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1 **Automatic Ice-Cream Characterization by Impedance Measurements for Optimal Machine**

2 **Setting**

3

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8

9 **Abstract**

10 Electrical characterization of products is gaining increasing interest in the food industry for quality
11 monitoring and control. In particular, this is the case in the ice-cream industry, where machines
12 dedicated to store ice-cream mixes are programmed “ad hoc” for different groups of products. To
13 this purpose, the present work shows that essential product classification (discrimination between
14 milk based and fruit based ice-cream mixes) can be done by means of a technique based on the
15 measurements of non-linear response in the electrical behavior of the electrode-electrolyte interface.
16 The addition of pH measurements allows to further reach the three parts classification occasionally
17 required for advanced applications. The proposed idea is validated by means of measurements on
18 21 ice-cream mixes, different for producers and composition.

19

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

22

23 **1. Introduction**

24 While in the early stage of the food industry the competition was mainly focused on costs, today
25 product quality and safety are a primary concern. Consequently, products are routinely screened for

26 important organoleptic characteristics (such as smell, aroma, color,...) as well as to guarantee that
27 microbial content is below the maximum allowed threshold concentration.

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

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

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

49 At present, specific machine parameters for these three ice-cream groups (but often differences are
50 considered only among milk and fruit based mixes) are set manually: hence an operator is needed
51 every time the stored ice-cream mix type is changed. Instead, if the product type could be

52 discriminated by means of an electronic system embedded in the machine, such an intervention
53 would be no longer necessary, with significant advantages in terms of costs, time and error
54 reduction.

55 Electrical Impedance Spectroscopy (EIS) is often used for electrical characterization of food
56 products. In EIS the sample under test is placed in direct contact with electrodes and stimulated
57 with a sinusoidal test voltage $V_{in}(t) = V_M \sin(\omega t) = V_M \sin(2\pi f t)$ with fixed amplitude V_M in a
58 definite range of frequencies. The current $I_{in}(t)$ through the electrodes due to the test signal is
59 measured and, if the system electrode-electrolyte can be considered linear (i.e. if $V_{in}(t)$ is the
60 weighted sum of several signals, then $I_{in}(t)$ is the weighted sum of the system response to each of
61 the signals), the complex impedance Z can be calculated as $Z = |Z|e^{j\text{Arg}(Z)} = V_{in}(j\omega)/I_{in}(j\omega)$, where
62 $V_{in}(j\omega)$, $I_{in}(j\omega)$ are the Steinmetz phasors of the sinusoidal signals $V_{in}(t)$ and $I_{in}(t)$ respectively, $|Z|$ is
63 the impedance modulus and $\text{Arg}(Z)$ the impedance phase. The acquired spectra can be represented
64 with different graph types, such as Bode plots, where $|Z|$ and $\text{Arg}(Z)$ are plotted as function of the
65 test signal frequency, or Nyquist plots where the impedance imaginary component
66 $\text{Im}(Z) = |Z|\sin(\text{Arg}(Z))$ is plotted vs. the real component $\text{Re}(Z) = |Z|\cos(\text{Arg}(Z))$ for different
67 frequencies.

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

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

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

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

77

78 **2. Experimental approach**

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

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

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

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

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

103

104 **3. Measurement setup**

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

106 The setup used for the experiments is illustrated in Fig. 1 (a): the product samples are incubated in a
107 thermal chamber WTC Binder providing the target temperature with an uncertainty of 0.1 °C.
108 Measures have been carried out at two different temperatures (4 °C and 35 °C). The two
109 temperatures have been chosen according to the following rules: 4 °C is the standard temperature
110 the ice-cream mixes are stored while 35 °C is the temperature used in a microbial biosensor system
111 recently developed by the authors [13]. Thus, the choice has been made with the idea of a future
112 implementation in industrial environment as a sensor integrated in the tank of the storing machine
113 (4 °C) or in a separate chamber controlled with the embedded biosensor system (35 °C). However,
114 the measures at 4 °C resulted in poor repeatability (see Supplementary Material for more
115 information). This can be related to the fact that at 4 °C the ice-cream mixes are in a semi-viscous
116 frozen state and also small temperature variations can produce relatively large changes in the
117 product structure. Thus, in the following, only measures at 35 °C are discussed. Electrical
118 characteristics of the sample ($|Z|$ and $\text{Arg}(Z)$) are measured with an LCR meter Agilent E4980A,
119 controlled via USB interface by a PC system that is also used to acquire measured data and further
120 data processing. The sample under test is placed in a 10 ml container with cap shaped stainless steel
121 electrodes. Two types of sensors are used: sensor A (Fig. 1 (b)) consists of two electrodes while
122 sensor B (Fig. 1 (c)) has four electrodes that are shorted together in couples as shown in the figure.
123 The difference between the two sensors is related to the generated electric field. Both sensor
124 geometries have been simulated using the software Comsol Multiphysics v4 (Comsol Inc, Palo
125 Alto, USA). The electric field distribution is also shown in Fig. 1 (b) and (c). Sensor B is
126 characterized by more homogeneous electric field with higher values than sensor A for both the
127 field and its gradient. All the ice-cream mixes have been tested with both types of sensors.

128

129 **4. Ice-cream mixes**

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

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

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

142

143 **5. Electrical circuit model**

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

152 The electrical model used to fit the data in the investigated frequency range is shown in Fig. 2 (b): it
153 is composed of a resistance R_m (accounting for the resistance of both the sample and the interface)
154 and a constant phase element CPE (resulting from the essentially capacitive component due to the
155 interface electrode–medium) in series. Since the ice-cream is an unstructured material no distinct

156 dispersion exists within the radiofrequency range up to several MHz. The sample impedance is thus
 157 purely resistive while the reactive component is essentially due to the electrode interface. The
 158 impedance of CPE is described by two parameters (Q and α) where Q represents the double layer
 159 capacitance, while α accounts for the non ideal electrode-medium interface (the case $\alpha=1$ refers to
 160 an ideal capacitance). The reason for using a CPE instead of a linear capacitor is the non ideal
 161 behavior of electrode interface [15]. Moreover, the calculated impedance using a linear capacitor
 162 results in $\text{Re}(Z)$ to be independent of frequency, contrary to the Nyquist plot of Fig. 2 (a).

