

FUNCTIONALIZATION-FREE MICROFLUIDIC ELECTRONIC TONGUE BASED ON A SINGLE RESPONSE

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Abstract: *The electronic tongues (e-tongues) are promising screening analysis platforms for applications in the industries and academy. As key limitations, the current e-tongues involve subsequent surface modifications and analyses to each one of the diverse sensing units. In addition, the recalibration of the system is usually necessary when sensing units are replaced. These aspects undermine the simplicity and velocity of the method. Herein, we introduce a microfluidic e-tongue that overcomes all such limitations. The key principle of global selectivity of the e-tongue was achieved by recording only a single response, namely, the equivalent admittance spectrum of an association of resistors in parallel. Such resistors consisted of non-functionalized stainless steel microwires (sensing units), which were short-circuited and coated with different films. Such wires were inserted in a chip composed of a single piece of polydimethylsiloxane (PDMS). Using impedance spectroscopy, the e-tongue was successfully applied in the classification of basic tastes and diverse chemicals used in oil industry. Our device may envisage the widespread dissemination of e-tongues with fast, reproducible, and robust data.*

Keywords: Screening analysis; Impedance; PDMS; Thin film; PCA.

Introduction: the electronic tongues (e-tongues) are composed of an array of sensing units, which statistically encodes diversified multivariate signals in distinct fingerprints in accordance with the types of samples. Such device relies on the concepts of global selectivity and cross-sensitivity, with sensors highly sensitive to several compounds in a sample without specific interaction. The e-tongues assure rapid tests including qualitative, semi-quantitative, and quantitative assays. In this regard, such platforms have emerged as promising methods toward different applications by addressing the challenges of continuous and accurate quality control.^{1,2} Compared with potentiometry and voltammetry, the electrical impedance spectroscopy displays advantages, namely, neither the analytes nor the sensing units need to be electroactive, the experimental set up is quite simple requiring just one or two polarizable electrodes without the use of a reference electrode, and the signal takes into account effects of all the mass phenomena. Hence, the use of background electrolyte (in excess) to avoid migration is unnecessary. In addition, it is worthwhile to highlight downsides related to the cell potential stability are not observed once the reference electrode is not used. The impedance-based microfluidic e-tongues reported in literature are based on interdigitated Au electrodes functionalized with different polymeric coatings. This functionalization is necessary because the signal must be diversified enough to assure the discrimination of different sample classes as well as quantitative assays. As limitations, these devices require subsequent surface modifications and measurements to each one of the diverse sensing units. In addition, the recalibration is usually needed when sensing units have to be replaced by a new one. It is imperative a screening platform exhibits high analysis velocity. Consequently, the aforesaid downsides critically undermine a more widespread use of the e-tongues in analytical chemistry field.

In this work, we address a new e-tongue that obviates all the limitations mentioned above. Our device assures the key principle of diversity in a single measurement regardless of the number of sensing units. This signal was associated with the equivalent real admittance spectrum of an association of resistors in parallel, which consisted of five wires in short-circuit. These wires were coated with different non-modified films (sensing units). Once this equivalent admittance depends on the admittance of each resistor, the single signal attained by our e-tongue comprised electrical transductions from all the sensing units. Thus, such signal was sufficiently diversified to get the classification of diverse samples by forming well-defined fingerprints. Additionally, the films that were used as sensing units (obtained by vapor phase deposition) show higher stability and reproducibility than the organic films that are usually applied in the e-tongues. Therefore, it is expected our device presents high inter-electrode precision as herein observed, eliminating the need of recalibrating the e-tongue when sensing units are replaced.

Experimental: the device (**Fig. 1(a,b)**) was obtained by the cleanroom-free, solventless, and bondless sequential steps of polymerization and scaffold removal (PSR) as shown in literature.³ The chip was composed of a single piece of polydimethylsiloxane (PDMS) with five parallel channels to insert the electrodes and one perpendicular channel on the top to pump the samples. The electrodes or sensing units relied on stainless steel wires (720- μm diameter and 10.0-cm length) coated with films of gold (Au), platinum (Pt), nickel (Ni), iron (Fe), and aluminum oxide (Al_2O_3) by electron beam vapor deposition. Such thin films were chosen by exhibiting distinct resistivities, thus providing different contributions to the single spectra of admittances. The gap between the electrodes was of

