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Supporting Information

Paper based electronic tongue – A low-cost solution for the distinction of sugar type and apple juice brand

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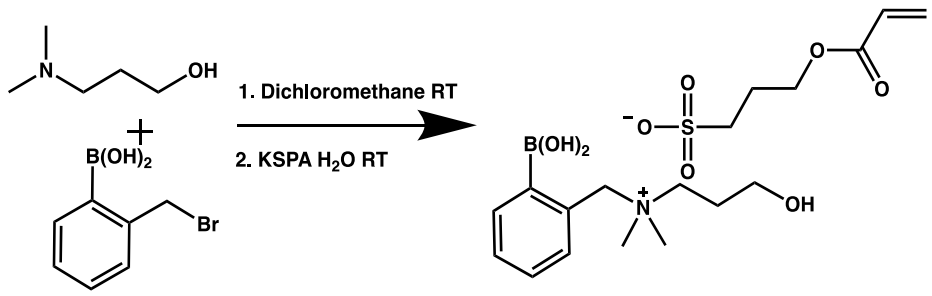
1. Materials and methods

2-(bromomethyl)phenylboronic acid, 3-Dimethylamino-1-propanol, potassium 3-sulfopropyl acrylate (KSPA), polyethylene glycol diacrylate (M_w ~ 320, 100 ppm MEHQ as inhibitor) (PEG256), N,N'-Methylenebis(acrylamide) (MBIS), 2-Hydroxy-2-methyl-propiophenone 97% (HMPP), ethanol (Chromasolv®, HPLC grade, ≥99.8%), dichloromethane, were purchased from Sigma Aldrich® and used as received. Deionized water (18.2 MΩ·cm^{-1}) (DI water) was purified using a Merck Millipore Milli-Q Water Purification System. Mass Spectrometry analysis was performed in Trinity College Dublin by Dr. Gary Hessman, using a Bruker micrOTOF-Q III spectrometer interfaced with a direct insertion probe, in Atmospheric-Pressure Chemical Ionization (APCI) mode. Masses were recorded over a range of 100-1600 m/z. ^{1}H (600 MHz), ^{13}C (150 MHz) and ^{11}B NMR (192 MHz) studies were carried out on a Bruker Avance Ultrashield 600 MHz NMR spectrometer.

2. Synthesis of N-(2-boronobenzyl)-3-hydroxy-N,N-dimethylpropan-1-ammonium 3-(acryloyloxy)-propane-1-sulfonate (DMA-PBA)



2-(bromomethyl)phenylboronic acid (1 g, 4.65 mmol) was dissolved in dichloromethane (50 mL). To this, 3-dimethylamino-1-propanol (2 mL) was added drop wise and the solution stirred overnight (18h). The solvent was then removed in vacuo. The metathesis reaction to form the polymerisable ionic liquid was then carried out following a modified procedure from Tudor et

al.[1] by dissolving the resulting oil in deionised water (25 mL) and adding potassium 3-sulfopropyl acrylate (1.14 g, 5 mmol). The reaction mixture was then stirred for 24h at room temperature. After this time, the solvent was removed by evaporation. The product was dissolved in absolute ethanol, and the solvent evaporated using on a rotary evaporator. The product was dried under vacuum on a high vacuum line and was collected as a thick, viscous oil.

^{1}H NMR (600 MHz, 20 °C, D_2O), δ: 7.60 (1H, *t, J=6 Hz*), 7.43 (3H, *m*), 6.29 (1H, *dd*), 6.08 (1H, *d*), 5.82 (1H, d), 4.62 (2H, *s*), 4.14 (2H, *m*), 3.67 (2H, m), 3.08 (2H, m)2.94 (2H, *m*), 2.85 (6H, *s*), 2.0 (4H) ppm.

^{13}C NMR (150 MHz, 20 °C, D_2O), δ: 215.3 (1C), 168.5 (2C), 134.4 (2C), 133.8 (1C), 132.3 (2C), 130.1 (1C), 127.5 (1C), 126.4 (1C), 67.3 (1C), 63.5 (1C), 62.6 (1C), 47.7 (2C), 23.6 (2C) ppm.

^{11}B NMR (192 MHz, 20 °C, D_2O), δ: 29.03 (1B, $B(OH)_2$) ppm.