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

$$164 \quad Z = R_m + Z_{CPE} = R_m + \frac{1}{Q(j\omega)^\alpha} = R_m + \frac{e^{-j\frac{\pi}{2}\alpha}}{Q\omega^\alpha} = R_m + \frac{\cos(\frac{\alpha\pi}{2})}{Q\omega^\alpha} - j\frac{\sin(\frac{\alpha\pi}{2})}{Q\omega^\alpha} \quad (1)$$

165 Thus:

$$166 \quad \text{Re}(Z) = R_m - \text{ctg}\left(\frac{\alpha\pi}{2}\right) \times \text{Im}(Z) \quad (2)$$

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

174 The electrical characterization in the non-linear region for the electrode-medium system is
 175 investigated measuring $|Z|$ with a sinusoidal voltage signal of fixed frequency and V_M in the range
 176 10 mV to 2 V (with logarithmic spacing). Fig. 4 shows $|Z|_{10\text{mV}} - |Z|$ vs. V_M (logarithmic scale) for
 177 different frequencies in the case of the Angelito mix (# 9 in Table 1) and sensor A. The value of $|Z|$
 178 is almost constant for small signal amplitude (i.e. $V_M \ll V_{MT}$, with V_{MT} never lower than 200 mV),
 179 while for higher values of V_M , it decreases linearly with $\text{Log}_{10}(V_M)$, thus producing an increase of

180 $|Z|_{10mV} - |Z|$. The results clearly indicate that increasing the test signal frequency results in an increase
 181 of the cut-off amplitude V_{MT} and a decrease of the slope in the non-linear region.

182 In order to characterize the electrical response in the non-linear region for the tested products, the
 183 curves have been fitted with the empirical model $|Z| = |Z|_{10mV} + \beta_1 \cdot \text{Log}_{10}(1 + (V_M/V_{MT})^{\beta_2})$, where
 184 $|Z|_{10mV}$ is the value of $|Z|$ for small signal amplitude (i.e. linear response region), V_{MT} the cut-off
 185 amplitude (separating the linear from non-linear region) while β_1 and β_2 are empiric parameters
 186 used to fit the curve. Fitting procedure has been carried out by LMA. The iterative algorithm has
 187 been run with the following initial guess for parameters $|Z|_{10mV}=300$ $\beta_1=0.6$ $V_{MT}=600$ $\beta_2=11$ for all
 188 ice-cream mixes and both sensors. Fitting procedure resulted in high determination coefficient ($R^2 >$
 189 0.99), thus validating the empirical model. The slope λ in the non-linear region has been estimated
 190 with the following procedure: when $V_M \gg V_{MT}$ the empirical model function can be simplified as

191 $|Z| \approx |Z|_{10mV} + \beta_1 \cdot \text{Log}_{10}(V_M/V_{MT})^{\beta_2} = |Z|_{10mV} + \beta_1 \cdot \beta_2 \cdot \text{Log}_{10}(V_M/V_{MT})$, thus:

$$192 \quad \lambda = \frac{\partial |Z|}{\partial \text{Log}_{10}\left(\frac{V_M}{V_{MT}}\right)} \approx \beta_1 \cdot \beta_2 \quad (3)$$

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

197

198 **6. Results and discussion**

199 *6.1. Electrical impedance spectroscopy*

200 The ice-cream mixes have been tested following the procedures described in section 2 and section
 201 5. The experimental results are illustrated in Fig. 5. Statistical analysis of the presented data
 202 indicates that significant differences exist between fruit based and both creamy and frozen yogurt
 203 mixes in the case of R_m . Fruit based mixes are generally characterized by higher values of R_m than

204 milk based mixes. In particular, mean values of R_m for fruit based mixes are 838.9 Ω and 276.2 Ω
205 for sensor A and sensor B, respectively. Instead, the corresponding values for creamy mixes are
206 328.7 Ω and 95.3 Ω , while for frozen yogurt products these values are 406.9 Ω and 74.1 Ω .
207 However, a small number of fruit based mixes (banana and kibana based mixes, # 17 and 20,
208 respectively) exhibit values of R_m comparable with those of the milk based group, due to the
209 presence of potassium salts that greatly enhances conductivity.

210 Conductivity for the dairy products is mainly related to fats and salt content: higher concentration of
211 milk fats results in higher values of R_m , while the increase in salt concentration leads to resistance
212 decrease, as can be clearly seen comparing the values of R_m for mixes 1 and 2. However,
213 comparison between mixes 2 and 3 clearly indicates that pasteurization temperature also plays a
214 role in the measured electrical characteristics, since the same mix subjected to high temperature
215 pasteurization cycle (85 °C) results in a higher value for R_m than that of the mix pasteurized at
216 lower temperature (65 °C). On the other hand, it is known that differences in pasteurization
217 temperature can significantly alter some organoleptic characteristics of the product: for instance,
218 [16] showed that ice-cream mixes pasteurized with high thermal cycle (between 75 °C and 82 °C)
219 exhibit lower fat clumping, viscosity and freezing time, and higher protein stability. To investigate
220 if repeated pasteurization cycles can effectively alter the product electrical characteristics, mix 2 has
221 been subjected to low temperature pasteurization cycles (65 °C) at time intervals of 1 day and the
222 electrical parameters have been measured after each cycle : no correlation was observed between
223 the electrical parameters and the number of pasteurization cycles, thus showing that only thermal
224 cycling with high temperature significantly affects the product characteristics, while repeated
225 cycling at lower temperature produces no detectable change.

226 As far as values of Q are considered (expressed as $10^6 s^a/\Omega$), fruit based and frozen yogurt mixes
227 exhibit values significantly higher than those of creamy mixes: mean values of 66.6 and 64.6 for
228 sensor A and 121.9 and 114.7 for sensor B as compared to 51.5 and 93.5 for creamy mixes. Once

229 again, overlapping values of Q exist among different groups and no significant difference between
230 frozen yogurt and fruit based mixes is detected.

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

233

234 *6.2. Electrical response in the non-linear region*

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

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

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

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

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

257

258 *6.3. Correlation between electrical and pH measures*

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

265 Better results are obtained for the correlation of pH with λ (0.444 and 0.489) and Q (0.533 and
266 0.492). However, the determination coefficient never higher than 0.533 is not satisfactory,
267 preventing a reliable estimate of pH with electrical measures. Multiple regression analysis has been
268 carried out to test if expressing pH as linear function of more than a single electrical parameter
269 significantly increases the correlation. The best results are obtained (for both sensors) by using Q
270 and λ as independent variables, namely: $\text{pH} = b_0 + b_1 * Q + b_2 * \lambda$, where b_0 , b_1 and b_2 are numerical
271 parameters. In this way, however, the determination coefficient R^2 (corrected for the use of multiple
272 variables) increases only slightly in the case of the data obtained with sensor A (0.621) while no
273 improvement is found in the case of sensor B.

