Short communication

CCD camera full range pH sensor array

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Abstract
Changes in colors of an array of optical sensors that responds in full pH range were recorded using a CCD camera. The data of the camera were transferred to the computer through a capture card. Simple software was written to read the specific color of each sensor. In order to associate sensor array responses with pH values, a number of different mathematics and chemometrics methods were investigated and compared. The results show that the use of “Microsoft Excel’s Solver” provides results which are in very good agreement with those obtained with chemometric methods such as artificial neural network (ANN) and partial least square (PLS) methods.

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1. Introduction

Sensors have traditionally been considered to respond selectively to a component in a mixture. But only a few numbers of sensors are selective. Sensors with different selectivity coefficients are widely used in many areas for chemical analysis. Nonselectivity was once considered as their drawback. These sensors when used as arrays and when they have different responses toward different components can be used for multicomponent analysis. In the course of calibration, arrays produce large amounts of data and thus quantitative and qualitative information are mixed up. This type of data can only be manipulated with mathematical and chemometrics methods [1]. Solid-state sensors used to detect gases are usually quartz crystal microbalance or metal oxide semiconductors sensors [2]. In the liquid state mostly different electrochemical methods are used [3]. The arrays which either detect the gaseous components (electronic nose) or components in aqueous form (electronic tongue) measure the electrical properties of the system under study.

Optodes, which fall in neither of the above categories, have been long used in practical cases such as clinical analysis, environmental analysis, and process control. They are suitable for sensing wide range of organic and inorganic materials. Several optodes have been designed to determine pH [4–8], but all suffer from limited measuring range. Artificial neural networks (ANNs) have shown to be very successful in extending the response range of an optical pH sensor. The application of ANN enabled the extension of the useful pH response range of an optode from its narrow linear range (pH 5–7.25) to much wider range of pH (2.51–9.76) [9]. In another work multilayer feed-forward ANN was used to model the input–output data of an optical-fiber pH sensor at three different wavelengths. The resulting model was tested with 70 solutions of pH 1.60–10.17. The average prediction error was 0.2 pH units [10]. Recently we described the development of an optical pH sensor based on immobilization of a mixture of two dyes on a triacetylcellulose membrane [11]. The sensor has a useful pH range at low and high pH values, where glass electrodes show acidic and alkaline errors, respectively. Application of a back-propagation artificial neural network (ANN) model extended the measuring range of the proposed optode to the whole pH range. Another strategy in extending pH range using optodes is based on dynamic method of analysis [12].

Usually the quantitative and qualitative data of optodes are obtained photometrically [4]. CCD cameras can also obtain similar data. The color and intensity (power) data as obtained by the camera are usually 24 bit data. These are three colors red (R), green (G) and blue (B). The intensity of each color has 8 bits or 256 levels. In this color Scheme $256 \times 256 \times 256 = 16777216$ colors are obtained and the value zero refers to black and 16777215 is pure white and other colors are in between, which has no resemblance to the white light spectrum. In harmony with
the electronic tongue and nose, which relate to human sense of taste and olfaction, this system, which is related to human sense of sight, can be termed as an electronic eye. Although this term has previously been used to refer to a light intensity measurement device, it is also very suitable in this context. Also it should be noted that in contrast to conventional optodes, which are transmissive, this technique could also be reflective.

CCD camera detection system is used in many areas of science and industry and has been employed in many areas of chemical experimentation [13]. Lavigne et al. [14] analyzed the transmitted light through a series of polymer beads that were derivatized with some complexing agents in micromachined wells by a CCD camera. They determined species such as Ca^{2+}, Ce^{3+}, and simple sugars at different pH values. Recently, we have reported the use of a CCD camera as a detection system for simultaneous determination of Al(III) and Fe(III) in alloys, using chromazaurol S (CAS) as the chromogenic reagent [15].

In an effort to extend the measuring range of pH optodes, in this communication we explain the design of an array of five partially selective reflective optodes for pH measurements. The responses of these optodes cover the whole pH range. Frames are taken by the CCD camera and are transferred to the computer. The frames were analyzed for red, green and blue components.

2.2. Instrumentation

Optode array responses were recorded using a Sony CCD TR750E video Hi8 Handycam. Setting all controls to manual, its video output was connected to a PV-8T6-48 video capture card on an IBM compatible personal computer. Fig. 1 shows a schematic set-up diagram for the sensor system. Image analysis program was written in Visual Basic. For comparison purposes spectrophotometric measurements were performed using a Jasco V-530 UV–vis spectrophotometer attached to an IBM compatible personal computer.

2.3. Optode preparation

The triacetylcellulose membranes were produced from waste photographic film tapes. These were previously treated with commercial sodium hypochlorite for several seconds in order to remove the colored gelatinous layers. The tapes simply were treated with a clear solution of indicators in ethylene diamine (about 5 × 10^{-3} g mL^{-1}) for 5 min at room temperature. Then, they were washed with water to remove ethylene diamine and loosely trapped dyes. These membranes were washed with hot ethanol for removing extra dyes. Finally, the membranes were washed with detergent solution and water, and kept under water when not in use.