APCI-MS (m/z) (positive mode) for cation $C_{12}H_{21}BNO_3^+$ calculated: 238.16145 found: 238.161132; (negative mode) for anion $C_6H_9O_5S^-$ calculated 193.01762 found: 193.017852

3. Sugar sensing mechanism

Figure S1 shows the electrical responses of the hydrogel before and after sugar addition. The electric field was applied between the electrodes modifying the dielectric properties of the hydrogel and consequently the capacitance and impedance between the electrodes. In Figure S1 (A) the capacitance was measured in the case of the hydrogel hydrated with buffer only. Upon sugar addition an increase in the capacitance value is observed, as depicted in Figure S1 (B), which corresponds proportionally to the binding of diols to the phenyl boronic species, resulting in the formation of cyclic boronate esters and swelling of the hydrogel. The increase in the volume of hydrogel results in a change in dielectric properties and permeability of ions by diffusion, increasing the current passage that can be measured via impedance spectroscopy. Electrical impedance spectroscopy measurements were performed using a Solartron 1260 impedance analyzer. The impedance spectrum was acquired by applying 20 mV across the interdigitated electrodes in a frequency range from 0.1 to 10 MHz with 5 points per decade. Additional information regarding the sensing mechanism can be found in the work of Daikuzono

et al.[2] in which hydrogel modified paper-based electrodes have been used for monosaccharides detection.

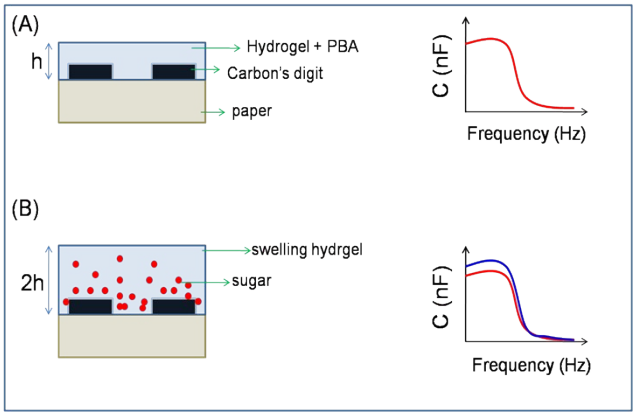


Figure S1. Diagram showing the capacitance response of the hydrogel before and after sugar addition.

4. Capacitance measurements and IDMAP plots

The changes in the capacitance spectra of bare electrodes caused by deposition of such hydrogels are small for pure water and PBS, as shown in Figures S2(A) and S2(B). The largest change in capacitance was observed for the DMA-PBA hydrogel-modified electrode, in both water and PBS.

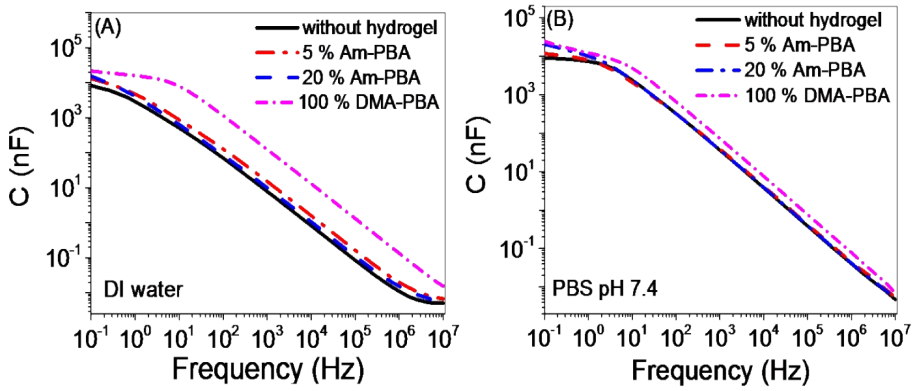


Figure S2. Capacitance spectra for sensing units modified with 5% Am-PBA,20% Am-PBA and 100% DMA-PBA and bare electrode (without hydrogel) in (A) deionized water and (B) PBS solution (pH 7.4).