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

275 The overall results from the study are presented in Table 2. Regarding the primary discrimination
276 between milk based and fruit based mixes, although the resistive component of the impedance R_m is
277 characterized by statistical significantly different values for the two groups, the discrimination is not
278 reliable due to few fruit based mixes characterized by higher conductivity. On the contrary, the
279 parameter λ measured in the non-linear region can provide reliable discrimination between the two

280 groups (in particular using sensor B). The second level discrimination of milk based mixes in
281 creamy mixes and frozen yogurts can be reliably achieved by pH measure, while electrical
282 parameter Q (although characterized by significantly different values for the two subgroups) doesn't
283 provide a reliable solution due to overlapping values between the two subgroups.

284

285 **7. Conclusions**

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

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

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

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

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

305

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309

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#	Ice-cream mix	pH
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384	1	<i>Soft serve mix (low fat content – pasteurization at 65 °C)</i>	6,2
385	2	<i>Soft serve mix (high fat content – pasteurization at 65 °C)</i>	6,3
386	3	<i>Soft serve mix (high fat content – pasteurization at 85 °C)</i>	6,2
387	4	<i>Egg based ice-cream mix</i>	6,6
388	5	<i>Fiordilatte ice-cream mix</i>	6,6
389	6	<i>Chocolate ice-cream mix</i>	7
390	7	<i>Fabbri soft serve Chocolate mix</i>	6,8
391	8	<i>Pregel soft serve Chocolate mix</i>	6,7
392	9	<i>Angelito Vanilla Flavour Dairy Ice Cream Mix</i>	6,4
393	10	<i>Mondi ice-cream mix</i>	6,9
394	11	<i>Pregel Yogursprint mix</i>	4,6
395	12	<i>Pregel Yogursprint mix + fresh yogurt</i>	4,4
396	13	<i>Yogurt mix</i>	5,1
397	14	<i>Yogurt soft serve mix</i>	5,2
398	15	<i>Orange based ice-cream mix</i>	3,5
399	16	<i>Prickly pear based ice-cream mix</i>	6,2
400	17	<i>Banana based ice-cream mix</i>	4,8
401	18	<i>Strawberry based ice-cream mix</i>	3,6
402	19	<i>Pear based ice-cream mix</i>	4,5
403	20	<i>Kibana based ice-cream mix</i>	3,8
404	21	<i>Lemon based ice-cream mix</i>	2,7

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

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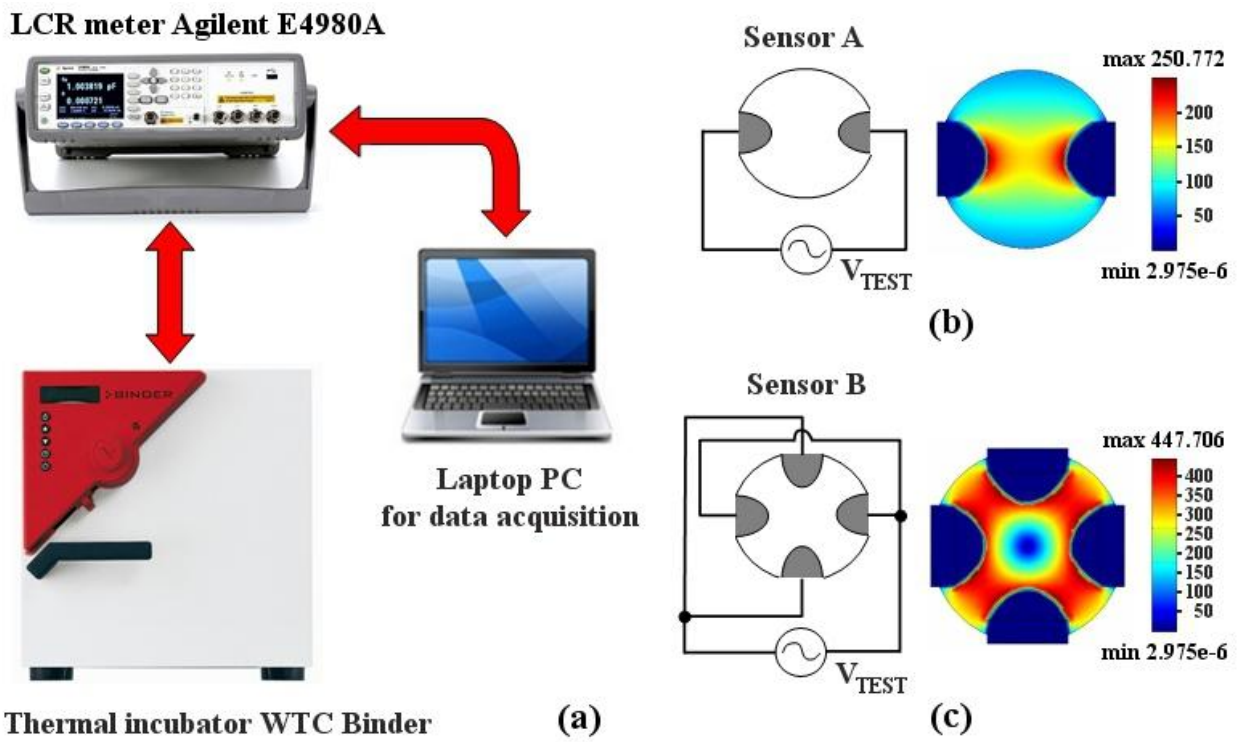
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	SENSOR A			SENSOR B			pH
	R _m	Q	λ	R _m	Q	λ	
Milk based mixes/Fruit based mixes	*		X	*		X	*
Creamy mixes/Frozen Yogurt mixes		*			*		X

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.

