Electrochemical measurements on a droplet using gold microelectrodes

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Abstract. Facile methods of ion recognition are important for the fabrication of electronic tongue systems. In this work, we demonstrate performing pulsed conductometry on microliter electrolyte droplets dropped on gold microelectrodes vapor deposited on soda lime glass slides. A droplet is dropped between two microelectrodes when a voltage waveform from a preprogramed power supply is applied on them. The temporal variation of the electric current passing through the droplet is recorded, digitized and stored. The obtained data are compared with the database formed out of the previous experiences for the classification of the sample electrolytes. It is shown that the shape of the voltage waveform is the important parameter of the process. We devised a method for the optimization of the voltage waveform profile for obtaining the maximum of discriminating information from the recorded current variations.

1. Introduction

Electronic tongues are usually formed by arraying a number of miniaturized electrochemical cells [1-3] providing uncorrelated information on an electrolyte [4-8]. The drift of array components, particularly due to the electrochemical corrosion on the electrodes, affects the performance of the system and system responses shift away from the training-based calibrations [9-13]. Moreover, owing to the rapid advancement of the microfluidics, it has become important to develop analytical methods compatible with these techniques and can be performed on microliter volumes of the analyte electrolyte [9, 14].

In the standard conductometry, the conductance of an electrolyte is measured by measuring the electric current passing through it when an AC voltage is applied between two conductive electrodes immersed in the liquid [15-17]. The measurements are carried out at the steady state of the system. The results of these standard tests can hardly be used for the recognition of the ionic species responsible for the conduction. The data provided by the standard conductometry can only be utilized as measures of the overall concentration of a predetermined ionic substance. For identifying unknown ionic species in electrolytic solutions in the standard procedure, a complex combination of the conductometry data and other physicochemical phenomena is used [18-20].

Here, we are reporting conductometry with gold microelectrodes on microliter droplets of different electrolytes. The applied voltage is a time varying pulse train which causes a transient current in the electrolyte with temporal variations depending on the nature of the mobile ions present in the electrolyte. The voltage waveform applied is specifically selected to obtain the maximum of diagnostic information out of the current vs. time diagrams. It is shown that the information extracted from these
data is enough to facilitate correct classification of a number of electrolytes containing different concentrations of KF, KCl, and KF. The device and measurement system are cost effective and easy to use.

2. Experimental

Gold electrodes are deposited on soda lime glass substrates by physical vapor deposition in vacuum. As shown in Figure 1, each substrate contains 8 gold electrode couples with varying effective electrode areas. Experiments are carried out on 2 different electrode sizes, but those with smaller electrode area, evidently, rendered better results. The results reported here are related to the smaller area electrodes marked in Figure 1.

Three target electrolytes are prepared by dissolving 800 mg of the analytically pure salts in doubly distilled water. The conductivities of the obtained electrolytes are all adjusted at 2 mS/cm and are kept in a clean glass bottle as backups. Each sample is prepared by mixing 1 cc of the backup electrode with appropriate volume of distilled water. For each experiment 2 microliter from the sample electrolyte is dropped at the line separating two gold electrodes, as shown in Figure 1.

The measurement system is schematically shown in Figure 2. It comprises a programmable pulse generator capable of providing voltage waveforms applied to the electrodes [21] and a data acquisition unit which samples the voltage drop on a resistor connected in series with microcell. The sampling rate is 100 s\(^{-1}\), and the data is recorded by the computer connected to the data acquisition system. Due to the low current levels involved, the measurement system is placed in a Faraday cage for noise reduction. The wire connections from the system to the microelectrodes are shown as an inset in Figure 2. To prevent electrolyte evaporation during the experiment, the experiments were carried out in a closed chamber with 90% humidity level. The temperature in the chamber is 25 ±1°C.

The voltage waveform applied to the electrodes is shown in Figure 3. Experiments are carried out on KCl, KL and KF samples. After dropping the solution between the electrodes, the voltage pulse train is applied to the electrodes and the voltage on the series resistor shown in Figure 2, which is proportional to electric current passing through the droplet, is measured and its temporal variations are recorded. The recorded temporal profiles obtained for various electrolytes are given in Figure 3, confirming that each solution has its particular response profile (see the inset).

![Electrodes](image)

**Figure 1.** The glass substrate and gold electrodes with different effective surface areas used for the conductometry on electrolyte droplets.
Figure 2. The schematics of the experimental setup. The inset shows the voltage connection to the gold microelectrodes.

Figure 3. The voltage waveform applied to the electrodes and the temporal responses recorded for different electrolytes each at five different concentrations.
3. Result
According to Figure 3, recorded waveforms for different electrodes are clearly distinct. For distinguishing the recorded waveforms, 48 features are extracted from each response profile. The selection of the features is heuristic and based on the most dissimilar regions of the responses collected. Applying principle component analysis (PCA) reduces the feature space dimensions from 48 to 3 and allows visualization in a 3-dimensional feature space. The heuristic feature extraction and the dimension reduction method for feature space visualization is similar to those utilized in references [21, 22]. This facilitates observation of the different sample classes from each other in the feature space. The results obtained are shown in Figure 4, where unfilled markers are the verification results. Verification experiments are carried out independently in a different work session.

![PCA of responses](image)

**Figure 4:** Successful classification of the stated analytes in the 3-dimmensional feature space. The unfilled markers are related to the verification tests.

4. Conclusion
A simple and fast method was presented for performing conductometry on electrolyte droplets. It was shown that the information acquired from a simple conductometry is enough for distinguishing between three different potassium halides. The method uses only 2 µl of the electrolyte and is a good match to the common microfluidic systems and techniques.

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