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Handheld colorimeter for determination of heavy metal concentrations

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Abstract. A portable instrument that measures heavy metal concentration from a colorimetric sensor array is presented. The use of eight sensing membranes, placed on a plastic support, allows to obtain the hue component of the HSV colour space of each one in order to determinate the concentration of metals present in a solution. The developed microcontroller-based system captures, in an ambient light environment, an image of the sensor array using an integrated micro-camera and shows the picture in a touch micro-LCD screen which acts as user interface. After image-processing of the regions of interest selected by the user, colour and concentration information are displayed on the screen.

1. Introduction

The detection and determination of heavy metals in the area of analytics and drug control are important and demanding tasks, and, therefore, drug analysis and quality control require increasingly better analytical methods and procedures to solve specific problems in pharmaceuticals and in the industrial production of medicines [1]. A recent trend to obviate the difficulties of obtaining single analyte sensors based on specific receptors – problems of selectivity – is to combine non-specific sensors in an array that produce a set of analytical signals (electronic tongue for gaseous species/electronic nose for species in solution). This information with higher dimensionality, encoded in the overlapping measurements, can be processed to extract qualitative and quantitative information through advanced mathematical procedures of pattern recognition and/or multivariate analysis [2,3], improving in this way the performance of the sensors [4].

Different principles have been used for the preparation of sensor arrays for electronic tongues, with the most widely used being: tin oxide catalytic sensors, conducting polymer sensors, acoustic wave sensors, quartz crystal microbalance sensors, sensors based on MOSFET technology, systems based on ion mobility spectrometry as well as mass spectrometry techniques like API and PTR, and lastly, optical techniques, principally fibre optics and fluorescence [5].

The basic requirements for the optical tongue systems, in reference to the sensing array, which is the key of the system, is that sensors should present low selectivity or high cross-sensitivity, and that they have reproducible analytical characteristics. Moreover, it is necessary to look for sensors to be more sensitive and more robust, which is contradictory to a certain degree, since usually the more

sensitive a sensor is, the less robust it becomes [6]. One solution is to use disposable sensors which are, therefore, not integrated into the device. Additional requirements refer to cost and portability.

Most different optical approaches used for tongues are based on the measurement of colour using different colour spaces obtained from the image captured principally by imaging devices, mainly CCD cameras or scanners. By far, the most commonly used space is RGB, whose coordinates are used for processing with multivariate techniques. However, in this work, we used the HSV colour space, whose main characteristic is that it represents the useful information of the colour in one single parameter, the coordinate H (hue). Previous studies from our group have shown that the use of the H coordinate in bitonal sensors that produce a change in colour by reaction yields a substantial improvement in resolution and repeatability [7].

We approached the analysis of heavy metals using the concept of an optical tongue using an array of membranes placed on a transparent support that contains immobilized conventional chromogenic reagents [8]. Their usual drawback, i.e. their lack of selectivity, is used here as the source of non-selective information about the metals present, considering their usual good sensitivity.

2. Preparation of the sensing array

Different chromogenic reagents for heavy metals were tested for immobilization using different strategies such as ion-exchange, adsorption, and entrapment using as criteria for selection the conditions of no leaching, change in tonal colour coordinate by reaction and non-selective behavior.

As chromogenic reagents for this proof of concept study, 1-(2-pyridylazol)-2-naphtol (PAN) and zincon (ZIN) were used and the needed amounts of polymers, reagents, plasticizers and lipophilic salts were optimized. For characterization of sensing films, individual membranes were prepared by using a spin-coating technique from the cocktails containing all the reagents in THF or in ethanol:water mixture on the sheets of Mylar-type polyester. In addition sensing arrays were prepared on a Mylar support covered by an adhesive and transparent PVC layer with 12 holes, 5 mm in diameter each. The array was produced by placing 8 μL of the corresponding cocktail in each hole.

3. Description of the instrument

The portable instrument here developed is a microcontroller-based system that allows to calculate the H component of the HSV colour space from an image of a colorimetric sensor array obtained with a micro-camera. The colour information is used to determinate the concentration of metals in a solution. The block diagram of the prototype described is in Figure 1.