The interdigitated electrodes coated with 100% DMA-PBA were immersed in different types of sugar solution (fructose, glucose and sucrose); the change in capacitance is greatest in the presence of fructose (Figure S3). However, when exposed to a mixture of sugars, the 100% DMA-PBA was ineffective at differentiating between relative sugar concentrations (Figure S4).

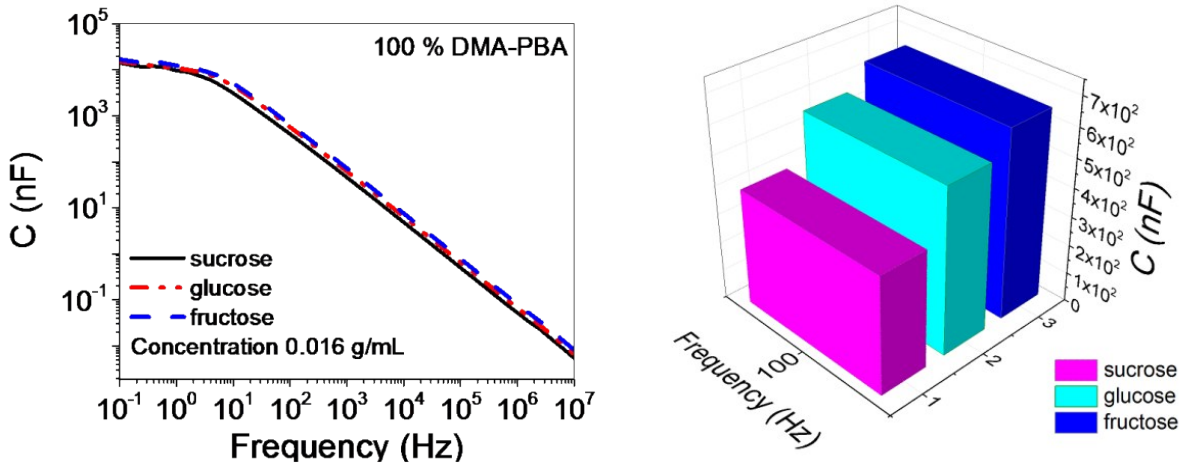


Figure S3. (A) Capacitance spectra for sucrose, glucose and fructose at 0.016 g.mL^{-1}for an electrode coated with 100% DMA-PBA; (B) 3D plot of capacitance at 100 Hz for the 3 types of sugar.

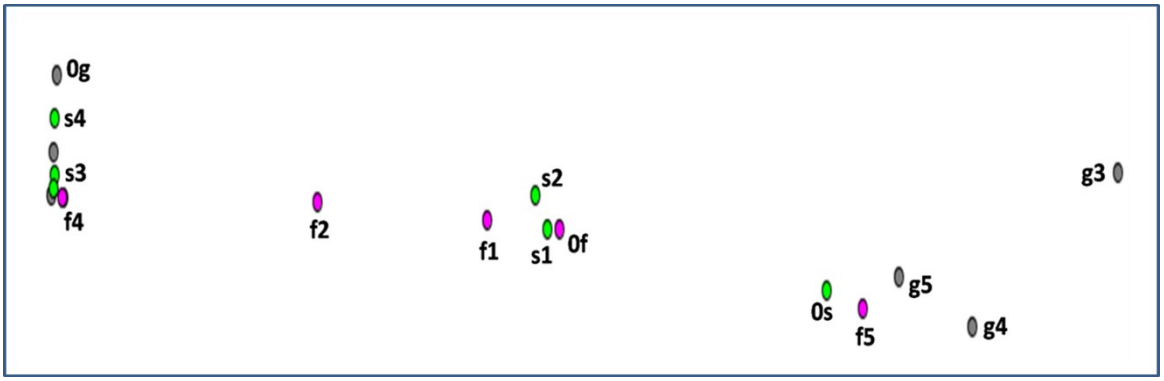


Figure S4. IDMAP plot for the capacitance data taken with only the 100% DMA-PBA-coated electrode for different concentrations of the sugars at 1 kHz.

Figure S5 shows that even though standard solutions of sucrose, fructose, and glucose could be separated from each other and the PBS sample, it was not possible to differentiate different concentrations of the same sugar.

