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# Integrated, paper-based potentiometric electronic tongue for the analysis of beer and wine

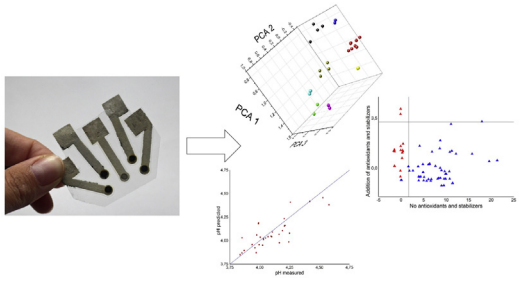
Emilia Witkowska Nery [a, b, *], Lauro T. Kubota [a, b]

[a] Department of Analytical Chemistry, Institute of Chemistry – UNICAMP, P.O. Box 6154, 13084-971 Campinas, SP, Brazil
[b] National Institute of Science and Technology in Bioanalytics, Institute of Chemistry – UNICAMP, P.O. Box 6154, Campinas, Brazil

## HIGHLIGHTS

- Novel paper-based electrochemical electronic tongue is proposed.
- Integrated paper-based device comprises of four ion-selective electrodes and a Ag/AgCl reference.
- Device is able to work with as low as 40 μL of sample.
- Measurements could be performed with a standard multimeter.
- Device allowed discrimination and analysis of 34 beer and 11 wine samples.

## GRAPHICAL ABSTRACT

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## ABSTRACT

The following manuscript details the stages of construction of a novel paper-based electronic tongue with an integrated Ag/AgCl reference, which can operate using a minimal amount of sample (40 μL). First, we optimized the fabrication procedure of silver electrodes, testing a set of different methodologies (electroless plating, use of silver nanoparticles and commercial silver paints). Later a novel, integrated electronic tongue system was assembled with the use of readily available materials such as paper, wax, lamination sheets, bleach etc. New system was thoroughly characterized and the ion-selective potentiometric sensors presented performance close to theoretical. An electronic tongue, composed of electrodes sensitive to sodium, calcium, ammonia and a cross-sensitive, anion-selective electrode was used to analyze 34 beer samples (12 types, 19 brands). This system was able to discriminate beers from different brands, and types, indicate presence of stabilizers and antioxidants, dyes or even unmalted cereals and carbohydrates added to the fermentation wort. Samples could be classified by type of fermentation (low, high) and system was able to predict pH and in part also alcohol content of tested beers. In the next step sample volume was minimalized by the use of paper sample pads and measurement in flow conditions. In order to test the impact of this advancement a four electrode system, with cross-sensitive (anion-selective, cation-selective, $Ca^{2+}/Mg^{2+}$, $K^{+}/Na^{+}$) electrodes was applied for the analysis of 11 types of wine (4 types of grapes, red/white, 3 countries). Proposed matrix was able to group wines produced from different varieties of grapes (Chardonnay, Americanas, Malbec, Merlot) using only 40 μL of sample. Apart from that, storage stability studies were performed using a multimeter, therefore showing that not only fabrication but also detection can be accomplished by means of off-the-shelf components. This manuscript not only describes new paper-based, potentiometric sensors but also

* Corresponding author. Present address: Institute of Physical Chemistry, Polish Academy of Sciences, 44/52. Kasprzaka street, 01-224 Warsaw, Poland.
*E-mail address:* ewitkowskanery@ichf.edu.pl (E.W. Nery).

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according to our knowledge is the first description of an electrochemical paper-based electronic tongue with integrated reference.



## 1. Introduction

The first systems mimicking the olfactory [1] and gustatory [2] organs were proposed in the 1980's. From that time the desire to model, replace and improve human olfactory and taste systems drove scientists to develop new sensor arrays for gaseous and liquid samples. Design of those devices resembles biological recognition systems in which arrays of non-specific sensors present in the tongue or nose are used to gather information. This complex data is later processed and analyzed in the brain which provides decision about the sample (recognition, identification or quantification). Instead of a brain, arrays of chemical sensors use methods of artificial intelligence and chemometry [3,4]. Applications of such systems include the food industry (quality control, optimization of bioreactors, control of aging and automated control of taste), the chemical industry (detection of functional groups, purity assessment), they are employed for medical use (clinical *in vivo* monitoring, non-invasive diagnostics, assessment of taste of pharmaceuticals, growth of cell cultures) and environmental monitoring [4–8]. More information about electronic tongue and electronic nose systems can be found in the literature e.g. Refs. [4,9–11].

