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Characterization of a carbon nanotube polymer composite sensor for an impedimetric electronic tongue

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Abstract. In a previous report on a multicomponent sensor array for electronic tongues, carbon nanotube (CNT) composite sensors were identified as the most reproducible and sensitive. To further elucidate the response mechanisms and optimize the working parameters of CNT composite sensors, we focused on a single polymer CNT combination and tested its response to the 5 tastes in a variety of measurement modes. The results demonstrate that an acquisition frequency of 200 Hz is the most suitable in terms of concentration discrimination, and that this sensor was extremely sensitive to all tastes except sweet, indicating that the recognition is based on charge interactions between the sensor matrix and the analyte.

Keywords: Carbon nanotube composite sensor; impedimetric electronic tongue; taste discrimination

Electronic tongues are now coming to the forefront having been shown to be more robust and reproducible than their e-nose counterparts. One of the main problems with e-noses is that of humidity as a major source of interference. By their very nature, of being immersed in water, e-tongues do not have this problem. Several different types of sensors for e-tongues have been proposed, the most common of these are based on either polymeric or lipid bilayer membranes on associated voltammetric electrodes [1, 2]. Some authors [3] have used conducting polymer sensors while certain groups have employed ISFETs [4]. Sensors based on carbon nanotube (CNT)/polymer composites have been shown to have excellent sensitivity and reproducibility in e-tongue sensors [5]. Carbon nanotubes are in fact noted for their ability to interact with several classes of organic molecules and gases through charge transfer mechanisms, which in turn can induce electrical variations within the sensing matrix [6, 7]. One of the major problems of CNTs is their tendency to aggregate, thus rendering processibility and fabrication of CNT based devices rather difficult. A dual solvent approach can be used to obtain CNT polymer composites with a uniform dispersion of CNT within a polymer matrix, which can be deposited on electrodes or membranes using a plotter or dispenser. Recently, we showed that a multicomponent composite array with a CNT/polymer sensor, a conducting polymer sensor and a carbon black/polymer composite sensor based on impedimetric measurements could be used to identify the 5 different tastes: bitter, sweet, salty, umami and sour [8].

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Following the analysis of data obtained from an intensive and randomized testing scheme consisting of over 500 measurements, a ranking order was given to the sensors according to their performance in terms of solution discrimination, reproducibility and sensitivity to concentration. Of all the sensors used, the CNT based sensor showed the best performance. In this work the objective was thus to optimize a composite CNT/polymer sensor in terms of the quantity of CNT and to standardize an impedimetric measurement protocol using appropriate frequencies. The sensor was tested with five compounds with different chemical characteristics (a carbohydrate, two salts, a weak organic acid and an aminoacid) able to elicit different kinds of gustative perceptions (glucose, sodium dehydrocholate, sodium chloride, citric acid and glutamic acid) representing the 5 classic tastes. For each compound, 3 measurements of impedance were carried out at 3 different frequencies (100, 150 and 200 Hz) and at 10 concentration levels of each solution comprising the human sensitivity range to evaluate the discrimination capability of the sensors.

