Accepted Manuscript

Disposable electrochromic polyaniline sensor based on a redox response using a conventional camera: a first approach to handheld analysis

M. Porcel Valenzuela, J. Ballesta-Claver, I. de Orbe-Payá, F. Montilla, L.F. Capitan-Vallvey

Please cite this article as: M. Porcel Valenzuela, J. Ballesta-Claver, I. de Orbe-Payá, F. Montilla, L.F. Capitan-Vallvey, Disposable electrochromic polyaniline sensor based on a redox response using a conventional camera: a first approach to handheld analysis, *Journal of Electroanalytical Chemistry* (2014), doi: http://dx.doi.org/10.1016/j.jelechem.2014.12.002

Disposable electrochromic polyaniline sensor based on a redox response using a conventional camera: a first approach to handheld analysis

M. Porcel Valenzuela[a,b], J. Ballesta-Claver[a]*, I. de Orbe-Payá[a], F. Montilla[b], L.F. Capitan-Vallvey[a].

[a]ECsens. Department of Analytical Chemistry, Campus Fuentenueva, Faculty of Sciences, University of Granada, E-18071 Granada, Spain.

[b]Institute of Materials, Faculty of Sciences, University of Alicante, E-03080 Alicante, Spain.

*E-mail: juliosci@ugr.es

Abstract

We present a disposable optical sensor for Ascorbic Acid (AA). It uses a polyaniline based electrochromic sensing film that undergoes a color change when exposed to solutions of ascorbic acid at pH 3.0. The color is monitored by a conventional digital camera working with the hue (H) color coordinate. The electrochromic film was deposited on an Indium Tin Oxide (ITO) electrode by cyclic voltammetry and then characterized by atomic force microscopy, electrochemical and spectroscopic techniques. An estimation of the initial rate of H, as $\Delta H/\Delta t$, is used as the analytical parameter and resulted in the following logarithmic relationship: $\Delta H/\Delta t = 0.029 \log [AA] + 0.14$, with a limit of detection of 17 μM. The relative standard deviation when using the same membrane 5 times was 7.4 % for the blank, and 2.6 % (for n = 3) on exposure to ascorbic acid in 160 μM concentration. The sensor is disposable and its applicability to pharmaceutical analysis was demonstrated. This configuration can be extended for future handheld configurations.

*Corresponding author; E-mail: juliosci@ugr.es

1. Introduction

Direct sensing schemes using chemical sensors cannot be applied if the analyte or analytes do not show adequate intrinsic analytical properties. In that case, reagent-mediated sensing is used in a huge variety of schemes and materials [1, 2].

An interesting group of materials using optical sensing are those that show electrochromism, a reversible optical change in a material induced by an electron-transfer (redox) process or sufficient electrochemical voltage [3]. Examples of electrochromic materials include metal oxide films (tungsten oxide), viologens (4,4'-bipyridylium salts), conjugated conducting polymers (polymeric thiophenes and pyrroles), and metal coordination complexes (transition-metal polypyridyl complexes) [4]. Electrochromic materials can be classified in different ways; one of the most simple consist on consider the solubility of each redox state that is categorized in three types [5]. Type I, such as methyl viologen, numerous metal complexes and organic redox indicators, is soluble in both reduced and oxidized states. Type II includes materials that are soluble in one redox state but form a solid film on the surface of an electrode following electron transfer. Examples are reversible electrodeposition of metals and heptyl viologen [4]. In type III electrochromic materials, both or all redox states are solid, such as WO_3 or conjugated conducting polymers.

Conjugated conducting polymers are very sensitive to the microenvironment within the polymer matrix due to the delocalization of π-bonded electrons over the polymeric backbone [6]. Many of these materials are electrochromic as thin films. Conducting polymers can be transformed from an electrically insulating state to conducting materials through several doping techniques such as: (1) chemical doping by charge transfer groups, (2) electrochemical doping, (3) doping by acid–base chemistry, (4) photodoping and (5) doping by charge injection [7]. Among them, polyaniline (PANI) is the most interesting because of its ease of synthesis, low-cost monomer, tunable properties, and better stability compared to other conducting polymers [8]. PANI film has been used as the active layer in electrochromic devices since it can reversibly change colors upon electrochemical doping and de-doping treatments [9] and also for modifying functional material by inkjet-printing [10].

The unsubstituted PANI presents problems of insolubility and infusibility; the emeraldine base is soluble in some polar organic solvents, but it is an insulator, whereas emeraldine salts are conductive but usually insoluble and non-processable. To improve

the solubility and induce fusibility of this polymer required for any application, various procedures have been adopted ranging from doping with functionalized protonic acids to copolymerization or the incorporation of polar functional groups [7].

PANI films show multiple color changes depending on their redox state: a) leucoemeraldine, the fully reduced form that is colorless and electrically insulating; b) pernigraniline, the fully oxidized form, violet in color and also electrically insulating, and c) emeraldine, a half oxidized and stable intermediate green color that has significant electrical conductivity [11].

The color of PANI depends on their absorption characteristics, appearing around 320 nm, 400 nm and 850 nm. The band at 320 nm, attributed to the band gap, is the principal one in reduced PANI leucoemeraldine, in addition to a small band around 850 nm. With the oxidation of PANI, the 320 nm band steadily decreases, growing a new band at about 400 nm, and the 850 nm band increases and shifts to 750 nm. These bands are attributed to the polarons and bipolarons associated with the formation of the quinoid units due to the oxidation of the amine to imine groups [12].

The use of PANI for optical sensing refers mainly to pH determination and pH related analytes because the degree of oxidation of the polymer depends on the pH [13]. Thus, films of chemically polymerized PANI are proposed to optically measure the pH between 2-12 in the NIR [14] or in the visible region [15, 16]. Another approach consists of the immobilization of PANI onto the core of a silica optical fiber, measuring the intensity of the NIR evanescent field for pH between 3-12 [17]. The immobilization of PANI coating microfluidic channels is also studied for pH measurement via absorbance and color by means of a digital camera, which makes it possible to detect pH gradients using an imaging technique [18]. The modification of cellulosic paper with PANI nanoparticles has been carried out for the determination of acidic analytes such as HCl both in solution and gas, measuring the color by means of a scanner [19]. In a similar way, covering PANI films with a layer of silicone permits the determination of analytes in solution such as acetic acid and ammonia [15]. An optical gas sensing device for ammonia was developed using a LED-photodiode setup and a PANI layer deposited on glass [20] or on poly(methyl methacrylate) and polystyrene blend films [21]. A copolymer of aniline and anthranilic acid was used as the support for the immobilization of urease allowing the spectrophotometric determination of urea [22]. Another strategy is the use of PANI type polymers containing boronic acid side groups capable of recognizing saccharides such as fructose by inducing spectral changes [23]. The ability

3

of some fiber/net membranes containing PANI to trigger a series of redox and doping reactions including complex formation with metal ions is the basis of a naked-eye procedure for Cu(II) identification and quantification based on RGB coordinates calculated from reflectance spectra [24].

