C)*	Water, Skimmed Milk Powder, Whipping Cream, Pregel Base Diamant 100 and Sugar in the following composition: Sugar (11.9%), Fat (4%), Milk Solids-nonfat (8.9%), Stabilizers (0.3%)
2	*Soft serve mix (high fat content – pasteurization at 65 °C)*	Water, Skimmed Milk Powder, Whipping Cream, Pregel Base Diamant 100 and Sugar in the following composition: Sugar (17.2%), Fat (11.2%), Milk Solids-nonfat (12%), Stabilizers (0.3%)
3	*Soft serve mix (high fat content – pasteurization at 85 °C)*	Water, Skimmed Milk Powder, Whipping Cream, Pregel Base Diamant 100 and Sugar in the following composition: Sugar (17.2%), Fat (11.2%), Milk Solids-nonfat (12%), Stabilizers (0.3%)
4	*Egg based ice-cream mix*	Whole Milk (66.5%), Skimmed Milk Powder (8%), Fresh Whipping Cream @ 35% (8.2%), Sucrose (15.6%), Dextrose (2%), Egg Yolk (7.5%), Pregel Base Diamant 50 (3.4%)
5	*Fiordilatte ice-cream mix*	Whole Milk (70%), Skimmed Milk Powder (1,.3%), Fresh Whipping Cream @ 35% (8.2%), Sucrose (15.4%), Dextrose (1.7%), Pregel Base Diamant 50 (3.4%)
6	*Chocolate ice-cream mix*	Whole Milk (63%), Fresh Whipping Cream @ 35% (10%), Sucrose (15.6%), Dextrose (2%), Cocoa Powder (24%), Pregel Base Diamant 50 (3.4%)
7	*Fabbri soft serve Chocolate mix*	Sugar, Cocoa Powder, Whole Milk Powder, Skimmed Milk Powder, Maltodextrins, Stabilisers (E412, E466), Emulsifiers (E471), Flavouring in the following composition: 2.25 liters by water and 1 Kg by powder
8	*Pregel soft serve Chocolate mix*	Sugar, Cocoa Powder, Skimmed Milk Powder, Hydrogenated Vegetable Fat, Dextrose, Dehydrated Glucose Syrup, Stabilisers (E412, E410, E466), Emulsifiers (E471,E472a, E472b), Acidifier (E330)
9	*Angelito Vanilla Flavour Dairy Ice Cream Mix*	Skimmed Milk, Sugar, Butter, Skimmed Milk Powder, Dried Glucose, Syrup, Emulsifiers (E477, E471), Stabilisers (E466, E412, E407, E451), Flavouring
10	*Mondi ice-cream mix*	Sugar, Coconut Oil, Dextrose, Glucose Powder, Milk Proteins, Stabilisers (E412, E410, E466), Emulsifiers (E471, E473), Flavouring in the following composition: 17.5 Kg by powder and 30 liters by water
11	*Pregel Yogursprint mix*	Sugar, Dextrose, Skimmed Milk Powder, Skimmed Yogurt Powder, Maltodextrins, Acidifier (E330), Flavouring, Hydrogenated Vegetable Fat, Stabilisers (E412, E410, E466), Emulsifiers (E471,E472a, E472b, E477) in the following composition: 2.5 liters by Whole Milk and 1 Kg by powder
12	*Pregel Yogursprint mix + fresh yogurt*	Sugar, Dextrose, Skimmed Milk Powder, Skimmed Yogurt Powder, Maltodextrins, Acidifier (E330), Flavouring, Hydrogenated Vegetable Fat, Stabilisers (E412, E410, E466), Emulsifiers (E471,E472a, E472b, E477) in the following composition: 2 liters by Whole Milk, 500 g by Fresh Skimmed Yogurt and 1 Kg by powder
13	*Yogurt mix*	Skimmed Yogurt (2 liters), White Base (1 liters), Sucrose (450 gr), Skim Solids (8 gr) with White Base in the following composition: Milk (1 liters), Skimmed Milk Powder (50 gr), Whipping Cream (258 gr), Sucrose (250 gr), Dextrose (25 gr), Glucose (33 gr), Skim Solids (8 gr), Proteins (25gr)
14	*Yogurt soft serve mix*	Whole Milk (482 gr), Skimmed Yogurt (300 gr) and Yosoft Powder (220 gr) with the following ingredients: Sucrose, Vegetable Fiber, Skimmed Milk Powder, Skimmed Yogurt Powder, Dextrose, Emulsifiers (E471, E472b, E472, E477), Acidifier (E330), Stabilisers (E410), Flavouring
15	*Orange based ice-cream mix*	Orange (69.3%), Water (4.9%), Sugar (20.8%), Fruit Base 50 (3.5%), Lemon Juice (1.5%)
16	*Prickly pear based ice-cream mix*	Prickly Pear (50%), Water (25.5%), Sugar (22%), Fruit Base 50 (2.5%), Lemon Juice (1.5%)
17	*Banana based ice-cream mix*	Banana (50%), Water (27.6%), Sugar (20.4%), Fruit Base 50 (2%), Lemon Juice (1.5%)
18	*Strawberry based ice-cream mix*	Strawberry (50%), Water (23,5%), Sugar (24%), Fruit Base 50 (2.5%), Lemon Juice (1.5%)
19	*Pear based ice-cream mix*	Pear (50%), Water (25%), Sugar (22.5%), Fruit Base 50 (2.5%), Lemon Juice (1.5%)
20	*Kibana based ice-cream mix*	Kiwi (35%), Banana (15%), Water (24.9%), Sugar (23%), Fruit Base 50 (2.1%), Lemon Juice (1.5%)
21	*Lemon based ice-cream mix*	Lemon Mashed Fruit Pulp (69.3%), Water (4.9%), Sugar (20.8%), Fruit Base 50 (3.5%), Lemon Juice (1.5%)