Experimental methods

Sensor fabrication

A 0.2 g mL^{-1} solution of polycaprolactone (PCL, Sigma, www.sigmaaldrich.com, molecular mass 65000) in chloroform was prepared. The polymer was chosen at this particular concentration because it has excellent viscous properties which enable it to be processed using a variety of microfabrication techniques [9]. Multiwalled CNTs (kindly supplied by Prof. Ciardelli, Department of Chemistry, Pisa) in 3 concentrations, 24, 30 and 36 mg mL^{-1} were dispersed in benzene using a pulsed sonicator. The sensor support substrates were alumina plates containing two vacuum evaporated gold electrodes 1 mm wide, 15 mm long. A 400 μm inner gap of 5 mm in length at one end formed a sensing zone for impedance measurements. The substrates were cleaned in acetone prior to use. When the substrates were ready for deposition of the CNT/polymer composite, the PCL solution was mixed with the CNT suspension in a 1:1 ratio using pulsed sonication for 1 min. The 3 solutions thus had a final PCL concentration of 0.1 g mL^{-1} and 12, 15 and 18 mg mL^{-1}, respectively of CNTs. Ten microlitre of each solution was dispensed onto a substrate ensuring that the drop covered the sensing zone completely. The sensors were then dried in air for a week, while the resistance across the electrodes was measured daily. Prior to the taste testing sessions, the bare sensor electrodes were coated with a transparent polyurethane resin (RS195–984, RS Components Ltd, www.rs-components.com) to ensure that the impedance of water across the electrodes did not interfere with the impedance of the sensing zone. The resin effectively insulates and isolates the gold electrodes from the solution, so that the impedance measured is due only to the CNT/polymer composite and not to the impedance of the solution. This effect was cross checked by using a control sensor with a bare sensing zone, which was subject to the same measurement protocol. A sensor substrate with a CNT/polymer composite drop deposited on the sensing zone and the gold electrodes covered by the resin is shown in Fig. 1.

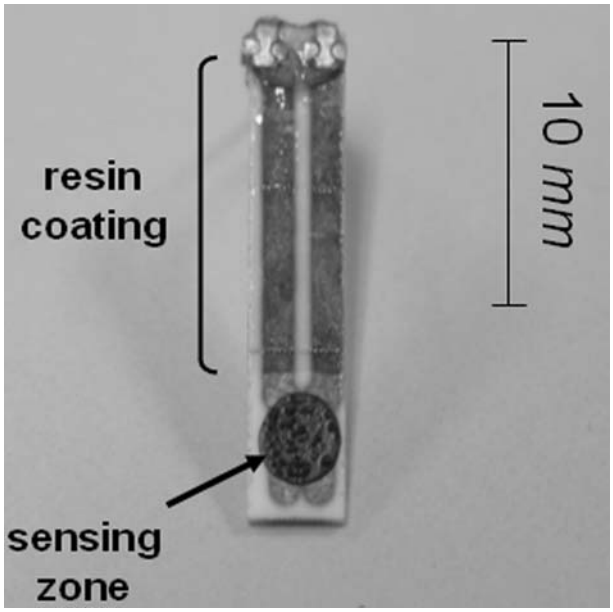

Fig. 1. A sensor showing the sensing zone where the CNT/polymer composite is deposited and the area covered by the resin

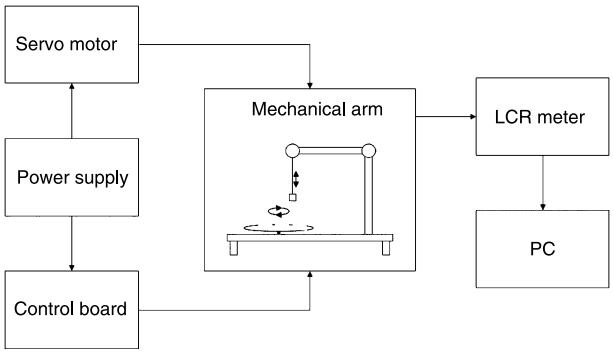

Fig. 2. A scheme of the experimental set-up

Experimental setup

The experimental set-up was realized by means of hardware and software modules (Fig. 2). The sensors were connected to an impedance meter (Agilent E4980A, www.agilent.com), and prior to performing the taste measurements, an impedance spectrum was acquired from 0 to 200 Hz with an input amplitude of 5 V and a DC offset of 0 V. In a recent paper [10] the charging process of a CNT/polymer matrix is described by considering the system to be an electrochemical capacitor charged and discharged by the diffusion of charged moieties through the matrix which form a double layer around the nanotubes. A simple RC lumped parameter system was used to model this behaviour. We therefore conducted measurements at low frequencies to limit capacitive coupling effects, which cannot be assessed using the experimental set-up described. Three frequencies in the range 100–200 Hz (100, 150 and 200 Hz) were chosen for the taste analyses, with a sampling rate of 0.7 Hz. A

