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Sensors and Actuators B 113 (2006) 857–865

www.elsevier.com/locate/snb

Speciation of iron(II), iron(III) and full-range pH monitoring using paptode: A simple colorimetric method as an appropriate alternative for optodes

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Received 2 December 2004; received in revised form 27 March 2005; accepted 29 March 2005

Abstract

A new methodology for construction of a sensor array, to acquire signal patterns, is discussed in this article. This sensor is constructed by immobilizing an ionophore on a piece of paper (or porous material such as thin layer chromatography (TLC) plate) followed by charge coupled device (CCD) camera-based detection. This allows us to use non-transparent porous materials as a support for immobilization of ionophore. Changes in RGB values of color spots on pH paper or TLC strips create a pattern. The obtained pattern was analyzed using Microsoft Excel Solver. Full-range pH monitoring and speciation of ferric and ferrous ions in solution are discussed. A commercial multi-color pH strip was used as a typical prototype for full-range pH monitoring, and 4-methyl-2,6-bis (hydroxymethyl)phenol (or its halo-derivatives) and 1,10-phenanthroline were used as ionophores for determination of Fe(III) and Fe(II), respectively. Results of analyzed patterns showed a good correlation between predicted and true values of pH ($r = 0.9986$), Fe(II) ($r = 0.9989$) and Fe(III) ($r = 0.9978$) with acceptable relative standard error.

Keywords: Paptode; CCD camera; Scanner; 1,10-Phenanthroline; 4-Methyl-2,6-bis(hydroxylmethyl)phenol; Fe

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1. Introduction

In recent years, the mimic of an olfactory system has been developed and the term of “electronic nose” has entered in the analytical chemistry. In a typical electronic nose, the resistance of a series of different conducting polymers is changed by the absorption of volatile molecules and then creates a pattern. This pattern can be related to certain quality or substances by analysis using the mathematical methods such as multivariate analysis or artificial neural network [1,2].

It is clear that the electronic noses posses several limitations. The most significant deficiencies are that they are not suitable for solution phase analysis. For many important medical, biochemical, environmental and food analysis, identification and determination of analytes in vapor phase are very difficult or even in some cases is impossible to volatilize without decomposition. Therefore, the electronic tongues for liquid analysis, based on the organizational principles of biological sensory systems, developed rapidly during the last decade. The strategy is to artificially mimic information transduction as in living organisms [3–5]. An electronic tongue is composed of several kinds of liquid/polymer membranes for transforming information of chemical substances into electrical signals. The sensor output shows different patterns for these materials, which have different qualities and quantities [6]. These systems include acoustic wave devices [7,8], microelectrodes [9–11], arrays based on conducting polymers [12], polymerized crystalline colloidal arrays (PCCA) [13] and fiber optic-based array sensors [14,15].

Recently, in 1998, scientists of Texas University at Austin described a chip-based microsphere arrays platform (a new type of electronic tongue) had potential to mimic many of the features exhibited by the human sense of taste. That is, multi-analyte mixtures could be analyzed and intelligent decisions

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0925-4005/$ – see front matter
doi:10.1016/j.snb.2005.03.119

could be made in relation to the chemical composition of solution phase. Samples could be made rapidly and accurately with this detection modality. In this electronic tongue the output signal was obtained from a charge couple device (CCD) instead of electrical signal output. They applied advanced micromachining techniques and efficient rapid data acquisition by a CCD camera along with known chemical indicators that could create a single sensor. This was described as an "electronic tongue" [16]. This research team developed a chip-based sensor array composed of individually addressable polystyrene-poly (ethylene glycol) and agarose microspheres. The microspheres were selectively arranged in micromachined cavities on silicon wafers. These cavities were created with an anisotropic etching served as miniaturized reaction vessels and analysis chambers. A single drop of fluid provided sufficient analysis media to complete ∼100 assays in these microetech pits. This group demonstrated the power and utility of this new microbead array detection methodology, for analysis of complex fluids containing a variety of important classes of analytes including acids, bases, metal ions, metabolic cofactors and antibody reagents [17].