2.4. Sensor array

Five different pH optodes were prepared by coating TY, VB, SC, CR, and, NB indicators on the membrane. The sensor array was formed from five membranes over a white background. The sensors were arranged randomly in a glass container. The system was stable over 40 successive pH measurements in the pH range of 0–14, after that a minor leaching of the dye materials was observed. Sensor array was kept under water when not in use.

2.5. RGB values

The response of the sensor array at each pH value was first obtained as a single frame taken by the CCD camera. The analytical data that a digital camera returns are a standard trichromatic response, with 8-bit red, green and blue channels, respectively. Hence, a value is returned to the user ranging from 0 to 255 for each channel. The data which were transferred to the computer were analyzed by a program written in Visual Basic and was then transported to Excel.

3. Results and discussion

3.1. Analytical signals

In this technique the three-dimensional RGB values of pixels of the pH optodes’ pictures were taken as analytical signals,
instead of the one-dimensional absorbance values of the pH optodes (at their wavelength of maximum absorption). As an example, the response of blue component as a function of pH for the optode array is shown in Fig. 2.

Thus, for each pH, a series of 15 signals (3 colors × 5 optodes) were recorded. In order to correlate sensor array responses to pH values, the resulting patterns were analyzed using different mathematical or chemometrical methods. The data were randomly split into calibration and validation sets consisting of 29 and 14 frames for model definition and evaluation, respectively.

For comparison, spectroscopic studies on TY, VB, SC, CR, and NB pH optodes were performed at $\lambda_{\text{max}}$ of 510, 430, 650, 600, and 645 nm, respectively (see Fig. 3). It is to be noted that spectrophotometric measurement with one wavelength per optode cannot cover the whole range of pH.

### 3.2. Measuring ranges

The two limiting activities at which the slope of the response function reduces to quarter of its maximum value have been used to quantify the practical pH measuring ranges of the pH optodes described herein (Fig. 3). Estimation of the best fitting curves on the curves of RGB light intensity values versus pH for slope calculation was performed by Table Curve windows software [16].

### 3.3. Calibration procedures

For the data set described above, different methods were used for processing the data in order to obtain the best results. The calibration set of data was used as the input for ANN, Microsoft Excel’s Solver (generalized reduced gradient nonlinear optimization algorithm), and partial least squares (PLS).

The data obtained from the image were processed by ANN, which was trained with the back-propagation of errors learning algorithm. In this study, the calibration and prediction sets were prepared randomly. Twenty-nine solutions were selected as the calibration set and 14 were selected as the prediction set. The structure of network was comprised of three layers, an input, a hidden and an output layer. The parameters of the network were optimized based on the minimum error of prediction of the testing set. The optimum learning rate of 0.3 and momentum of 0.2 for two nodes in the hidden layer gave minimum error of prediction. Continued training up to 2000 iterations resulted in the best network’s prediction performance.

A multi-linear model ($Y = C_0 + C_1 X_1 + C_2 X_2 + \ldots + C_{15} X_{15}$) estimates pH values ($Y_i$) from RGB patterns ($X_{i1} \ldots X_{i15}$). Solver was used to optimize the values of coefficients ($C_0 - C_{15}$) to obtain the best fit of the experimental pH values with the estimated pH values.

To select the number of factors in PLS and in order to model the system without over-fitting the pH data, a cross-validation method [17], leaving out one sample at a time, was used on the validation data. Nine factors gave the best performance.

Table 1, shows some results on prediction of pH values using different methods. This table shows that a very good correlation exists between true and predicted pH values using different chemometric and mathematical methods. Comparison of the correlation coefficients obtained between the true and predicted pH values using different methods reveals the suitability of the user friendly Excel’s Solver for data analysis in here which in fact eliminates the need to use chemometrics methods for untrained experimentalists.

### 3.4. Interferences

The proposed immobilized indicators were tested in the appropriate buffer solutions for any possible interference from ions, which have been previously reported [18,19] to react with free indicators (Table 2).

No interference from the ions was observed when the indicators were immobilized on the proposed optodes.
Table 2
List of reported interferences for the free indicators

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>NB</td>
<td>–</td>
</tr>
<tr>
<td>VB</td>
<td>–</td>
</tr>
<tr>
<td>TY</td>
<td>Mg²⁺ (pH 12.5) [18]</td>
</tr>
<tr>
<td>CR</td>
<td>Hg²⁺ (pH 5.5) [19]</td>
</tr>
<tr>
<td>SC</td>
<td>Ca²⁺, Cd²⁺ (pH 11.5), Mg²⁺, Mn²⁺, Zn²⁺ (pH 10) [19]</td>
</tr>
</tbody>
</table>

4. Conclusions

Imaging pH measurements with the potential of simultaneous detection of many samples, not only yields wider measuring ranges, but it also offers other measuring ranges, which could not be obtained from spectrophotometric measurement (at a single wavelength) (see Fig. 3). One of the best features of such an optode array is its ability to measure pH values at high and low extremes of the pH range, where glass electrodes encounter alkaline and acid errors, respectively. The mathematical and chemometric models show good performance for association of three-dimensional imaging data to one-dimensional chemical data. The presented methodology allows rapid determination of pH values in a full pH range. The good correlation that exists between the true and predicted pH values warrants the applicability of the method to different samples.

Acknowledgement

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References

[16] http://www.systat.com/products/TableCurve3D.