Table 1. The ten concentration levels (expressed in mol L^{-1}) chosen for each of the five compounds

	Sour (Citric acid)	Bitter (Sodium dehydrocholate)	Sweet (Glucose)	Salty (Sodium chloride)	Umami (Glutamic acid)
C_1	0.0050	0.0001	0.0010	0.0010	0.0010
C_2	0.0162	0.0003	0.0032	0.0032	0.0032
C_3	0.0275	0.0006	0.0055	0.0055	0.0055
C_4	0.0388	0.0008	0.0076	0.0076	0.0076
C_5	0.0500	0.0010	0.0100	0.0100	0.0100
C_6	0.1400	0.0028	0.0280	0.0280	0.0200
C_7	0.2300	0.0046	0.0460	0.0460	0.0300
C_8	0.3200	0.0064	0.0640	0.0640	0.0400
C_9	0.4100	0.0082	0.0920	0.0820	0.0500
C_{10}	0.5000	0.0100	0.1000	0.1000	0.0600

software module was realized to communicate with the impedance meter, to acquire the data, and to store all the information into a centralized database. One servomotor was employed to enable the system to dip the sensors into six glass containers (one for each compound and one filled with distilled water). Since a vertical movement was obtained, the glass containers were placed over a rotating plate actuated by another servomotor. The servomotors were connected to a ASC-16 device to communicate with the PC using the RS-232 protocol. An automatic system was realized by means of a software module that performed the control of the mechanical platform and the storage of the timing information into the database. A single automatic session consisted in applying the measurement protocol over the 5 compounds at a fixed concentration level, with 3 repeated measurements. In order to perform the analysis over different concentration levels, 10 sessions were carried out.

Measurement protocol

The electrical impedance of the sensor array was monitored at different frequencies: 100, 150 and 200 Hz. The data acquisition was performed with a data acquisition rate of 0.7 Hz. The following measurement protocol was adopted:

1. Start of data acquisition;
2. For each repeated measurement #m = 1,. . .,3;
3. For each solution #s = sour, bitter, sweet, salty, umami in random order;
4. Sensor in air (10 sec);
5. Sensor dipped in distilled water (10 sec);
6. Sensor in air (10 sec);
7. Sensor dipped into the s-th solution (10 sec);
8. Next #s;
9. Next #m;
10. Sensors in air, stop acquisition;

The classification capability of the device was tested on fifty solutions of the five compounds at ten concentration levels (Table 1) chosen so as to cover the human range of sensitivities.

Data analysis

The timing information belonging to the actuation of the mechanical platform was used to evaluate the data acquired from the impedance meter. For each measurement of each compound at each concentration level, the variation of impedance at the three frequencies was