The use of PANI for ascorbic acid determination has been carried out using different strategies in the literature, with electrochemical being the most common. The preparation of modified electrodes by electrodeposition of gold on polyaniline films prepared on titanium was employed for the electrooxidation of AA [25]. Another modified electrode based on a film that contains immobilized laccase with a cysteine self-assembled monolayer coated with functionalized quantum dots is capable of retaining its activity to oxidize AA [26]. Polyaniline is used to modify electrodes improving the electrochemical properties, especially with screen-printed carbon electrodes [10] or with doped agents such as dodecylbenzene sulphonic acid by drop-casting technique [27]. One interesting option is the use of polyaniline film as a molecularly imprinted polymer where AA was used as a template molecule for electrode fabrication [28].

Additionally, PANI films have been used for the spectrophotometric determination of redox analytes such as hydrogen peroxide by chemical polymerization of aniline in the microwells of microtiterplate and glucose by enzyme immobilization [29]. Bossi et al. use coated microplates based on monitoring the changes in optical absorption of the PANI film resulting from the reduction process from AA [30].

The aim of this study is to develop a disposable optical sensor for ascorbic acid based on monitoring the color changes of an oxidized PANI film with a conventional digital camera. The film is prepared by electrochemical doping on an ITO electrode, which achieves precise control of the doping level and higher precision in the preparation than with the usual chemical doping discussed above. We describe the use the HSV hue-oriented color space, whose initials indicates Hue, Saturation and Value, that represents the color information by using one single parameter, the H coordinate (hue). The H coordinate is a qualitative signal independent from reagent concentration and the optical path, meaning that it will not be affected by differences in thickness or the lack of membrane homogeneity, or the reagent concentration between batches of sensors, which reduces the precision of measurements [31].

2. Experimental section

4

2.1 Chemicals

Saline buffer was prepared in 0.2 M sodium chloride (Panreac Química S.L, Barcelona, Spain. http://www.panreac.es/) and 0.5 M sodium dihydrogen phosphate (Panreac), adjusted to pH 3.0 by adding HCl (35%, Panreac). Aniline solution, grade 99 %, was obtained from Sigma-Aldrich (Sigma-Aldrich Química S.A., Madrid, Spain, https://www.sigmaaldrich.com/spain.html). Ascorbic acid 99 % (AA) was purchased by Sigma-Aldrich. Different standard solutions of AA were prepared by weighing and solution in buffer. Acetone and acetic acid were obtained by Panreac. A 0.2 M solution of aniline (Sigma) was prepared in 0.5 M sulfuric acid (95%, Panreac). Reverse-osmosis type quality water (Milli-Q Plus185 from Millipore, Molsheim, France) was used throughout.

2.2 Apparatus and software

The potentiostat Autolab PGSTAT 128N (Metrohm Autolab B.V., Utrecht, The Netherlands) with conventional electrochemical cell has been used for electrochemical studies containing: platinum counter electrode, Ag/AgCl reference electrode and ITO coated glass (15 – 25 Ω/sq surface resistivity) or ITO coated plastic working electrode (60 Ω/sq surface resistivity) both obtained by Sigma. We used ITO coated glass in all the optimization study in order to reuse the electrodes after an acid washing process. The ITO coated plastic offer only a single use and cheap sensor. An electrochemical quartz crystal microbalance (EQCM) module made it possible to perform a mass change per unit area by recording the change in resonant frequency of a quartz crystal oscillator where 6 MHz EQCM Crystal Au/TiO$_2$ was used.

For the spectroelectrochemical measurement, a PalmSens handheld potentiostat / galvanostat (B.V., Utrecht, The Netherlands) with ultraviolet-visible diode array spectrophotometer HP 8453 (Nortwalk, CT, USA) with Chemstation software package was used. A Canon PowerShot G12 photographic camera was used for H parameter acquisition (Figure 1). Micro-Raman Spectrometer Dispersive JASCO NRS-5100 with Spectrum Manager Software (2011) was used for Raman spectroscopic data. The conditions for Raman spectra were an exposure time of 15 s and a laser wavelength of 785.11 nm, scanning from 350 cm^{-1} to 1750 cm^{-1} with a laser intensity of 0.2 mW with 12 accumulations. Atomic Force Microscopy (AFM) measurement was carried out with a Multimode Nanoscope IIIa from Digital Instruments (Veeco Metrology Group, Santa

Barbara, CA, USA); other instruments consisted of a Crison digital pH-meter (Crison Instruments, Barcelona, Spain) with combined glass-saturated calomel electrode.

Different software was used for the treatment and acquisition of data: Statgraphics centurion software package (Manugistics Inc. and Statistical Graphics Corporation, USA, 2007); Origin 8.0 (OriginLab Corporation, Northampton, USA), Microsoft Office Suite 2010 (Microsoft Corp., Redmond, WA, USA); Digital Photo Professional (Canon INC. 2010); and Matlab r2007b (The MathWorks, Inc, Natick, MA, USA), which was programmed for H value achievement.

2.3 Sensor preparation

First, ITO electrodes were washed with acetone in an ultrasonic bath for 10 minutes. Then, the electrode was immersed in a solution containing 0.2 M aniline in 0.5 M sulfuric acid. The electropolymerization of the aniline was performed by cyclic voltammetry with three sweeps from -0.2 to 1.1 V at 0.05 $V \cdot s^{-1}$. After that, the PANI/ITO electrode was dried for 30 minutes at room temperature. Finally, a fixed potential of 1.1 V was applied to the electrode for 100 s in 0.5 M sulfuric acid to prepare PANI in blue-violet pernigraniline form.

2.4 Analytical setup

The change in color from blue-violet to green of the PANI film when reacting with AA in acidic medium was acquired with a digital camera using the H parameter. The camera was placed 10 cm in front of a homemade white wooden box with two LED lamps (each lamp contains 60 LEDs, 3528 SMD GU10, 220-240V AC, E609 model Bsuper mart, 4.5 W, 300 – 350 LM, 50 mm × 50 mm), placed at 90º with respect to the digital camera. A transparent rectangular methacrylate prism cuvette was positioned in the centre of the white box containing a PANI/ ITO sensor (Figure 1).

To evaluate the color change of the PANI/ITO sensors when reacting with an ascorbic acid solution placed in the cuvette described above, three photographs of the PANI/ITO sensors were taken every minute for 10 minutes, using a timer to obtain reproducible images. The acquisition of the images was in RAW format. Then, the images were cropped with Digital Photo Professional software into 168 × 154 pixels and saved in TIFF (True Image File Found) format. The TIFF images were processed with a set of scripts and functions developed by us with Matlab r2007b for H coordinate acquisition

from HSV space, as described in a previous work [31]. This was considered a qualitative signal, regardless of variations in the color intensity coming from the PANI concentration and optical paths.