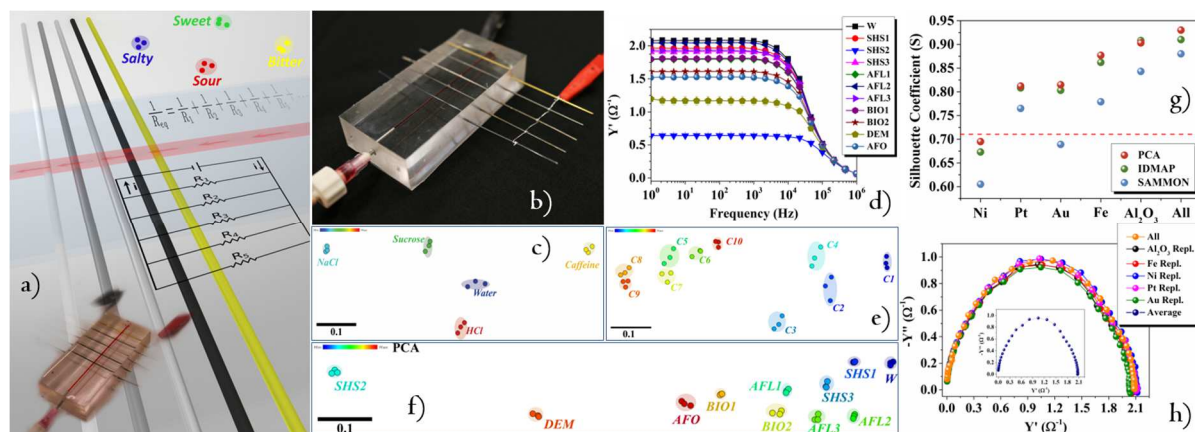


Fig. 1. Single response e-tongue. Image generically showing the concept of the method (a), chip with electrodes (b), PCA plot for the basic tastes (c), real admittance spectra for pure petrochemical species (d), PCA plots for these species (e,f), Silhouette coefficients calculated for all the arrays applied in this work to analyze the petrochemical compounds (g), and Nyquist plots recorded to evaluate the method reproducibility (h). In (e), the concentrations changed of 0.1% to 50.0% v/v. In (g), the dashed line in red is related to the minimum S for a strong classification. In (h), the average signal is shown in inset.

8.3 mm. Solutions were pumped into the chips with a syringe-pump at $1000.0 \mu\text{L h}^{-1}$. The real admittance of the whole wire surfaces was recorded at 25 mV ac and frequencies from 1 to 10^6 Hz. The admittances of the sensing units were analyzed by multivariate techniques (PCA, IDMAP, and SAMMON) to evaluate the classifications.

Results and discussion: the real admittances of the electrodes were calculated as $0.86 (\text{Al}_2\text{O}_3)$, $1.72 (\text{Pt})$, $2.08 (\text{Au})$, $2.14 (\text{Fe})$, and $2.34 \Omega^{-1} (\text{Ni})$ from Nyquist plots. In this case, deionized water was pumped into the chip. As a first proof-of-concept, the e-tongue was successfully applied in classification of basic tastes (Fig. 1(c)). Herein, aqueous media representing four basic tastes, namely, $100.0 \mu\text{mol L}^{-1}$ NaCl (salty), HCl (sour), caffeine (bitter), and sucrose (sweet) were tested. As quantitative analysis of the discrimination quality, the Silhouette coefficient (S; it changes of -1 to 1)² was 0.91, indicating a strong distinction of the different samples. Next, diverse species applied in oil industry were assessed. These compounds are applied as anti-fouling (AFL1, AFL2, and AFL3), scavengers of hydrogen sulfide (SHS1, SHS2, and SHS3), biocides (BIO1 and BIO2), demulsifier (DEM), and antifoam (AFO) in distinct oil processing stages. Satisfactory classifications were once again achieved (Fig. 1(d-f)) for pure (S of 0.93) and diluted compounds at diverse contents (S higher than 0.7). New tests were performed to assess if the single responses recorded by our e-tongue comprise the admittance changes from all the sensing units. For this purpose, analyses of pure petrochemical compounds were also conducted using microwires with the same resistance, i.e., the same coating film in short-circuit. Then, the values of S calculated for each case (Ni, Au, Pt, Fe, and Al_2O_3) were compared with the S recorded when integrating all the five films into the chip (Fig. 1(g)). The data confirmed this array with the different films provided the best discrimination, clearly suggesting the single admittance spectra obtained by our e-tongue incorporated contributions from all the electrodes. This aspect leads to diversified admittance spectra, explaining the strong distinctions of similar fingerprints provided by the single response e-tongue. Finally, Nyquist plots were also obtained to assess the e-tongue reproducibility (Fig. 1(h)). After the first measurement, each one of the five wires were subsequently replaced with new sensing units in the next assays. The average real admittance was $2.08 \Omega^{-1}$ with a confidence interval lower than $0.01 \Omega^{-1}$. Hence, the reproducibility was satisfactory eliminating the need of recalibrating the device if one sensing unit is replaced with another as expected. Currently, an e-tongue based on an association of capacitors in parallel (wires under and over the sample channel) have shown better sensitivity and classification ability than the device herein presented, which relies on an association of resistors in parallel. In addition, the possibility to use graphite pencil graduations as sensing units of our chip rather than the film-coated wires is being tested. Such graduations show distinct resistivities (data not shown) because they have different graphite/clay ratios.

Conclusion: to our knowledge, this is the first report of a single response e-tongue. Such unprecedented method may signify a breakthrough in the development of fast, simple, and reproducible e-tongues, contributing for a widespread dissemination of such platforms in academy and industry. One paper with the proof-of-concept data of our e-tongue was recently accepted for publication in ‘ACS Sensors’ (DOI: 10.1021/acssensors.7b00302).

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