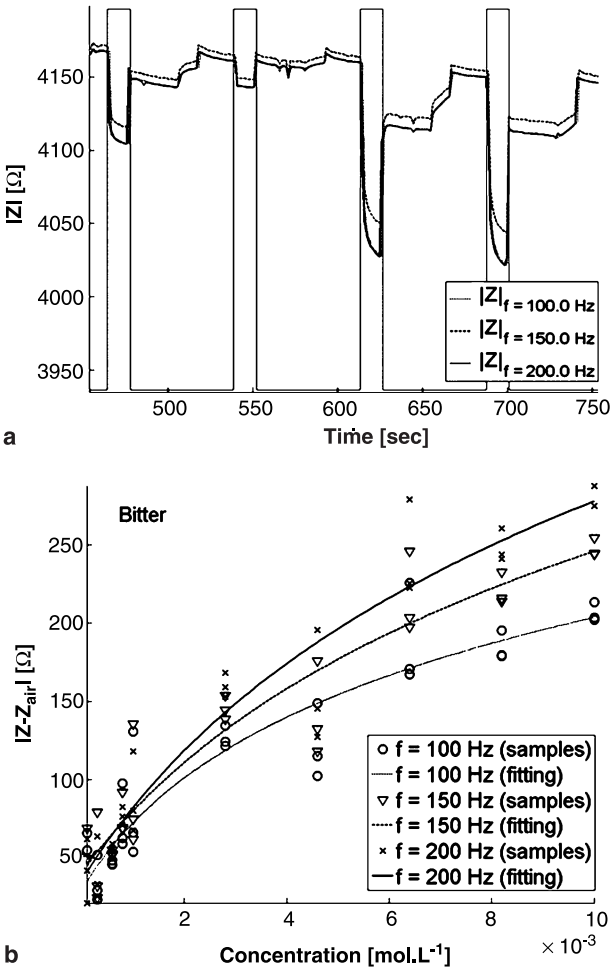

Fig. 3. a) Raw data belonging to the acquisition step. The impedance is acquired with a sampling rate of 0.7 Hz at three different frequencies. The rectangular wave represents the synchronization information supplied by the servomotor control process (high values represent the time interval of exposure of the sensor to the compound). b) The features and the fitting model plot of the bitter compound; the markers represent the values of $|Z(C) - Z_{air}(C)|$ obtained by the preprocessing step for each frequency

evaluated making use of two sets of data: the impedance of the sensors during the exposure to the air, and the impedance upon exposure to the compound (Fig. 3a). For each measurement the mean value of the first data set was used as a reference value (Z_{air}). The difference between the mean value of the second dataset (Z) and Z_{air} was used to characterize the sensors. A value of $Z_i = |Z - Z_{air}|$ was obtained for measurement. For each of the 5 tastes at 10 different concentrations, 3 repeated measurements were carried out at 3 different frequencies, therefore at the preprocessing step a total of 450 features (Z_i) were obtained (i.e. 30 features for each taste at a given acquisition frequency).

In order to assess the sensor response characterization, a fitting procedure was then carried out. A logarithmic equation was format to be the most suitable among those assessed (exponential, polynomial and logarithmic):

$$\hat{Z}(C) = Z_0 + A \cdot \log\left(1 + \frac{C - C_0}{\tau}\right)$$

where

- C is the concentration level expressed in $\mathrm{mol\,L^{-1}}$
- $Z_0[\Omega]$, $A[\Omega]$, $C_0[\mathrm{mol\,L^{-1}}]$, and $\tau[\mathrm{mol\,L^{-1}}]$ are the fitting parameters

The fitting error was evaluated according to the following formula:

$$E = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{\hat{Z}_i - Z_i}{Z_i}\right)^2$$

Results and discussion

Of the 3 CNT concentrations used, only the middle concentration of $30\,\mathrm{mg\,mL^{-1}}$ ($15\,\mathrm{mg\,mL^{-1}}$ in the final suspension) was found to be suitable for subsequent impedance measurements. The lowest concentration had very high resistance values in air ($>1\,\mathrm{M\Omega}$). In this case, the sensitivity of the sensor is limited, particularly in ionic solutions, because water short-circuits the sensor. The highest CNT concentration was found to have an extremely low resistance in air ($<0.1\,\mathrm{k\Omega}$), which resulted in very small DC impedance changes when immersed in solution. For each taste the equation parameters were estimated for each of the three frequencies. They are summarized in Table 2, where the fitting error is reported in the last column.

The logarithmic fitting equation has an acceptable fitting error for the bitter, salty and sour compounds, as shown in Figs. 3a, b, 4a, b and Table 2. The data show that sodium chloride and citric acid are easily recognized and distinguishable even at the lowest concentrations.

Glutamic acid and sodium dehydrocholate have acceptable errors too, of the order of a few %, with 200 Hz giving rise to the lowest errors for these two compounds (see Table 1).