The setting conditions used to photograph the sensors are summarized in Table 1. The most important question is to reduce the noise of the image to obtain a high definition picture. Therefore, we selected the lowest ISO speed that the Canon camera offers, which was 80 obtaining a higher tonal richness and image definition. Shutter speed and aperture value are interconnected. The digital camera offers an aperture value with a range of f/2.8-f/4.5. Using the exposure triangle [32], the shutter speed would be 1/200 or 1/60 respectively. However, a clear-cut image is obtained using a high shutter speed like 1/320, which is enough to work properly. Selecting a value higher than f/2.0, we can reduce the noise and we chose the value in the medium range, f/3.5 for better image quality.

Figure 1

Table 1

Different standards of AA from 46 to 520 µM were prepared in pH 3.0 phosphate saline buffer containing 0.2 M NaCl and 0.5 M NaH_2PO_4. Pharmaceutical samples containing ascorbic acid were prepared using appropriate weights, in 1 M HCl, and were then diluted to 100 ml in the same phosphate buffer.

3. Results and Discussion

The combination of conductive polymers with electrochromic properties and highly distributed imaging technology for optical sensing, such as a digital camera or a smartphone, extends their use for portable configurations. This is the main objective of this study: the use of PANI films as a redox responsive membrane using H value as the color coordinates for ascorbic acid quantification in pharmaceutical samples. Several aspects must be taken into account to prepare the films, as summarized in this section.

3.1 Electroformation of PANI on ITO electrodes.

To prepare the electrochromic sensor, a polymeric film of PANI sensing material is deposited on an ITO electrode by cyclic voltammetry from a solution containing 0.2 M aniline and 0.5 M H_2SO_4 working between -0.2 and 1.1 V (0.05 V × s^{-1}) [33, 34]. The layer thickness of PANI is related to the cycle number used. With the aim of obtaining a

7

sensor with an optimal electrochromic response and minimum preparation time, three cycles were selected. This parameter was fixed as starting condition.

Figure 2

3.2 PANI/ITO sensor characterization

In order to prepare an optical sensor for ascorbic acid, several techniques were used to characterize the prepared layer. Some characteristics, such as morphology, growing process, mass deposition, electrochromism, spectroelectrochemistry and colorimetric response (H value) are summarized.

The EQCM gives information about the change of frequency during the cyclic voltammetry process. Figure 2A shows the frequency variation during PANI film formation. The resonant frequency makes it possible – using the Sauerbrey equation (C_f = 0.0815 Hz $\times$ ng^{-1} $\times$ cm^{-2}) [35] – to calculate the mass of the deposited film after three cycles, which was (11.5 ± 0.2) µg $\times$ cm^2 (Figure 2B).

The Raman spectra provide additional information about the structural changes of the molecules. The color change of PANI is due to a modification in the polymer structure. This variation can be produced electrochemically or by chemical reaction (redox). To verify the structural changes, we observed the Raman spectra of PANI films obtained at the two selected potentials: violet-blue form (1.0 V) and the green form (-0.2 V). Similar peaks for both conditions have been obtained but with differences in intensity between 1625-1500 cm^{-1} and 1250-1150 cm^{-1}. The first range corresponds to C-C stretching vibrations of the quinonoid ring [36] where at 1602 cm^{-1} a peak in the green PANI is observed that is higher than the violet-blue PANI, in which only a plateau is observed. The position corresponds to the protonation of the polymer and the formation of semiquinoid rings [37], indicating the formation of the emeraldine structure. Another significant difference is observed in the second region, particularly at 1232 cm^{-1}, which is attributed to C–N stretching in semiquinoid and quinoid rings [38], ascribed to the violet-blue form of PANI, i.e., pernigraniline.

The AFM study shows the morphology and thickness of the PANI films on the ITO electrode (Figure 3). With respect to the distribution of the polymer on the electrode, a higher quantity is electropolymerized just on the top, at the aniline solution level. Figure 3 shows the two regions: first bottom layer: PANI polymer; second upper layer: ITO bare electrode. The PANI film appears using AFM as a rough inhomogeneous layer [34] with an average thickness of all surface of (0.46 ± 0.05) µm, which indicates a volume of PANI on ITO of 1.012×10^{-4} cm^3.

8

Figure 3

A spectroelectrochemical study was conducted by subjecting PANI/ITO to different potential values (from -0.2 to 1.1 V) for 100 seconds while absorption spectra (200-900 nm) were collected every 10 seconds. The obtained spectra showed characteristic absorption peaks at 373, 600 and 700 nm. The band at 373 nm due to π-π^* transitions of benzene rings, characteristic of the leucoemeraldine form, decreases when voltage increases, demonstrating the change to emeraldine form, which contains conjugated quinoid rings [39].

3.3 H value response

The H parameter gives analytical information about color tonal changes. As the colorimetric response (H value) of PANI film depends on the pH, the change in H of PANI/ITO sensing membranes by electrochemical doping at different pH values was studied in order to select the best conditions for their use as colorimetric sensors. Electrochemical doping at different pH values from 0.5 to 6.0 was studied chronoamperometrically applying different voltages from -0.2 V to 1.1 V, with a step potential of 0.1 V for 100 s (Figure 4A), obtaining the H value for each voltage. The change in H with voltage depends on the pH and it was observed that an increase in the pH means an increase in the slope ($\Delta H/\Delta V$) of the linear zone of the sigmoid presented in Figure 4A, obtaining the following relationship: $\Delta H/\Delta V = 0.14$pH $+0.79$. The change in color is faster when the pH increases, decreasing the ability of the sensing membrane to distinguish between different hue values, thus reducing the capacity of the sensor to discriminate among different potential values, trimming the potential response range. This decrease in the electrochromic response is due to deprotonation of the aniline rings at high pH values [33].

Additionally, the difference between the initial and the final color measured by H of the PANI/ITO membranes, i.e., the H range (ΔH), increases with the pH (Figure 4C), reaching a plateau at pH 3.0. In conclusion, although the electrochromic response decreases with pH and the difference in color (H) and the membrane response ($\Delta H/\Delta V$) increases with pH, we selected pH 3.0 as the working pH in order to select the best H range and adequate color discrimination (Figure 4B). This result agrees with the observations made by Prakash that the best pH for PANI electrochromic response was 2.5 [33]. Another reason for the pH selection is that the maximum degradation of AA

9

occurs at pH 4.0, near its acidity constant value (pK_a 4.04) [40], and a minimum occurs between pH 2.5 and 3.0 because of the different stability of the undissociated and monoanionic forms of AA [41]. One of the advantages of using the H value is the accuracy obtained. The reproducibility in the preparation of PANI/ITO membranes measured over 10 membranes at pH 3.0 has an H value of 0.52 ± 0.02 or 3.8%.