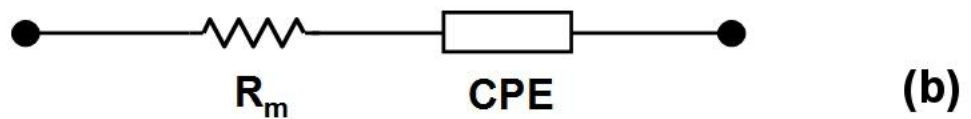
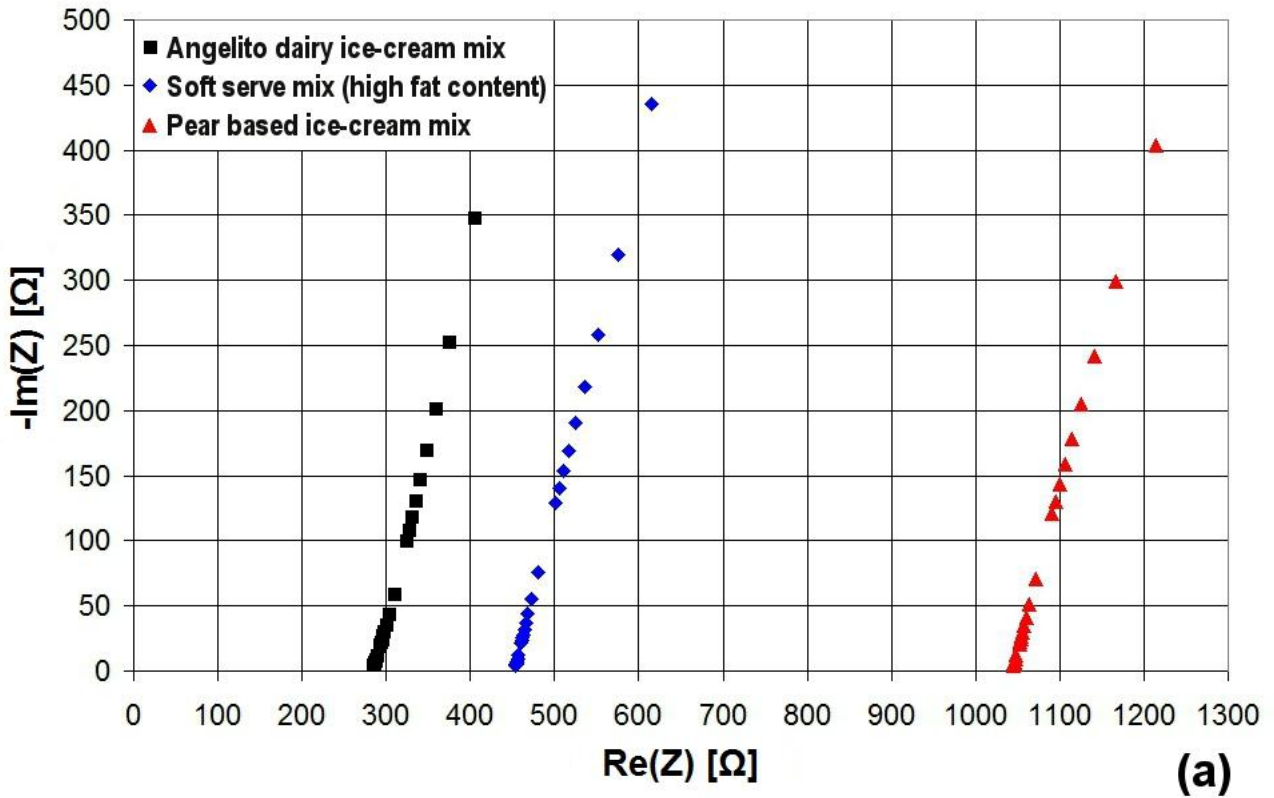
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Fig. 1 Measurement setup used in the electrical characterization of ice-cream mixes (a). Geometries and simulations of the generated electric field for sensor A (b) and sensor B (c).

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

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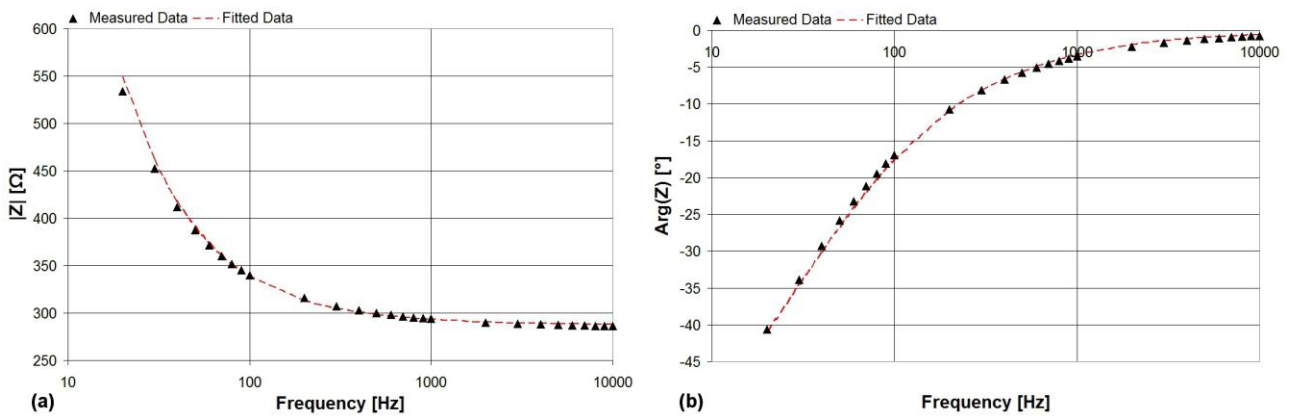
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469 **Fig. 3** $|Z|$ (a) and $\text{Arg}(Z)$ (b) vs. frequency of the applied test signal for the Angelito mix (# 9 in
470 Table 1) and sensor A. High correlation ($R^2 > 0.998$) is achieved for all ice-cream mixes and both
471 sensors between measured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