2. Electrical characterization in the frequency range 20 Hz to 2 MHz

Preliminary measurements have been carried out on a limited number of ice-cream mixes using a sinusoidal test signal of amplitude 100 mV and frequency in the range 20 Hz to 2 MHz for the incubation temperature of 35 °C. The Nyquist plot for the entire frequency range as well as a particular of the higher frequencies are shown in Fig. S1 for mix # 2 and sensor A (different mixes and sensor B result in similar behavior).

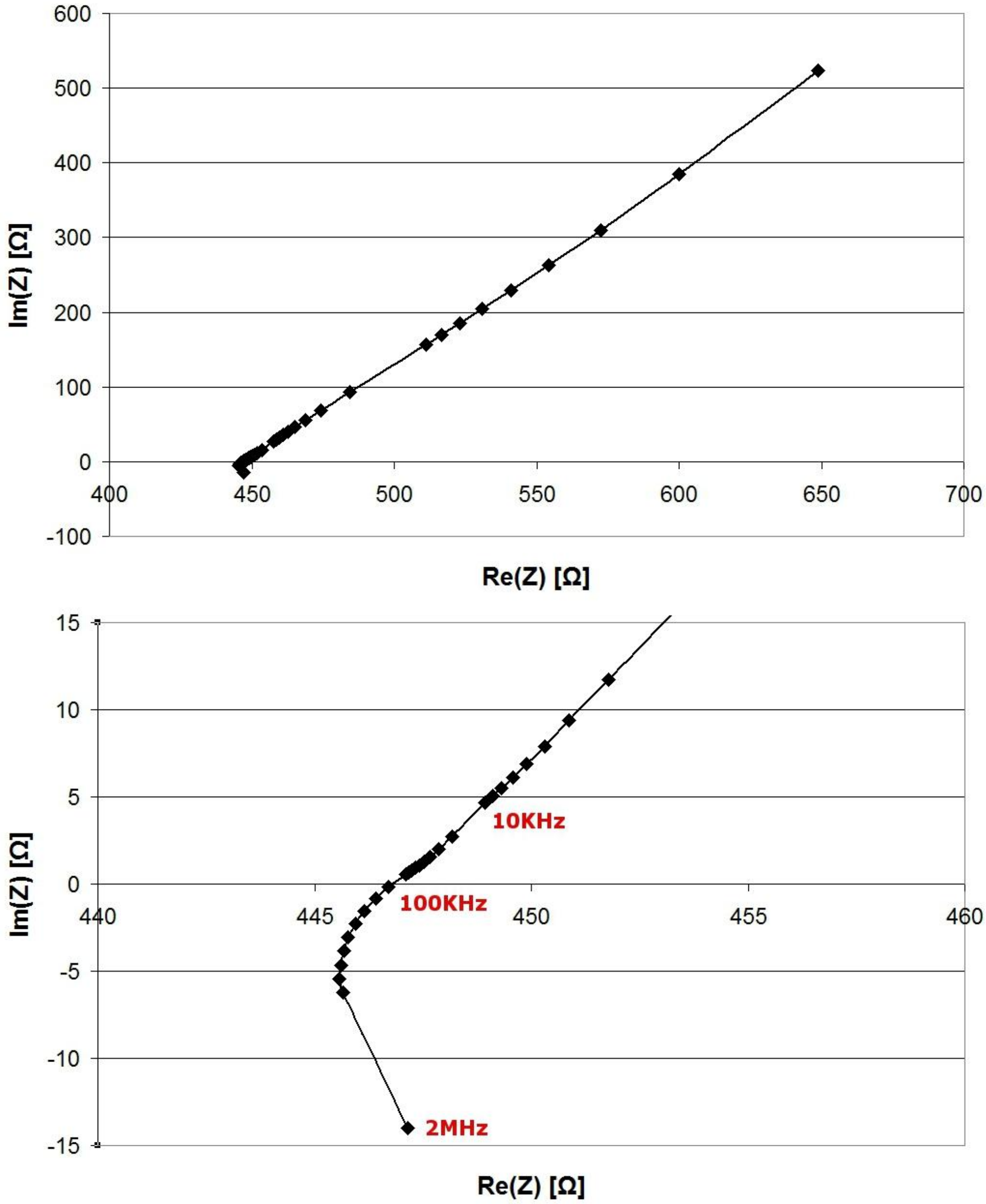

Fig. S1 Nyquist plot in the frequency range 20 Hz to 2 MHz for mix # 2 and sensor A at 35 °C.

The results from Fig. S1 clearly indicates that the electrical model featuring a resistance (R_m) and a CPE (Q) in series is adequate for frequencies up to 400 kHz. For higher frequencies a deviation from the model occours. The real component of the impedance Re(Z) was almost the same at 10 kHz and 2 MHz (differences lower than 0.2%). Repeated measures on the same ice-cream mix (# 2) were carried out to test the repeatability of the measures. The results show that Re(Z) results in comparable repeatability at 10 kHz and 2 MHz (with a ratio of standard deviation to mean value σ/μ of 0.03), while the imaginary component Im(Z) resulted in higher dispersion at higher frequency (with a σ/μ value of 0.19 at 2 MHz almost twice than at 10 kHz). The higher dispersion at higher frequencies can be related to some parasitic effects in the sensor that have to be further investigated. Since the less repeatability of the measures and the fact that, from preliminary measurements, data on the extended frequency range don't provide further informations, the investigated frequencies in the paper has been limited to the range 20 Hz to 10 kHz.

3. Measurements at 4 °C and 35 °C: results comparison

Mix # 2 from Table 1 in the paper has been analyzed in triplicate using EIS with a sinusoidal test voltage of amplitude 100 mV and frequency range from 20 Hz to 10 kHz with both sensors. In Fig. S2 the Nyquist plot is shown for the three measures at both temperatures of 4 °C and 35 °C for sensor A. Measures at 4 °C resulted in less repeatability than 35 °C. This can be related to the fact that at 4 °C the ice-cream mixes are in a semi viscous frozen state and also small temperature variations can produce relatively large changes in the product structure.