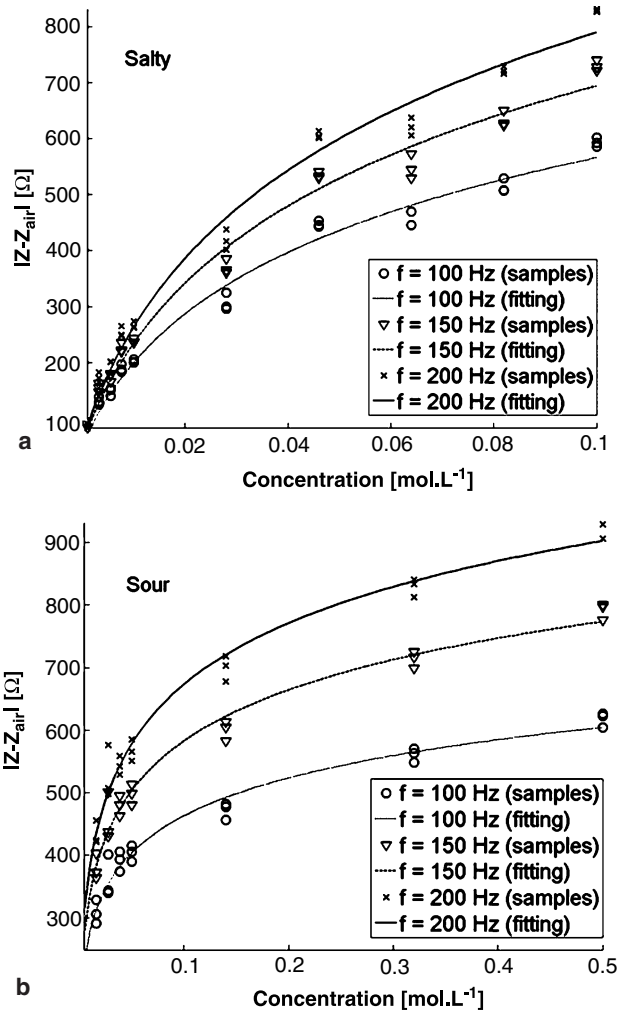

Fig. 4. a) The features and the fitting model plot of the salty compounds. b) The features and the fitting model plot of the sour compound; the markers represent the values of $|Z(C) - Z_{air}(C)|$ obtained by the preprocessing step for each frequency

The data for glucose and umami are reported in Figs. 5 and 6. The CNT/polymer sensor does not appear to interact specifically with the sweet compound at low concentrations, as the impedance only changes at very high concentrations. Glucose also had a large fitting error confirming that the sensor was unable to adequately distinguish this compound at all frequencies for the concentrations reported in Table 1. A linear relation between impedance and concentration was found with respect to the umami taste (Fig. 6), therefore the sensor can interact with this compound and distinguish between different concentrations. Although the logarithmic equation used was quite arbitrary, there is a good correlation between the fitting error and the ability of the sensors to distinguish and discriminate substances and concentrations.

Table 2. Estimate fitting parameters of the model $\hat{Z}(C) = Z_0 + A \cdot \log\left(1 + \frac{C-C_0}{\tau}\right)$ for each taste at three impedance acquisition frequencies. The fitting errors belonging to the sweet compound have the highest values