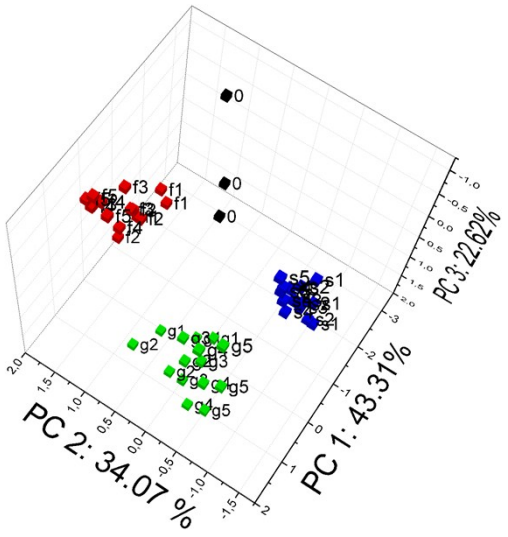


Figure S5. 3D PCA plot for different standard concentrations of fructose (red square), glucose (green square), sucrose (blue square) and PBS buffer (black square) analyzed by 3 e-tongues. For each sugar measurement a new buffer solution was used, which explains why the black squares are not close to each other.

However, using IDMAP, which is normally more effective in correctly clustering very similar samples, this distinguishing ability can be observed when the data for each sugar is plotted separately, in Figures S6-S8.

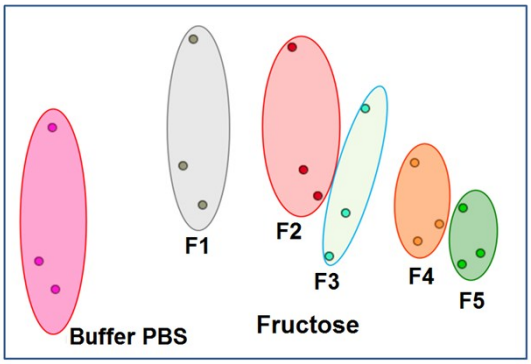


Figure S6. IDMAP plot for different concentrations of fructose and PBS buffer, obtained with 3 different e-tongues.

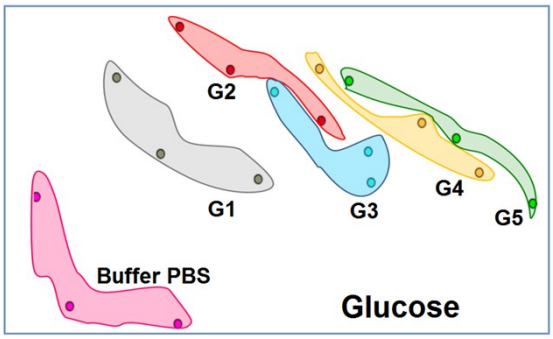


Figure S7. IDMAP plot for different concentrations of glucose and PBS buffer, obtained with 3 individual e-tongues.

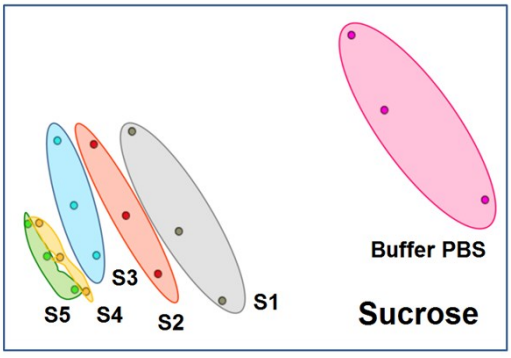


Figure S8. IDMAP plot for different concentrations of sucrose and PBS buffer, obtained with 3 distinct e-tongues.

The e-tongue was applied in the analysis of different apple juice brands. As in the measurements with the sugar samples, the electrode coated with 100% DMA-PBA hydrogel was the most important contributor in distinguishing the apple juices, as illustrated in Figure S9.