This work focuses on ion-selective potentiometric sensors, of solid contact type with liquid PVC membranes. Membrane allows selective extraction of ions from the solution, generating potential dependent on the concentration of the extracted ion. In case of solid-contact electrodes, without internal solution, membrane is in a direct contact with metal. In general, sensors of this type show poor stability and rely on blocked charge transfer across the interface between a purely ionic conductor (membrane) and a purely electronic conductor. Short time measurements (dozens of minutes) are possible due to potential stabilization based on side reactions with species penetrating the polymer. Oxygen is an especially good depolarizer in this case, but other redox species also present this effect. Advantages of this kind of sensors as compared with those of traditional architecture, are the possibility of miniaturization and low fabrication cost [12,13].

Recently, as a result of search for simple, low cost, and disposable systems paper was rediscovered as a valuable substrate for electronic applications, sensors and microfluidic platforms. Growing interest in paper during last few years can be attributed to its unique structural and mechanical properties (lightness, flexibility, capillary action, high surface-to-volume ratio), natural origin (biodegradability), easiness of modification and availability all over the world. Paper as a substrate for sensors has already become a subject of few review articles [14–16].

Until today few systems were proposed employing paper in potentiometric analysis. In the first approach paper was used to maintain continuous liquid stream during the flow-injection measurements. Electrodes of classical architecture were placed against a slip of paper that would carry the liquid. First attempts of this type appeared in mid-1980's e.g. system for the analysis of chloride in tap water and sewage [17] and another employed for trace analysis of fluoride [18]. First fully paper-based potentiometric sensor was described by Novell et al. [19,20]. In this work electrodes were based on a carbon nanotube impregnated filter paper. Later Whitesides group proposed a paper-based sensor with borders printed with wax, and screen-printed Ag/AgCl electrodes stacked against a ion-selective membrane [21]. Until the time of writing the only electrochemical electronic tongue with electrodes based on paper was described by our group. This system included four paper-based sensors with electrodes drawn with a pencil and a miniaturized reference electrode of traditional architecture. It was applied for the discrimination of forged mineral water samples [22].

Sensors developed in the aforementioned work presented rather low sensitivity, thus in the later stage of development we substituted pencil graphite with silver. Electrodes were integrated into one device, and the miniaturized reference electrode of traditional architecture was substituted with a newly developed paper-based Ag/AgCl reference. This integrated system was applied for the discrimination and analysis of beer samples. In the next step efforts were made to minimize the sample volume, as previous measurements were done by dipping the sensor matrix in the sample. Approaches intended to minimize the sample volume included use of paper sample pads and measurements in flow conditions. Final device was applied to discriminate 11 types of wine.

Electronic tongue systems are often used for the classification of alcohols, to detect falsification, classify samples by their geographical origin or taste factors. Both beer and wine industries demonstrated considerable growth during the past few years. In the case of beer annual revenue reached 494.4 billion US$ in 2014 with market consumption of 176.4 billion liters of beer (The Beer: Global Industry Guide, May 2015). Beer is currently the third most consumed beverage in the world (1st water, 2nd tea), and the first considering alcoholic beverages. On the other hand the total revenue for wine in 2013 was equal 25.7 billion €, which is an increase as compared with previous years (Report of the International Organization of Vine and Wine for the 2014).

Beers are usually categorized by factors such as color, flavor, alcohol content, production or fermentation method, type and origin. Traditionally, according to the purity law, beer was produced by the brewing and fermentation of malted barley and hops. At present, partial substitution of barley with corn, rice or sugars is a common practice. Additives also include chemical stabilizers and antioxidants. A growing discontent of consumers was observed due to insufficient description of such practices on the label. Manufacturers are also interested in the investigation of basic attributes of beer, in order to obtain products with accordance to consumer preferences, especially when developing novel products such as low-alcohol beers etc. [23–26]. In the case of wines, chemical classification is often based on grape variety, geographical origin, style (red, white, rose), relative age and taste factors (e.g. astringency).

Electronic tongues applied for the analysis of beers and wines described until today are based mainly on potentiometric or voltammetric sensors. In case of beer they were able to discriminate different beer types (pilsner, lager, ale etc.) and brands and often could predict the alcoholic strength, extract, polyphenol content and bitterness as well as indicate inappropriate storage conditions [25–35]. Wines were already assessed in terms of vineyards and wineries, astringency, aging periods, total and volatile acidity, pH, ethanol, tartaric acid, sulfur dioxide, total polyphenols and glycerol content [36–39].