	Frequency [Hz]	Z_0 [Ω]	A [Ω]	τ [mol L^{-1}]	C_0 [mol L^{-1}]	Fitting error
Bitter	100	0.00010	35.04000	0.01148	598.37348	0.02885
(Sodium	150	0.00010	45.27667	0.00690	301.95191	0.01601
dehydrocholate)	200	0.00010	41.14000	0.00584	300.92977	0.01439
Sweet	100	0.00100	54.27000	0.00010	0.07921	0.20727
(Glucose)	150	0.00100	57.88333	0.00013	0.13231	0.24496
	200	0.00100	62.17333	0.00014	0.15479	0.26289
Umami	100	0.00100	49.52667	0.00029	0.47317	0.03183
(Glutamic acid)	150	0.00100	58.54667	0.00021	0.36164	0.01779
	200	0.00100	70.12000	0.00020	0.34918	0.01542
Salty	100	0.00100	70.82333	0.00466	91.66490	0.00535
(Sodium chloride)	150	0.00100	80.63333	0.00362	82.84434	0.00635
	200	0.00100	87.91333	0.00315	82.12631	0.00683
Sour	100	0.00500	231.25333	0.01122	131.46213	0.00044
(Citric acid)	150	0.00500	279.62667	0.00829	119.48229	0.00050
	200	0.00500	315.76667	0.00689	113.04874	0.00058

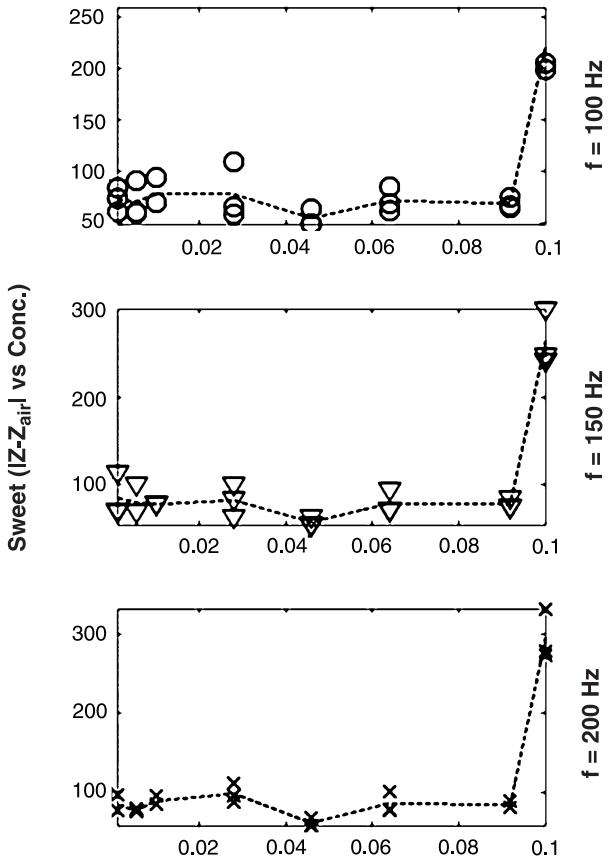

Fig. 5. Sweet (concentrations expressed in mol L^{-1})

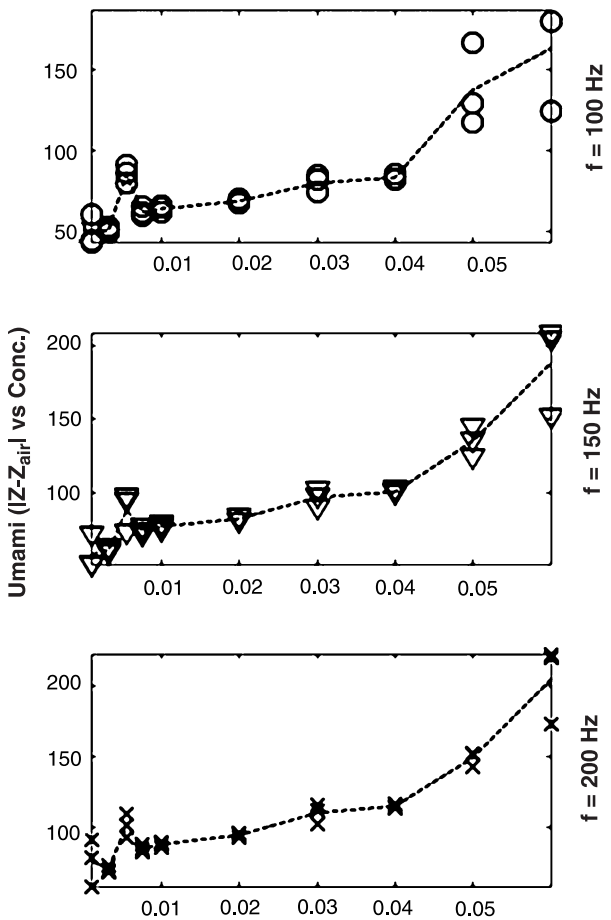

Fig. 6. Umami (concentrations expressed in mol L^{-1})