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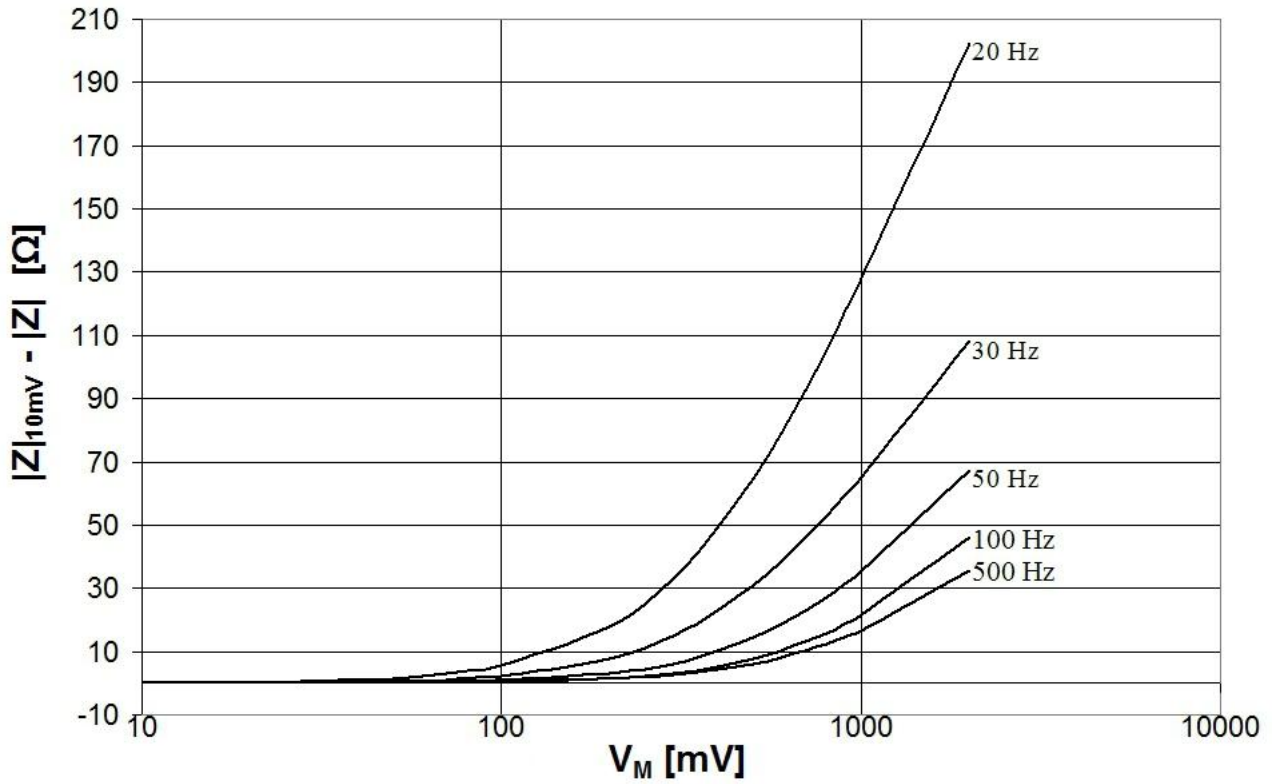
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488 **Fig. 4** $|Z|_{10mV} - |Z|$ vs. the amplitude V_M of the applied test signal for different frequencies in the
489 case of the Angelito mix (# 9 in Table 1) and sensor A. Non-linear response is stronger at low
490 frequencies.

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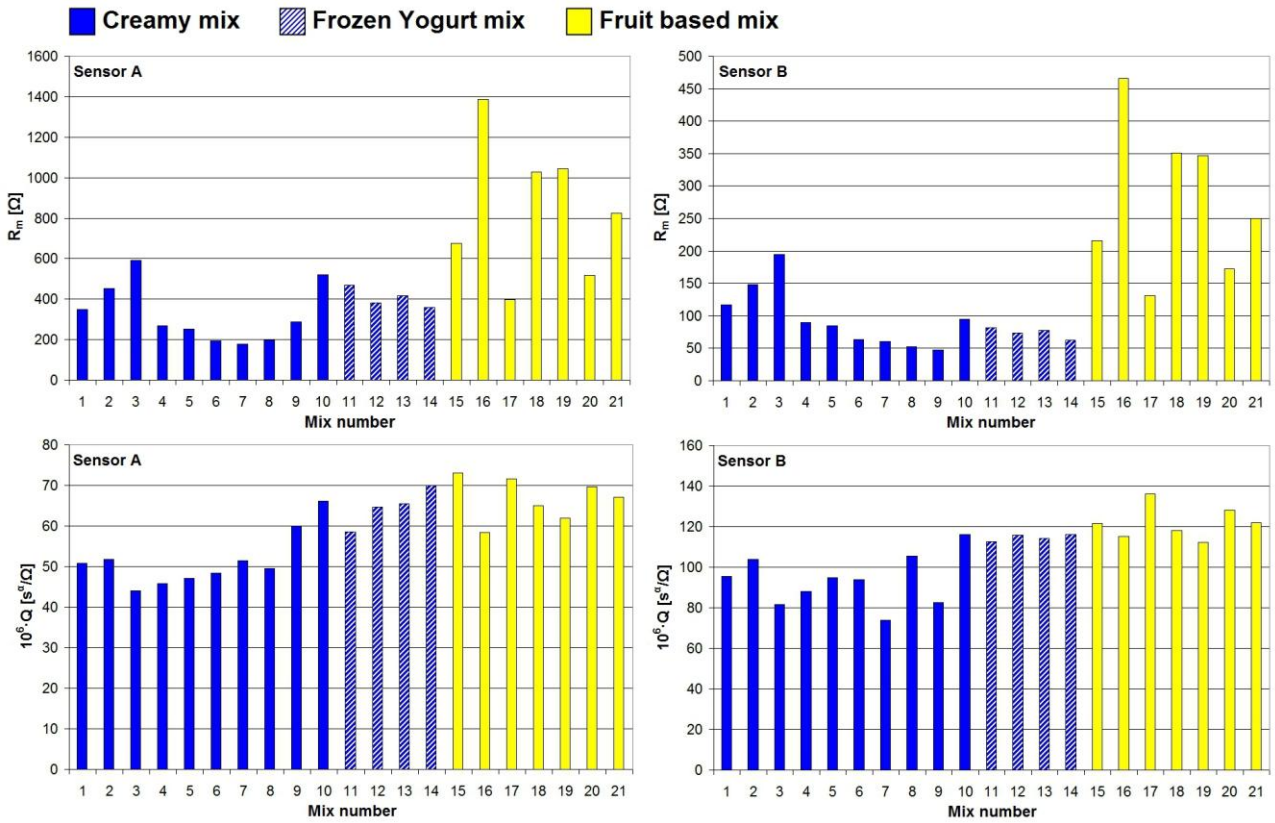
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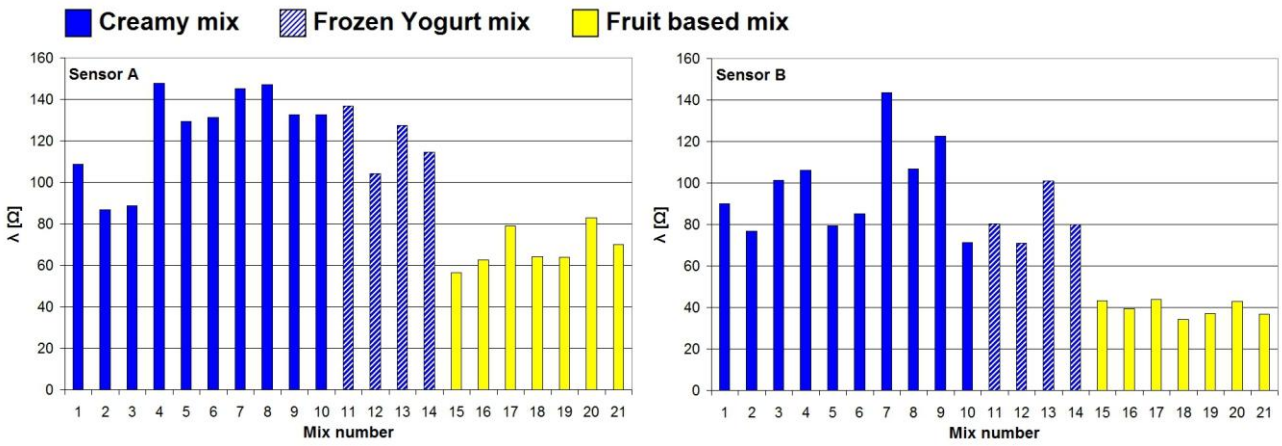