Figure 4

To work at pH 3.0, we tested different buffers, namely phosphate and acetic buffers. The best result was obtained using the phosphate buffer. That result agreed with observations by Yanfang Gao and co-workers [9] about the substitution of SO_4^{2-} in the PANI film by HPO_4^{2-} during the cyclic voltammetry, which means that the PANI film is doped with phosphate anions, maintaining an SO_4^{2-} ion size with the generation of some gap inside the PANI and increasing the internal impedance of the membrane, which results in a better resolution of the H value.

3.4 Analytical signal and characterization

The objective of the electrochromic PANI/ITO sensor is ascorbic acid determination by H value changes due to a redox reaction. In the previous section we studied chronoamperometrically the tonal change in the PANI/ITO membrane. In this section we study the tonal change of the membrane using solutions of ascorbic acid at pH 3.0 observing that the same color change occurs when the sensor is immersed in a solution containing ascorbic acid (chemical doping) as in the electrochemical procedure, although at a slow rate. The sensor gradually changes its color depending on the concentration of ascorbic acid. Working at 100 µM in AA, a typical value in pharmaceutical samples, the electrochemical process (100 s above mentioned) is a six times faster than the chemical reaction (600 s, see Figure 5A). Each AA concentration generates different sigmoidal curves over time, results that are obtained by photographing a PANI/ITO sensor immersed in the solutions are presented in Figure 5A.

As the reaction time was high, we tried to use the H value at a fixed time as the analytical signal. Different fixed times such as 5, 10, 20 and 30 minutes did not offer so much precision. Another possibility is using a kinetic study. The behavior we obtained in this work (sigmoidal curves) is very similar to the profile for an enzymatic study. The

response curves show three phases: 1) a lag phase that decreases when AA concentration increases; 2) a linear phase in which H decreases over time, and 3) a PANI depletion phase. The final H values obtained in all cases tend to have the same value. Generally, the linear phase (phase 2) of an enzymatic sigmoidal curve is always selected for initial rate estimation (v_H^0). Taking into account this procedure, different initial rates were obtained for each AA concentration. The results we obtained offer better accuracy and low analysis time than the fixed time method, selecting the initial rate as the analytical signal.

In all cases, the initial rate (v_H^0) was measured by measuring $\Delta H/\Delta t$ in the linear phase. Figure 5A shows the estimation of the different initial rates (dotted lines in the figure) and that an increase of AA concentration increases the negative slope value.

Figure 5

The different initial rate estimation obtained by several AA concentrations has a logarithmic dependence with the AA concentration according to: $v_H^0 = 0.029 \times \log$ [AA] + 0.14 (Table 2 and Figure 5B), with a limit of detection (LOD) of 17 μM according to a 3s criterion. The relative standard deviation (RSD) for the blank, using the same membrane ($v_{H_{blank}}^0$ of $(1.0\pm0.1) \times 10^{-3}$ H $\times$ min^{-1}) was 7.4 % (n = 5). This relatively high value of RSD is due to the low blank measured signals. The accuracy for AA determination in the medium level of the range was studied in two different ways: by using the same membrane (160 μM AA) with an RSD value of 2.6 % (n=3) and by preparing ten membranes of the PANI/ITO sensor according to the described procedure, obtaining a value of 3.6 % of RSD for the same concentration, which indicates good reproducibility in the procedure and in preparation of the membranes.

Table 2

Table 3

Comparing this method with others in the literature on ascorbic acid determination (Table 3), we observed that the procedure developed report a shorter working range as well as a lower detection limit than other procedures, although their precision is as good as or better than most of the procedures. Despite this, it is important to note the accuracy of the measurements and the simplicity of a setup that only uses a conventional camera.

Samples

Four pharmaceutical samples containing ascorbic acid were tested, including Aspirin C (Bayer®), Redoxon (Bayer®), Vitamin C (Acofarma®) and Vitamin C (Solgar®). Those samples were selected in order to test the viability of the methodology. For these analyses, the solid samples were dissolved using different weights in 1.0 M HCl and were diluted to 100 ml in a 0.5 M NaH_2PO_4, phosphate buffer containing 0.2 M NaCl. The reference method consisted of classic redox iodometric titration [42]. Table 4 shows the results obtained using the reference method and the presented method. With respect to the standard deviation, the H value is slightly higher than the reference method but in all cases, the statistical parameter (p-value), is higher than 0.5 %, that means a validated procedure.

Table 4

4. Conclusions

The use of the HSV color space, specifically the H value, in combination with an electrochromic PANI/ITO system offers the possibility of developing disposable sensors for ascorbic acid, applied here to pharmaceutical samples, thanks to sensitive changes in the hue. The preparation of electrochromic PANI film on an ITO electrode is quick because it only requires three voltammetric sweeps. The acquisition of the H value requires fixed variables, such as the position of the digital camera and sensor and constant illumination provided by two LEDs in horizontal distribution. These aspects can be automatized for future analysis. The analytical signal is the initial rate estimation, measured as the hue (H) change over time of the slow color change process. The analysis time is between 5 min (high concentrations) and 8 min (low concentrations). The system offers good accuracy (2.6 %, n=3, for AA 160 µM) using a conventional digital camera as a detector. This methodology offers a new approach for analytical measurements of redox changes in solutions providing an affordable system for handheld analysis. The possibility of developing conducting polymer combinations to extend the analytical performances with the use of the H parameter opens new possibilities for colorimetric sensor configurations.

Acknowledgements

Bibliography

1. J. Janata, Principles of Chemical Sensors, 2 ed., Springer, 2009.

2. H. H. Qazi, M. bin, M. Akram, Sensors, 12 (2012) 16522.

3. R. J. Mortimer, Annu. Rev. Mater. Res., 41 (2011) 241.

4. A. A. Argun, P. H. Aubert, B. C. Thompson, I. Schwendeman, C. L. Gaupp, J. Hwang, N. J. Pinto, D. B. Tanner, A. G. MacDiarmid, J. R. Reynolds, Chem. Mater., 16 (2004) 4401.

5. P. M. S. Monk, R. J. Mortimer, D. R. Rosseinsky, Electrochromism: fundamentals and applications, VCH, Weinheim etc., 2007.