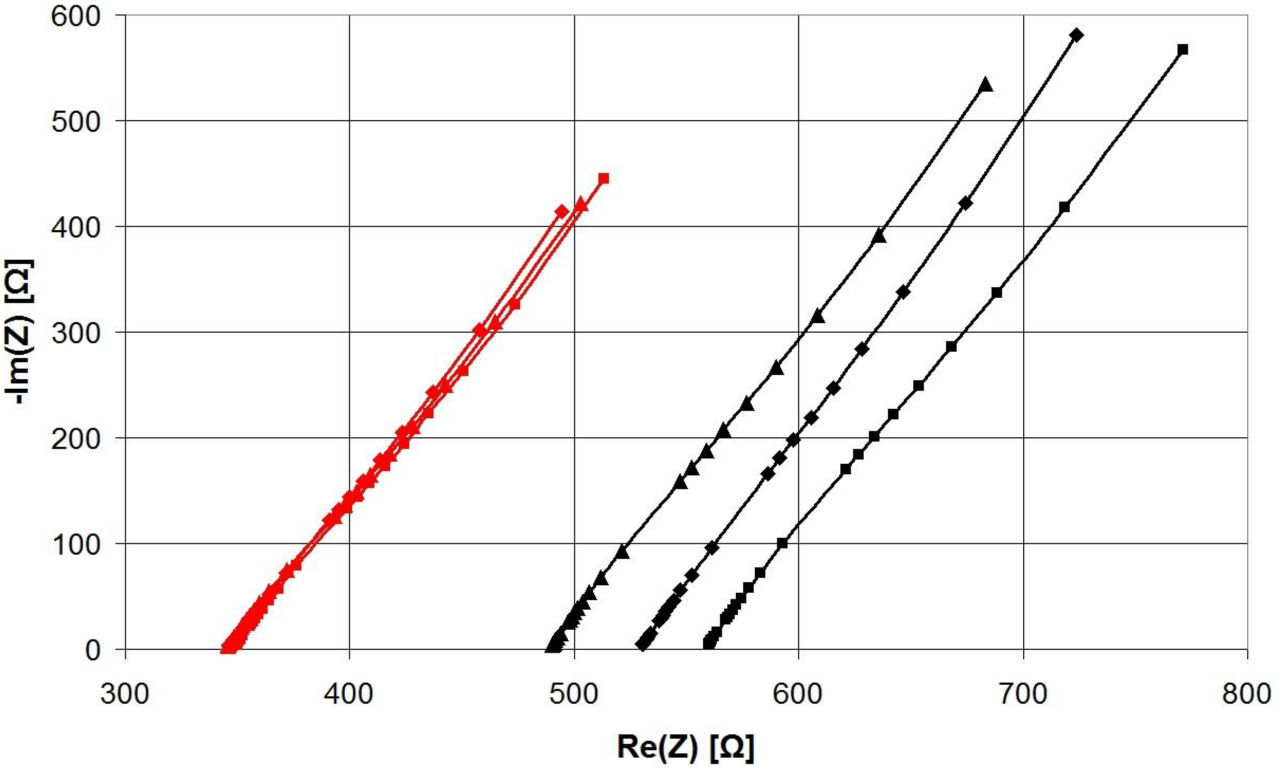

Fig. S2 Nyquist plot in the frequency range 20 Hz to 10 kHz for mix # 2 (measures in triplicate) and sensor A at two different incubation temperatures: 4 °C and 35 °C.

Statistical analysis has been carried out and mean value μ as well as the ratio of standard deviation to mean value σ/μ have been calculated for both sensors and temperatures. The results are presented in the following table.

		SENSOR A		SENSOR B	
		T = 4 °C	T = 35 °C	T = 4 °C	T = 35 °C
R_m	μ [Ω]	524.7	345.5	186	116.7
	σ/μ	0.066	0.005	0.055	0.005
Q	μ [$10^6 s^\alpha/\Omega$]	38.7	52.7	71.3	86.7
	σ/μ	0.08	0.03	0.18	0.09

4. Correlation between pH and electrical measures

The correlation between measured electrical parameters R_m, Q and λ for both type of sensors and pH has been investigated, and the results are presented in Fig. S3, where the values of pH are plotted versus the corresponding electrical parameter for all products tested and both sensors.