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505 **Fig. 5** Histograms of R_m and Q for all ice-cream mixes and both sensors used in this work. Creamy
 506 mixes bars are blue colored, frozen yogurt mixes are blue/white colored and fruit based ice-cream
 507 mixes are yellow colored.

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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

Marco Grossi, Massimo Lanzoni, Roberto Lazzarini, Bruno Riccò

1. Ice-cream mixes

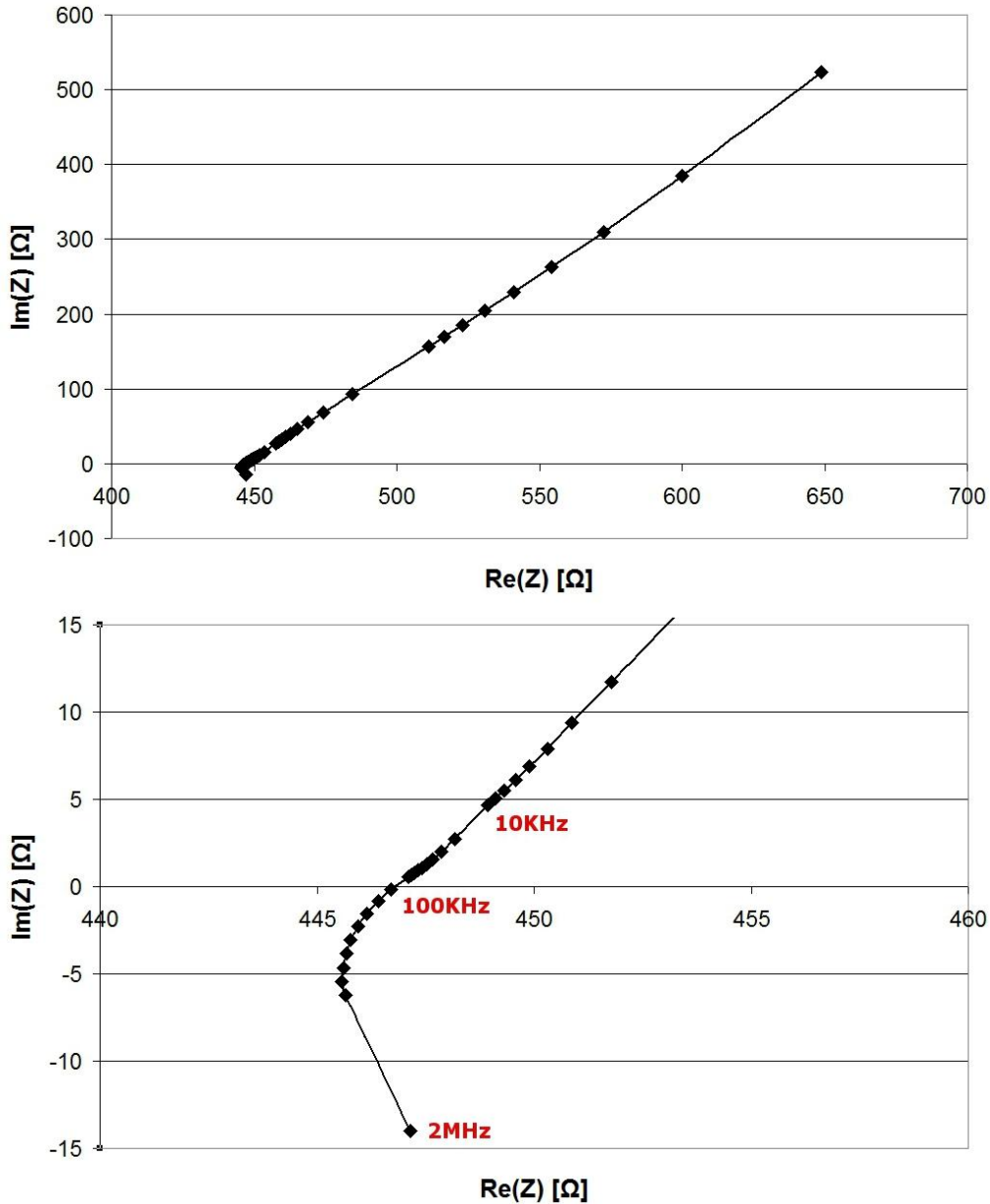
Measurements have been performed on a set of 21 ice-cream mixes, different for ingredients and producers. In the following, the recipes for every mix used in the study are presented.