6. M. Ates, Mat. Sci. Eng. A, 33 (2013) 1853.

7. M. Jaymand, Prog. Polym. Sci., 38 (2013) 1287.

8. S. Bhadra, D. Khastgir, N. K. Singha, J. H. Lee, Prog. Polym. Sci., 34 (2009) 783.

9. W. Zhang, X. Li, G. Jia, H. Wang, Z. Cao, C. Li, Y. Gao, J. Liu, Int. J. Electrochem. Sci., 8 (2013) 4142.

10. W. Kit-Anan, A. Olarnwanich, C. Sriprachuabwong, C. Karuwan, A. Tuantranont, A. Wisitsoraat, W. Srituravanich, A. Pimpin, J. Electroanal. Chem., 685 (2012) 72.

11. J. Tarver, Y. L. Loo, Chem. Mater., 23 (2011) 4402.

12. A. A. Nekrasov, V. F. Ivanov, A. V. Vannikov, J. Electroanal. Chem., 482 (2000) 11.

13. W. A. Marmisollé, M. I. Florit, D. Posadas, J. Electroanal. Chem., 707 (2013) 43.

14. U. W. Grummt, A. Pron, M. Zagorska, S. Lefrant, Anal. Chim. Acta, 357 (1997) 253.

15. S. De Marcos, C. Asensio, I. Urunuela, F. Gallarta, J. Galban, J. R. Castillo, Quim. Anal., 19 (2000) 99.

16. Z. Jin, Y. Su, Y. Duan, Sens. Actuators B, 71 (2000) 118.

17. Z. Ge, C. W. Brown, L. Sun, S. C. Yang, Anal. Chem., 65 (1993) 2335.

18. L. Florea, C. Fay, E. Lahiff, T. Phelan, N. E. O'Connor, B. Corcoran, D. Diamond, F. Benito-Lopez, Lab Chip, 13 (2013) 1079.

19. F. G. Souza, Jr., G. E. Oliveira, T. Anzai, P. Richa, T. Cosme, M. Nele, C. H. M. Rodrigues, B. G. Soares, J. C. Pinto, Macromol. Mater. Eng., 294 (2009) 739.

20. Y.-S. Lee, B. S. Joo, N. J. Choi, J. O. Lim, J. S. Huh, D. D. Lee, Sens. Actuators B, 93 (2003) 148.

21. M. Matsuguchi, A. Okamoto, Y. Sakai, Sens. Actuators B, 94 (2003) 46.

22. E. Pringsheim, E. Terpetschnig, O. S. Wolfbeis, Anal. Chim. Acta, 357 (1997) 247.

23. E. Pringsheim, E. Terpetschnig, S. A. Piletsky, O. S. Wolfbeis, Adv. Mater., 11 (1999) 865.

24. B. Ding, Y. Si, X. Wang, J. Yu, L. Feng, G. Sun, J. Mater. Chem., 21 (2011) 13345.

25. M. Hosseini, M. M. Momeni, M. Faraji, J. Mater. Sci., 45 (2010) 2365.

26. Z. Wang, Q. Xu, J. H. Wang, Q. Yang, J. H. Yu, Y. D. Zhao, Microchim. Acta, 165 (2009) 387.

27. A. Ambrosi, A. Morrin, M. R. Smyth, A. J. Killard, Anal. Chim. Acta, 609 (2008) 37.

28. A. K. Roy, V. Nisha, C. Dhand, B. D. Malhotra, J. Mol. Recognit., 24 (2011) 700.

29. S. A. Piletsky, T. L. Panasyuk, E. V. Piletskaya, T. A. Sergeeva, A. V. El´skaya, E. Pringsheim, O. S. Wolfbeis, Anal. Chem., 366 (2000) 807.

30. A. Bossi, S. A. Piletsky, E. V. Piletska, P. G. Righetti, A. P. F. Turner, Anal. Chem., 72 (2000) 4296.

31. K. Cantrell, M. M. Erenas, I. Orbe-Paya, L. F. Capitán-Vallvey, Anal. Chem., 82 (2010) 531.

32. L. Excell, Composition: From Snapshots to Great Shots, Second ed., Peachpit Press. Pearson Education, USA, 2014.

33. R. Prakash, J. Appl. Pol. Sci., 83 (2002) 378.

34. U. León-Silva, M. E. Nicho, H. Hu, R. Cruz-Silva, Sol. Energ. Mat. Sol. Cells, 91 (2007) 1444.

35. V. M. Mecea, Anal. Lett., 38 (2005) 753.

36. V. S. Jamadade, D. S. Dhawale, C. D. Lokhande, Syn. Met., 160 (2010) 955.

37. G. Cai, J. Tu, D. Zhou, J. Zhang, Q. Xiong, X. Zhao, X. Wang, C. Gu, J. Phys. Chem. C, 117 (2013) 15967.

38. E. Tomsík, Z. Morávková, J. Stejskal, M. Trchová, J. Zemek, Syn. Met., 162 (2012) 2401.

39. A. Malinauskas, R. Holze, Syn. Met., 97 (1998) 31.

40. D. R. Lide, CRC Handbook of Chemistry and Physics 2008-2009, 89th Ed ed., CRC Press-Taylor & Francis, Boca Raton, FL, USA, 2007.

41. T. Moura, D. Gaudy, M. Jacob, G. Cassanas, Pharm. Acta Helv., 69 (1994) 77.

42. L. Erdey, G. Svehla, Ascorbinometric Titrations, Akad. Kiado, 1973.

43. A. K. Roy, V. Nisha, C. Dhand, B. D. Malhotra, J. Mol. Recognit., 24 (2011) 700.

44. Z. Wang, Q. Xu, J. H. Wang, Q. Yang, J. H. Yu, Y. D. Zhao, Microchim. Acta, 165 (2009) 387.

45. M. U. Anu Prathap, R. Srivastava, Sens. Actuators B, 177 (2013) 239.

46. X. H. Yang, J. Ling, J. Peng, Q. E. Cao, L. Wang, Z. T. Ding, J. Xiong, Spectrochim. Acta A, 106 (2013) 224.

47. H. W. Park, S. M. Alam, S. H. Lee, M. M. Karim, S. M. Wabaidur, M. Kang, J. H. Choi, Luminescence, 24 (2009) 367.

Table 1. Digital camera parameters for H coordinate acquisition

Parameter	Selection
Shutter speed	1/320
Aperture value	3.5
ISO speed	80
Objective	6.1 – 30.5 mm
Focal distance	6.1 mm
Zoom	Off
Flash	Off
Image quality collection	RAW
AF mode	Continuous
AF mode rank	Macro
Level contrast, sharpness and saturation	Normal
Color space	sRGB
Shooting mode	Timed (10 seconds)

Table 2 Analytical parameters for PANI/ITO sensor

Parameter	Value	
Range, μM	46 – 520	
Ordinate	0.14 ± 0.01	
Slope	0.029 ± 0.002	
R^2	0.982	
LOD, μM	17	
LOQ*, μM	46	
RSD (%) blank (n=5)	7.4	
RSD (%) AA (n=3)	160 μM	2.6