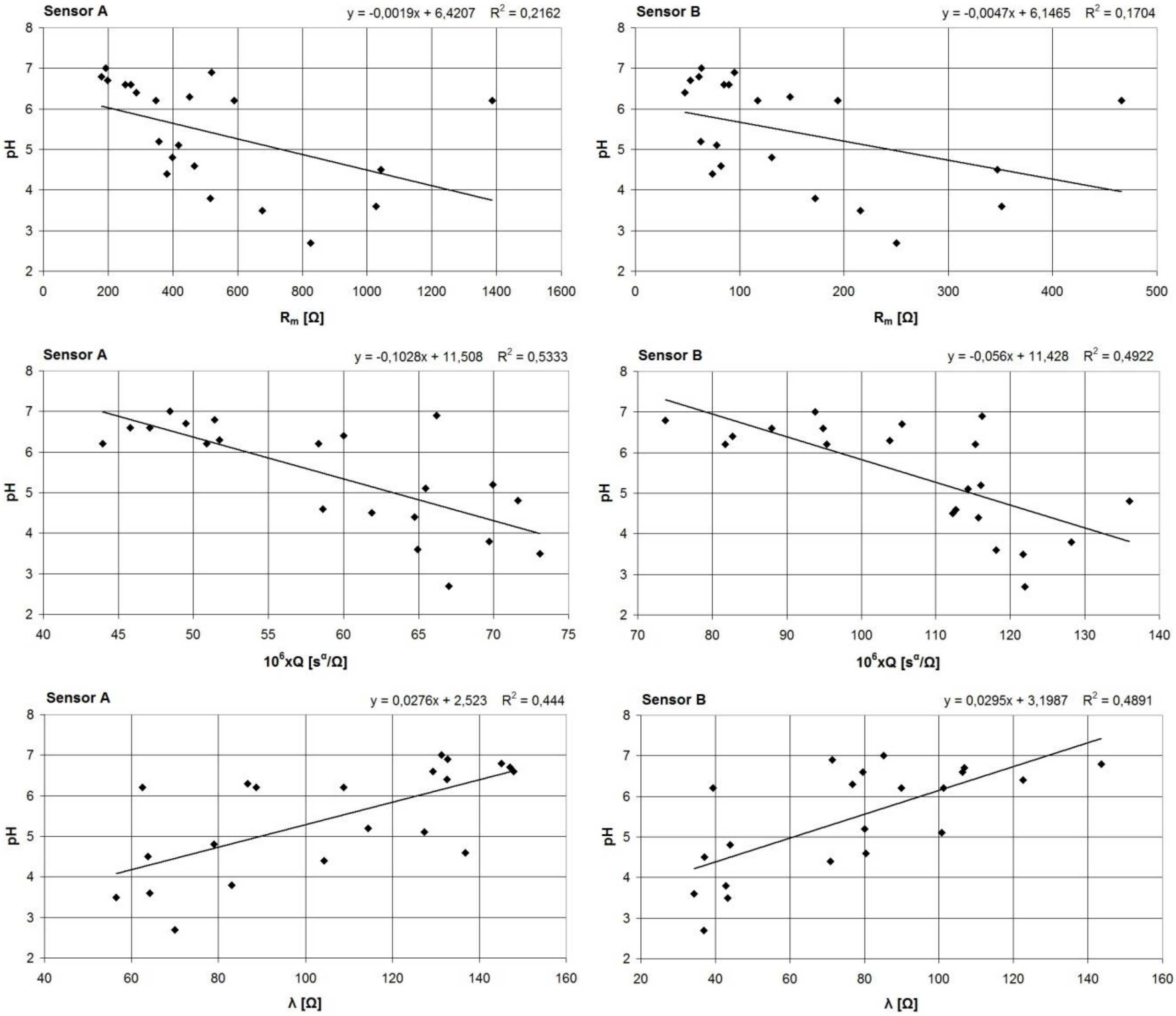

Fig. S3 Scatter plots of pH values vs. R_m, Q and λ for all tested mixes and both sensors. Linear regression lines as well as determination coefficient R^2 have been calculated.