#	Ice-cream mix	Composition
1	<i>Soft serve mix (low fat content – pasteurization at 65 °C)</i>	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	<i>Soft serve mix (high fat content – pasteurization at 65 °C)</i>	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	<i>Soft serve mix (high fat content – pasteurization at 85 °C)</i>	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	<i>Egg based ice-cream mix</i>	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	<i>Fiordilatte ice-cream mix</i>	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	<i>Chocolate ice-cream mix</i>	Whole Milk (63%), Fresh Whipping Cream @ 35% (10%), Sucrose (15.6%), Dextrose (2%), Cocoa Powder (24%), Pregel Base Diamant 50 (3.4%)
7	<i>Fabbri soft serve Chocolate mix</i>	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	<i>Pregel soft serve Chocolate mix</i>	Sugar, Cocoa Powder, Skimmed Milk Powder, Hydrogenated Vegetable Fat, Dextrose, Dehydrated Glucose Syrup, Stabilisers (E412, E410, E466), Emulsifiers (E471, E472a, E472b), Acidifier (E330)
9	<i>Angelito Vanilla Flavour Dairy Ice Cream Mix</i>	Skimmed Milk, Sugar, Butter, Skimmed Milk Powder, Dried Glucose, Syrup, Emulsifiers (E477, E471), Stabilisers (E466, E412, E407, E451), Flavouring
10	<i>Mondi ice-cream mix</i>	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	<i>Pregel Yogursprint mix</i>	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	<i>Pregel Yogursprint mix + fresh yogurt</i>	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	<i>Yogurt mix</i>	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	<i>Yogurt soft serve mix</i>	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	<i>Orange based ice-cream mix</i>	Orange (69.3%), Water (4.9%), Sugar (20.8%), Fruit Base 50 (3.5%), Lemon Juice (1.5%)
16	<i>Prickly pear based ice-cream mix</i>	Prickly Pear (50%), Water (25.5%), Sugar (22%), Fruit Base 50 (2.5%), Lemon Juice (1.5%)
17	<i>Banana based ice-cream mix</i>	Banana (50%), Water (27.6%), Sugar (20.4%), Fruit Base 50 (2%), Lemon Juice (1.5%)
18	<i>Strawberry based ice-cream mix</i>	Strawberry (50%), Water (23.5%), Sugar (24%), Fruit Base 50 (2.5%), Lemon Juice (1.5%)
19	<i>Pear based ice-cream mix</i>	Pear (50%), Water (25%), Sugar (22.5%), Fruit Base 50 (2.5%), Lemon Juice (1.5%)
20	<i>Kibana based ice-cream mix</i>	Kiwi (35%), Banana (15%), Water (24.9%), Sugar (23%), Fruit Base 50 (2.1%), Lemon Juice (1.5%)
21	<i>Lemon based ice-cream mix</i>	Lemon Mashed Fruit Pulp (69.3%), Water (4.9%), Sugar (20.8%), Fruit Base 50 (3.5%), Lemon Juice (1.5%)

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

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

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

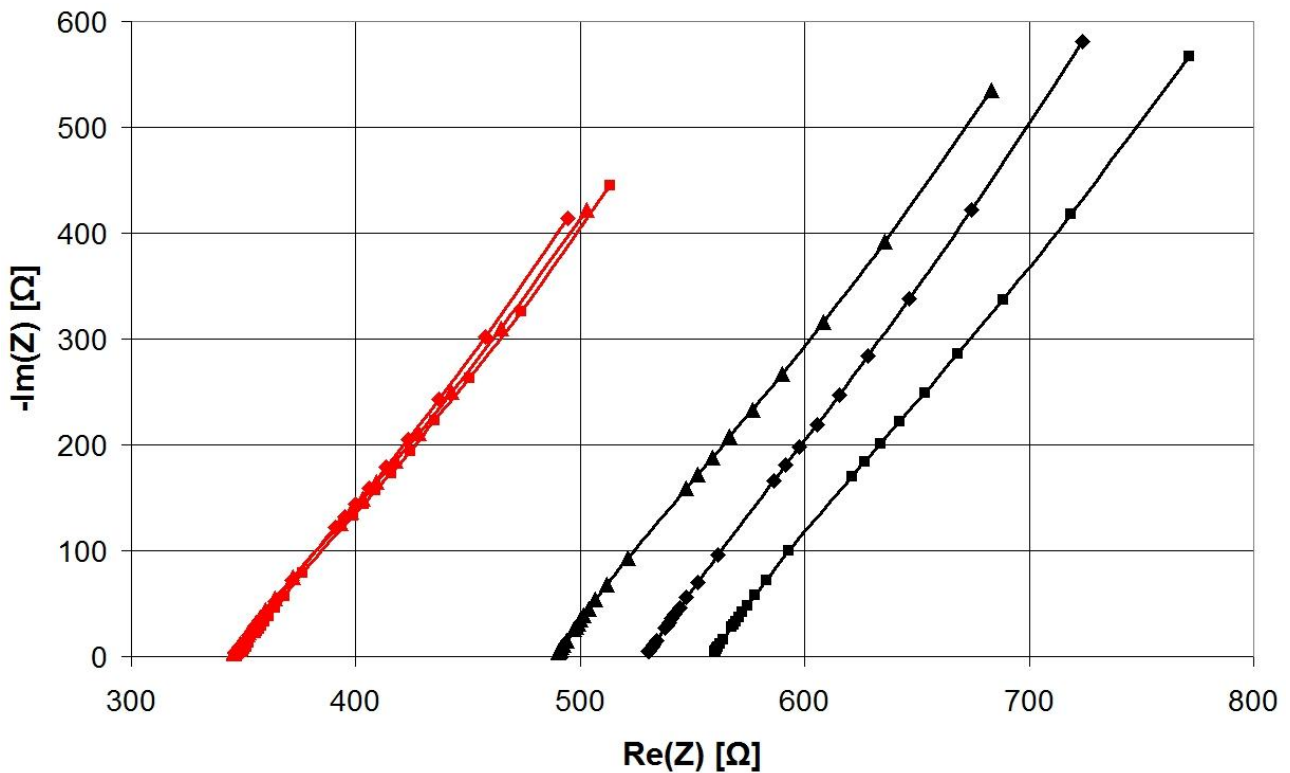
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554 The results from Fig. S1 clearly indicates that the electrical model featuring a resistance (R_m) and a
555 CPE (Q) in series is adequate for frequencies up to 400 kHz. For higher frequencies a deviation
556 from the model occurs. The real component of the impedance $\text{Re}(Z)$ was almost the same at 10
557 kHz and 2 MHz (differences lower than 0.2%). Repeated measures on the same ice-cream mix (# 2)
558 were carried out to test the repeatability of the measures. The results show that $\text{Re}(Z)$ results in
559 comparable repeatability at 10 kHz and 2 MHz (with a ratio of standard deviation to mean value σ/μ
560 of 0.03), while the imaginary component $\text{Im}(Z)$ resulted in higher dispersion at higher frequency
561 (with a σ/μ value of 0.19 at 2 MHz almost twice than at 10 kHz). The higher dispersion at higher
562 frequencies can be related to some parasitic effects in the sensor that have to be further