*LOQ: limit of quantification

Table 3. Analytical parameters of AA detection in recent papers

System	Linear range / μM	LOD / μM	Linearity	Detection	Reproducibility	Ref.
PANI/ITO	5–38	18	0.999	Electrochemistry	---	[43]
Laccase/Quantum dots	10–140	1.4	0.999	Electrochemistry	3.5 %	[44]
Metal-Mesoporous-PANI	10–300	6.5	0.999	Electrochemistry	2.9 %	[45]
Au-PANI	10-12000	8.2	0.999	Electrochemistry	5.9 %	[9]
BSA-silver nanoclusters	2–50	0.16	0.998	Absorption	2.7 %	[46]
Ag nanoparticles	4–100	0.1	0.998	Fluorescence	1.5 %	[47]
PANI plates	5–114	5.7	---	Absorption	10.0 %	[30]
PANI/ITO	46 – 520	17	0.982	Color (H)	2.6 %	This work

Table 4. Determination of AA in pharmaceutical samples using the PANI/ITO sensor and a reference procedure

Samples	Sensor	Reference procedure	p-value %	%*
Aspirin C (Bayer®)	(239 ± 10) mg/Tablet	(240 ± 1) mg/ Tablet	86.3	100.6
Vitamin C (Solgar®)	(498 ± 30) mg/ Tablet	(533 ± 10) mg/ Tablet	25.9	93.3
Redoxon (Bayer®)	(1027 ± 11) mg/ Tablet	(1007 ± 19) mg/ Tablet	32.6	102.0
Vitamin C (Acofarma®)	(34 ± 3) mg	(34.0 ± 0.2) mg	92.8	99.4

*RSD between presented method and reference method average values.

19

Figures

Figure 1. A) Experimental setup for PANI/ITO membrane image acquisition. B) The PANI color change is showed in the upper part of the figure. Each square corresponds to a decrease of 0.045 in voltage starting from the right obtained by the digital camera. Only one sensor appears in this figure.

Figure 2. EQCM study. A) and B) correspond to the frequency variation when consecutive sweeps were given of PANI on gold quartz electrode. A cyclic voltammetry of PANI using sweeps from -0.2 to 1.1 V at 0.05 V·s^{-1} by means of a solution of 0.2 M aniline in 0.5 M H$_2$SO$_4$ was carried out.

Figure 3. AFM images of PANI on ITO electrode. The preparation of the polymer shows two regions on the electrode: PANI polymer (green color) and bare ITO electrode. The AFM images show two profiles: 3D images on the left and a surface form above on the right. The medium value of the PANI electrode on ITO surface is 0.46 µm. The value of the roughness is given by the Root Mean Square (RMS) parameter, the root mean square average of the height deviations taken from the mean data plane. The figure shows two values: +RMS (upper data plane) and –RMS (bottom data plane).

Figure 4. Optimization of pH. A) Chronoamperometric response of PANI/ITO sensor. Observe the diminution of sensitivity and the increment of the slope when pH increases. B) On the right, the selected pH 3.0 shows a complete profile of the H response. C) ΔH influence vs. pH. Observe the plateau near pH 3.0.

Figure 5. Analytical quantification using the PANI/ITO sensor. A) Kinetic colorimetric response of different AA standards. Observe the acquisition of the different initial rates (v^0_H, dotted lines) by measuring ΔH/Δt in the linear phase obtaining different slopes; B) logarithmic dependence between AA concentration and initial rate.
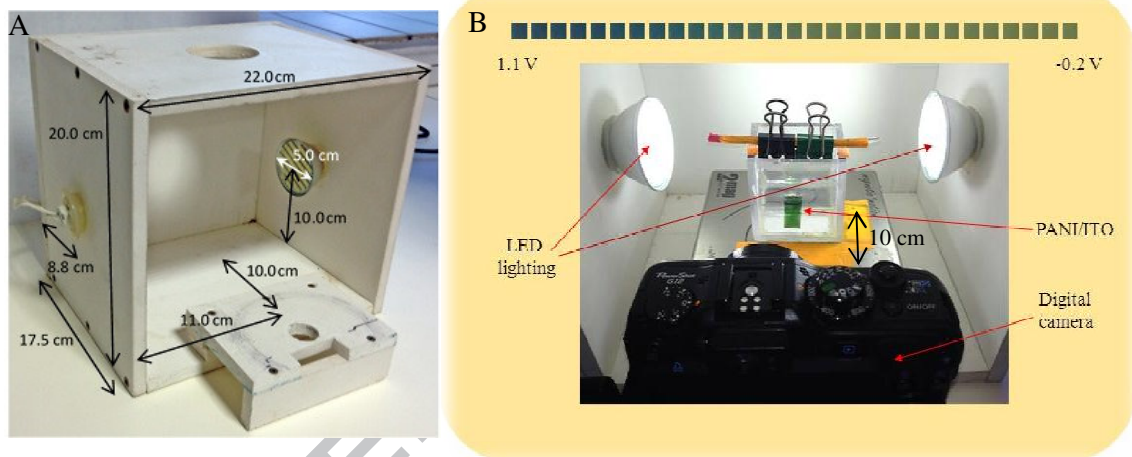
A