For the sake of comparison, the response of the control sensor with bare electrodes is also shown in Fig. 7. High values of the rectangular wave indicate exposure to the compounds, while low values indicate the exposure to the air. The values of the impedance over time measured during multiple measurements at the three different frequencies (100, 150 and 200 Hz) show a noisy response with high impedance values ($\sim 10^7$ Ω).

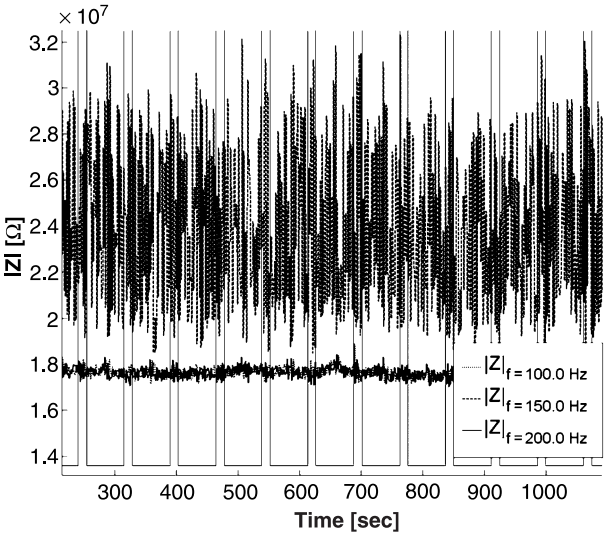

Fig. 7. The blank sensor response

The bare sensor has a flat response for all compounds, with little or no change in impedance with concentration. On the other hand, the CNT/polymer sensor shows significant variation both with compound as well as concentration, which is evidence for electrically dominated interactions between polarized or charged analytes and the matrix. It has been proposed that an electrical double layer can be formed around nanotubes immersed in a porous matrix permeated by an electrolyte [11]. The accumulation of charge depends, amongst other parameters, on the nature of the electrolyte and the applied potential. The sensing mechanism is therefore likely to be based on the diffusion of ions through the CNT/polymer and their interactions with the outer surface of the nanotubes. This would also explain the sensor's insensitivity to glucose, since this molecule is not charged.

Conclusion

The electrical impedance of a CNT-PCL composite sensor was measured by means of an impedance meter at three different frequencies ranging from 100 to 200 Hz. Although sensors were fabricated using a range of CNT concentrations, only one concentration (15 mg mL^{-1}) was found to be suitable for impedance measurements in liquids. The experimental set-up was designed in order to allow the automatic selection of a test solution and dipping of the sensor following a dedicated measurement protocol. Measurements were carried out on 50 different solutions eliciting 5 different tastes (sodium chloride, citric acid, glucose, glutamic acid and sodium dehydrocholate for salty, sour, sweet, umami and bitter, respectively) at 10 concentration levels comprising the human perceptive range. Regarding the bitter, salty and sour tastes, the data fitting analysis revealed a fairly good degree of association between the sensor response and the concentration level of each taste. The optimum measurement frequency was seen to be 200 Hz, since it resulted in the lowest fitting errors between the data and an empirical fitting model. While good and reproducible results were obtained also for umami, the sensor's exposure to the sweet compound provided a significant response only at high concentration levels. These results reflect those previously presented by the authors and indicate that in order to be able to better identify the taste ''sweet'', a sugar sensitive impedimetric sensor remains to be developed.

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