563 investigated. Since the less repeatability of the measures and the fact that, from preliminary
 564 measurements, data on the extended frequency range don't provide further informations, the
 565 investigated frequencies in the paper has been limited to the range 20 Hz to 10 kHz.
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568 **3. Measurements at 4 °C and 35 °C: results comparison**

569 Mix # 2 from Table 1 in the paper has been analyzed in triplicate using EIS with a sinusoidal test
 570 voltage of amplitude 100 mV and frequency range from 20 Hz to 10 kHz with both sensors. In Fig.
 571 S2 the Nyquist plot is shown for the three measures at both temperatures of 4 °C and 35 °C for
 572 sensor A. Measures at 4 °C resulted in less repeatability than 35 °C. This can be related to the fact
 573 that at 4 °C the ice-cream mixes are in a semi viscous frozen state and also small temperature
 574 variations can produce relatively large changes in the product structure.
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 578 **Fig. S2** Nyquist plot in the frequency range 20 Hz to 10 kHz for mix # 2 (measures in triplicate) and
 579 sensor A at two different incubation temperatures: 4 °C and 35 °C.
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581 Statistical analysis has been carried out and mean value μ as well as the ratio of standard deviation
 582 to mean value σ/μ have been calculated for both sensors and temperatures. The results are
 583 presented in the following table.
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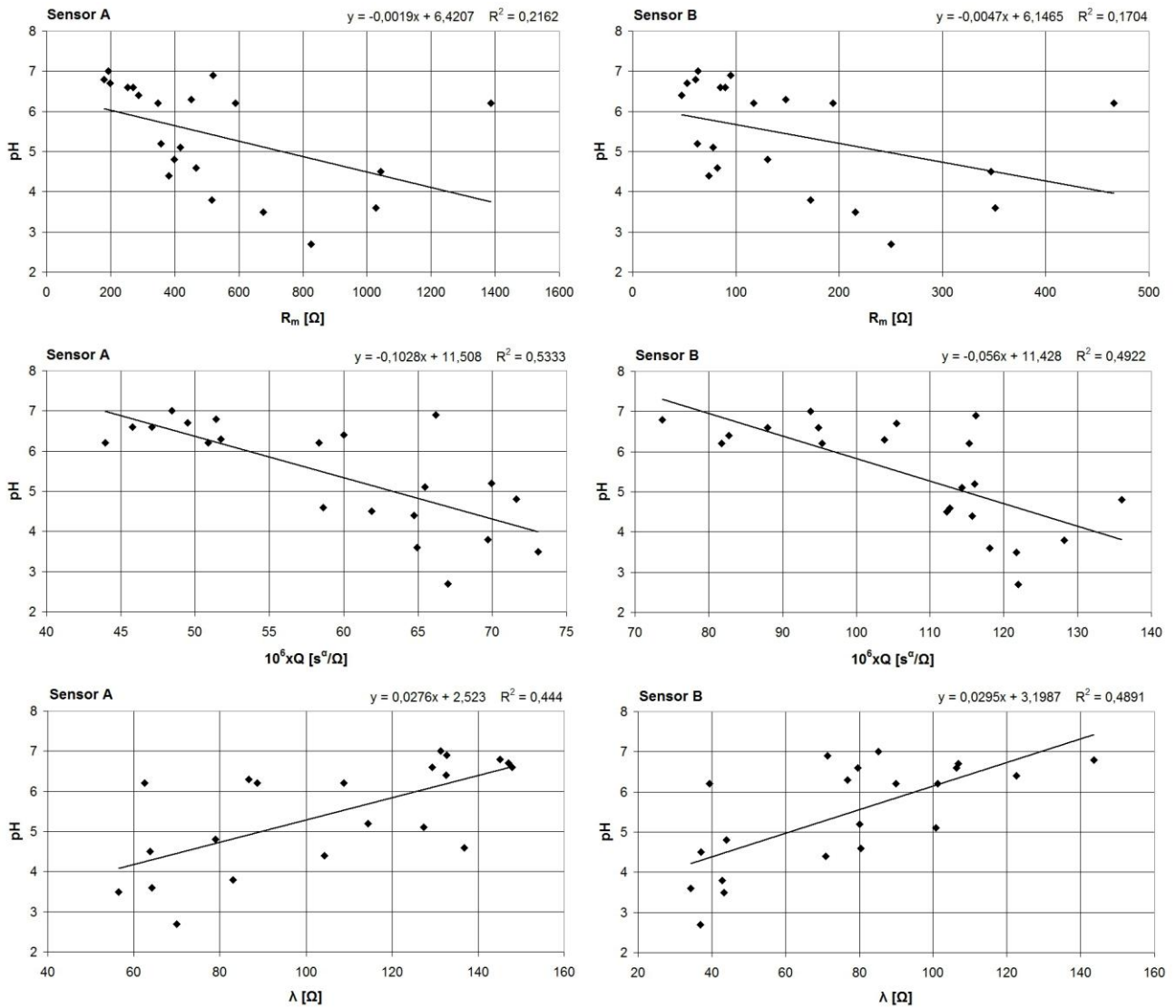
		SENSOR A		SENSOR B	
		T = 4 °C	T = 35 °C	T = 4 °C	T = 35 °C
R_m	μ [Ω]	524.7	345.5	186	116.7
	σ/μ	0.066	0.005	0.055	0.005
Q	μ [$10^6 s^{\alpha}/\Omega$]	38.7	52.7	71.3	86.7
	σ/μ	0.08	0.03	0.18	0.09

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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.



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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.

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