22.0cm

20.0 cm

5.0 cm

10.0 cm

8.8 cm

10.0cm

11.0 cm

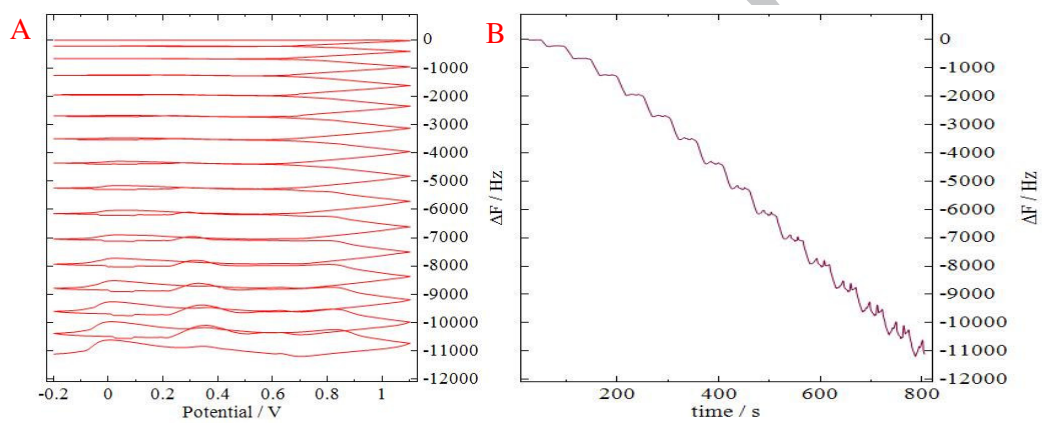17.5 cm

B

1.1 V   -0.2 V

LED lighting

PANI/ITO

10 cm

Digital camera

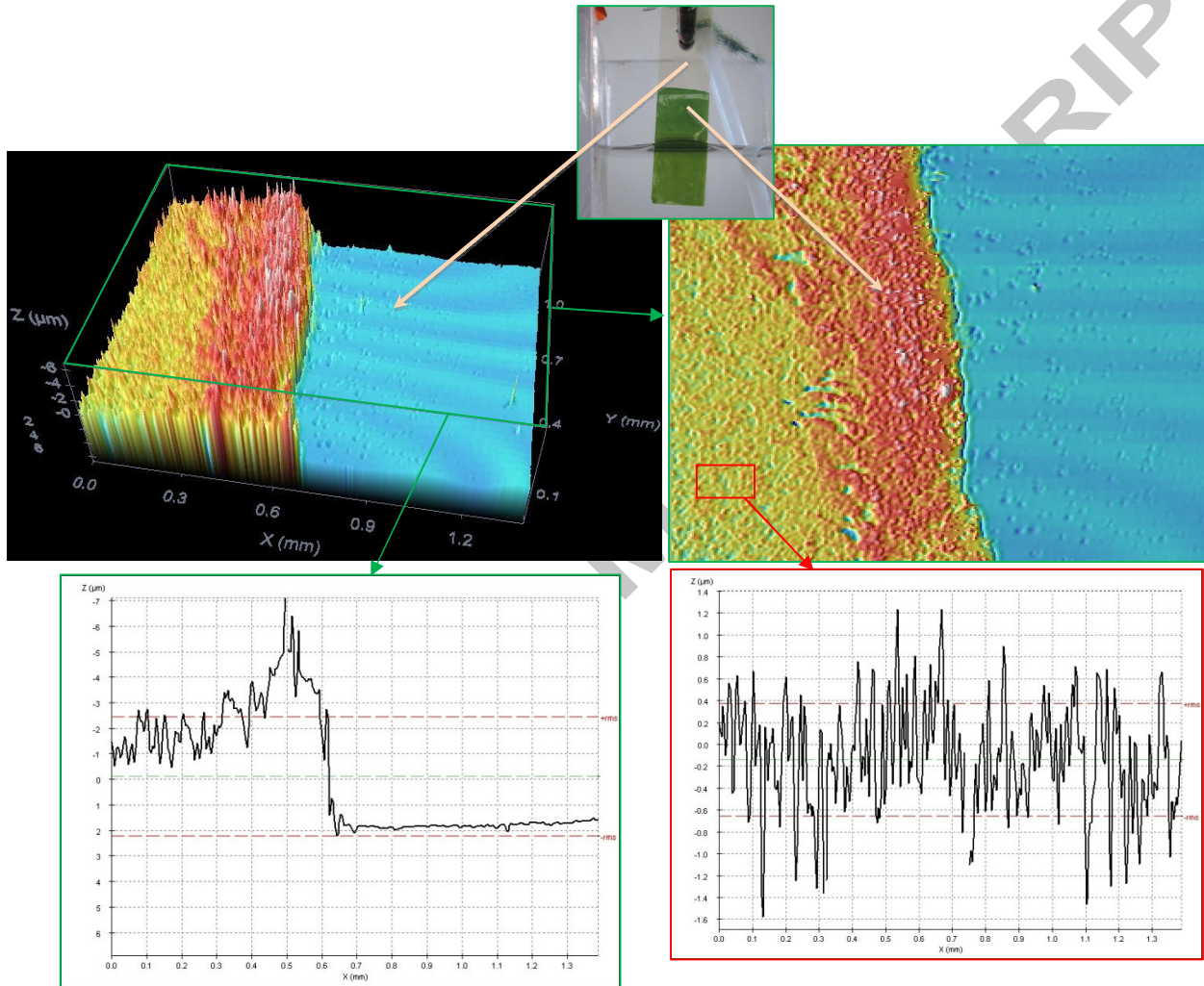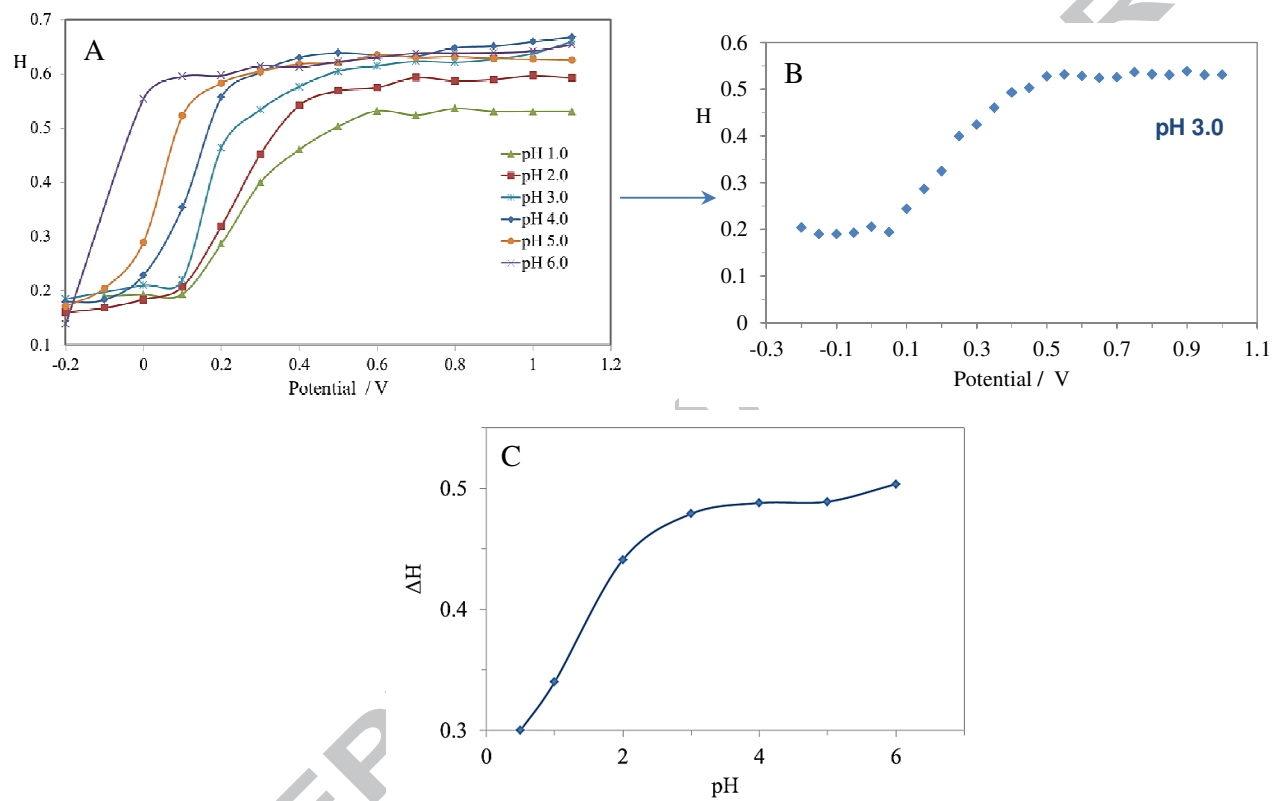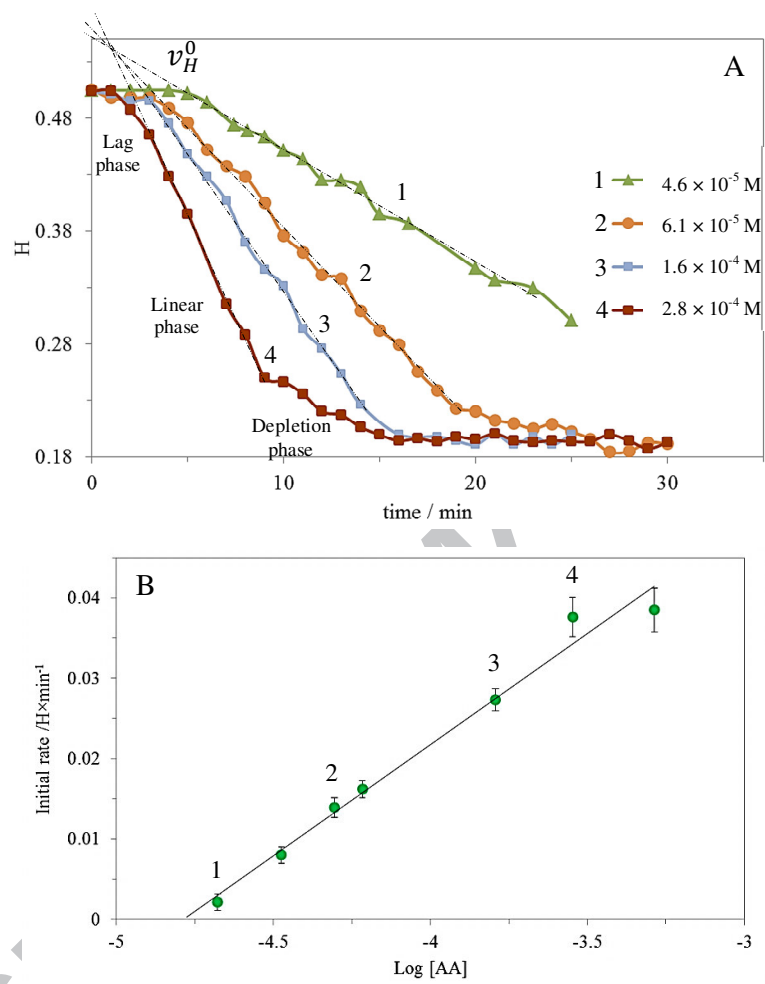Figure 1