Herein we describe a new device as electronic tongue that we called "*paptode*" (from paper optode). We choose this name, because this method is similar to *optode*, in many features. The theoretical bases of optodes have been reviewed in detail [18–20]. In paptode, instead of immobilizing an ionophore on a hydrophobic or hydrophilic polymer (as in optodes), simply a paper or other ordinary porous material such as cotton or clay and even TLC can be used as a substrate support for ionophore. Application of a CCD camera in these systems makes the use of non-transparent supporting substrates possible. Signal transduction was accomplished by analysis of the reflection properties of the paptode using a CCD camera. Data streams were composed of red, green and blue (RGB) light intensities. Use of a semitransparent TLC support based on video camera detection has been reported previously [21–23] and the application of a CCD camera in analytical instrumentation has been reported in several manuscripts [24–26]. Construction of paptode is very simple and does not require any advanced technique. In comparison of paptode and polymer sensors, as mentioned before, paptodes can be sterilized easily, whereas sterilization of optodes may be more difficult. It has also been claimed that electrode fouling due to protein adsorption on the electrode surface is a more serious in case of glass than for solvent polymeric membranes [27]. In the case of paptode also we expect that fouling with proteins is not very serious.

In this study, a simple approach to full-range pH monitoring and simultaneous determination of iron(II) and iron(III) in solution using selective indicator, which were immobilized on TLC plate based on a CCD camera detection method was described. These strips are a typically paptode. By using these types of platforms, the species can be measured simply. Commercial multi-color pH strip was used as a typical prototype for full-range pH monitoring, 1,10-phenanthroline was used as a suitable chromogenic reagent for Fe(II), and 4-methyl-2,6-bis (hydroxymethyl)phenol, 4-chloro-2,6-bis(hydroxymethyl)phenol and 4-bromo-2,6-bis(hydroxymethyl)phenol were used as specific reagents for Fe(III) [28,29].

We focused in this research on speciation studies, where two or more physicochemical forms of an element are determined, because it has received intensive attention in wide diversity areas such as ecotoxicology [30], chemical evaluation of geological material [31], automated analysis of process streams [32] and aquatic studies [33]. Numerous approaches have been developed for the speciation of Fe(II) and Fe(III) [34]. Determination of the oxidation state of iron in atmospheric (e.g., cloud, fog and rain) water is important in the light of ecological studies that iron may be limiting nutrient for phytoplankton growth in the open ocean. The chemical reactions that occur in water droplets affect the composition of the atmosphere and the atmospheric input to terrestrial and aquatic ecosystems. Fe(II) and Fe(III) are involved in many of these processes, particularly redox and radical chain reactions [35–37]. Most investigations of iron in atmospheric water have been limited to the determination of its total dissolved concentration, and relatively little is known about its oxidation state [37,38]. Among a variety of analytical techniques including UV–vis spectrophotometry, atomic absorption spectroscopy and spectrofluorimetry for the measurement of iron(II) and iron(III), only a few approaches have been developed to quantify the different oxidation state species of iron in a sample. Electroanalytical methods, e.g., polarography [31], and voltammetry [39] and flow injection procedures with and without electrochemical detection, have also been used for the simultaneous determination of iron(II) and iron(III) [40–42]. Chromatographic methods [43] have also been described. But paptode can easily be used for speciation of two or more physicochemical forms of an element or different species simultaneously. This method is very simple, efficient, portable, inexpensive technique and appropriate alternative for optodes. In addition, these devices can also be applied in situ environmental analysis.

2. Experimental

2.1. Apparatus and software

A Metrohm potentiometer (pH meter model 654) and a combined glass electrode were used for measurement of pH. A simple scanner (Genius, COLORPAGE HR6X) recorded the color changes of pH strips and iron species on TLC strips. We wrote software in Delphi 6 media to convert the recorded pictures of color bands (or spots) to RGB data. This software also calculated the average of involved pixels in each band. Microsoft Excel Solver was used to analyze the created pattern. This program was used to optimize the values of coefficients in a multi-linear model (Eqs. (1) and (5)), until the best fit of the experimental pH values to model estimate pH values were obtained. In the worksheet of Microsoft Excel,