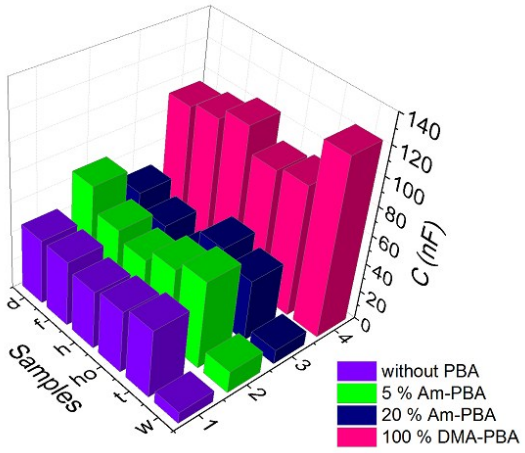


Figure S9. Capacitance at 1 kHz measured with the four sensing units for the 6 brands of apple juice.

The PCA plot in Figure S10 indicates that distinction of the 6 brands of juice is still possible in a second measurement with a sensor array, but the information contained in the first component is reduced from 94.6 % to 44.15 % of the variance, thus indicating a loss in performance. The same applied when IDMAP was used to treat the data in Figure S10, where the juices could still be distinguished from each other upon a second measurement, but the clear correlation with sugar content in the juices was lost. Therefore, the sensing units are suitable for single use only.

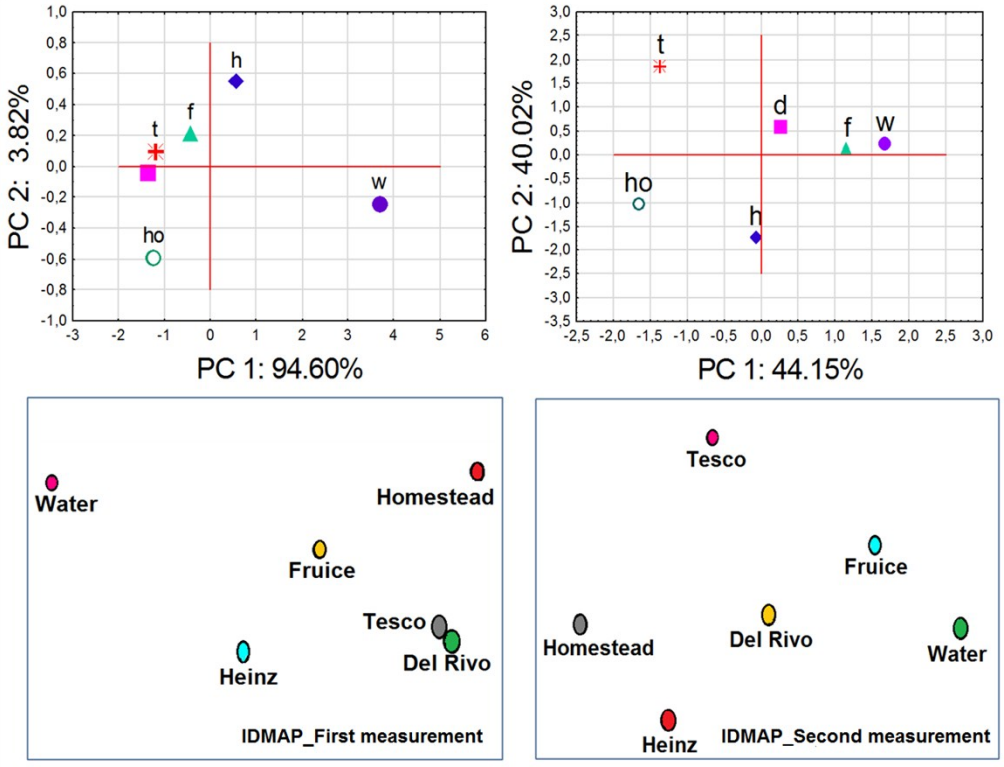


Figure S10. PCA (top) and IDMAP (bottom) plots for the capacitance at 1 kHz using the same set of sensing units of an e-tongue for apple juice samples, with the first and second measurements being shown on the left and right-hand sides, respectively.

References

1. Tudor, A., Florea, L., Gallagher, S., Burns, J., Diamond, D. Poly(Ionic Liquid) Semi-Interpenetrating Network Multi-Responsive Hydrogels, Sensors. 2016, vol 16.

2. Daikuzono, C.M., Delaney,C., Tesfay,H., florae, L., Oliveira, O.N., Morrin,A. and Diamond, D. Impedance spectroscopy for monosaccharides detection using responsive hydrogel modified paper-based electrodes, Analyst. 2017, 142, 1133.