ACCEPTED
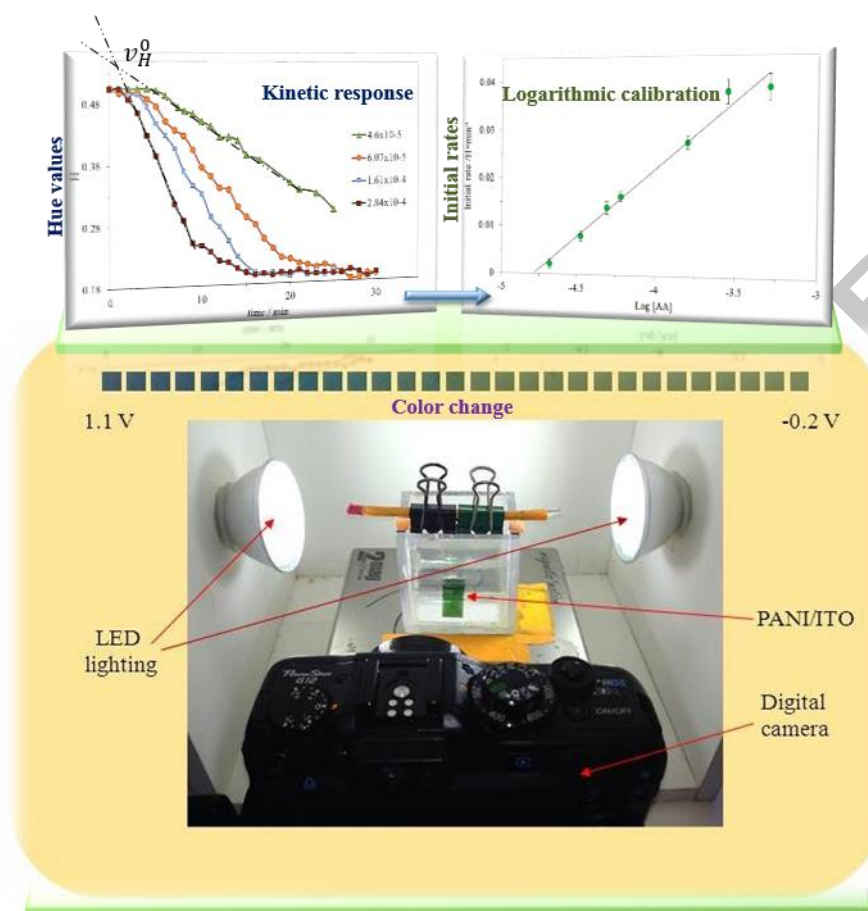
Figure 2

Figure 3

Figure 4

Figure 5

Graphical Abstract

This article presents how to obtain precise analytical information by using a digital camera. It is only needed a disposable electrochromic optical sensor making use of a polyaniline (PANI) that can be deposited on an Indium Tin Oxide (ITO) electrode by cyclic voltammetry, which can undergoes a color change if it is exposed to different solutions of ascorbic acid of pH 3.0. Color is monitored by a conventional digital camera working with the H coordinate (hue) of HSV color space. It can be observed the electrochemical scale of PANI color change in the upper of the image, where each square corresponds to a decrease of 0.045 in voltage starting from the right. An estimation of the initial rate of hue (H), defined as $\Delta H/\Delta t$, is used as the analytical information and resulted in a logarithmic relationship, with a detection limit of 17 μM. This configuration can be extended for future handheld configurations.

Highlights

➤ Use of electrochromic polymers for quantitative colorimetric response.

➤ Use of a conventional digital camera as an inexpensive analytical instrumentation for analytical quantification of analytes.

➤ Possibility of developing handheld systems for analytical quantification.

➤ Use of HSV color space, the hue parameter, for precise detection of color change from electrochromic polymers.