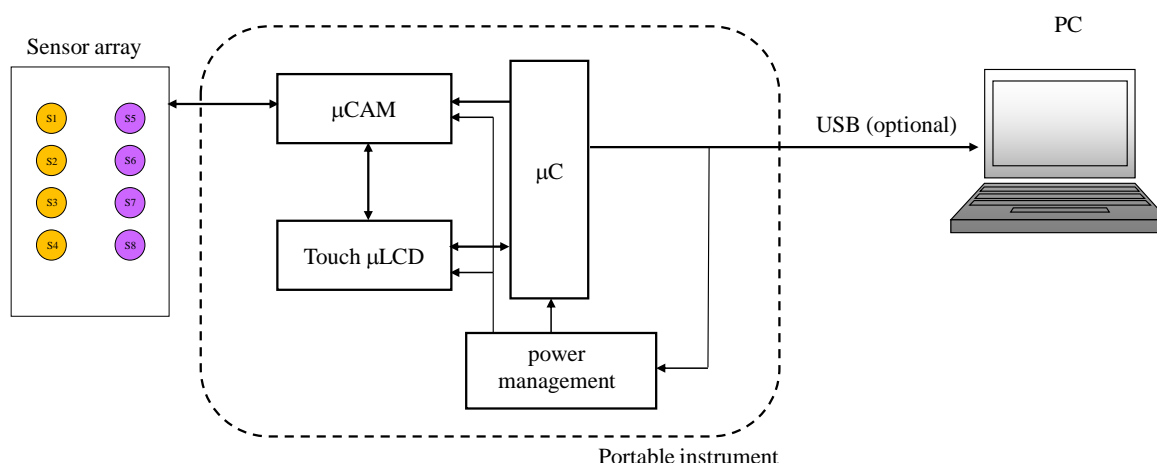


Figure 1: Block diagram of the instrument.

The model of microcontroller used in this instrument is the PIC18F2550 (Microchip Technology Inc., USA) which is a low cost device with an integrated USB module that has been used for developing and calibration purposes. The user can interact with the instrument through a touch micro-

LCD screen model μ LCD-32PT-SGC (4DSystems, Australia) included in the prototype, which also shows the colour information obtained from the sensors. Therefore, there is no need of external elements to handle the instrument. The touch micro-LCD screen integrates 4-wire resistive touch panel which has 240x320 QVGA of resolution and 65K colours. The dimensions of the screen are 56 x 77.6 x 3.7 mm and 3.2' diagonal, which are high enough to present an easy and clear interface to the user. Moreover, the screen integrates an on-board micro-SD memory card adaptor for multimedia storage and data logging purposes. The instrument makes use of a micro-camera model TTL-uCAM (4DSystems, Australia) to capture an image from the sensor array which is shown in the micro-LCD screen. The micro-camera is a module with serial output that allows to acquire images in JPEG or RAW format in different sizes and colour or gray-scale resolutions. Both the micro-camera and the touch-screen provide a set of embedded commands for an easy communication and programming. The main reasons for choosing this model of LCD-screen are the touch function to avoid external elements for user interaction and the high colour resolution which is enough for the explained purpose, achieving a handheld colorimeter.

For this work, a 16-bit colour RGB and RAW format was chosen because of the simplicity in the structure of this format which does not use any compression algorithm. Thanks to the compatibility between the micro-camera and the micro-LCD screen the RAW format permits direct communication between them with no action of the microcontroller or any external memory. However, since RAW is an uncompressed format, the received data from the micro-camera are heavier than JPEG format which increases the time required to obtain the image, but it makes possible a direct treatment of the pixels information with no need of a previous processing.

In Figure 2, a photography of the prototype described is presented. The micro-LCD screen shows an image of the sensor array in which are presented different membranes. The user can select, by touching the screen, the individual sensors to calculate the H coordinate and metals concentration, so that a defective sensor can be ignored. The sensor array is placed at the bottom of the instrument, in a hole built facing the micro-camera, covered by a transparent Mylar polyester sheet, to allow to capture the picture of the membranes which is processed in hindsight.

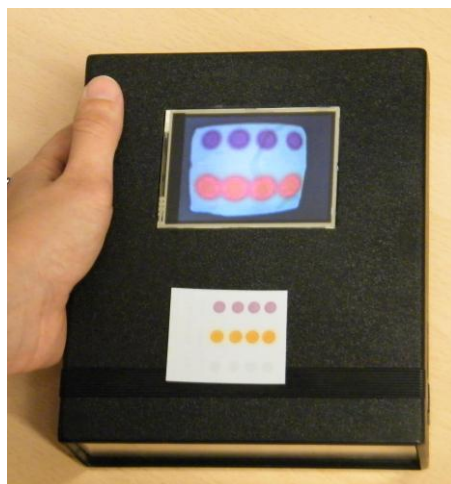


Figure 2: Photography of the instrument.

The prototype has multiple ways to obtain the power supply: from a PP3 battery of 9V through a voltage regulator to generate 5 V, from a AC/DC external adaptor or via the USB port.

3.1 Measurement procedure

The concentration of metals through colour determination of the sensor array is carried out after image processing from the picture of the membranes captured with the micro-camera. The image is taken in an ambient light environment; therefore the prototype has not need of a specific light source to obtain

a fine image. To avoid overexposure in the image, a thin white film of PVC is positioned between the sensor array and the light source to act as an intensity attenuator of the ambient light.

The sensor array is placed by the user in a holder situated facing the micro-camera. The aperture has a piece of transparent Mylar to place the sensor array for taking the image. After the sensor array is positioned in the instrument, the user starts the capture of the picture by touching the micro-LCD screen which was in a sleep mode.

Once the image is presented on the micro-LCD screen, the user can select a particular sensor to obtain its H component and the correspondent metal concentration, as it can be seen in Figure 3. The touch option offers the user the possibility of discarding defective membranes of the image and only takes into account good quality membranes to calculate the concentration of metals. On the other hand it is possible to determine the H component of every membrane at the same time. As the user can select a specific sensor by touching the micro-LCD screen, the position of the sensor array respect to the micro-camera is not critical since the H parameter is determined using the area selected by the user.

The algorithm used to obtain the H value consist of a pixel-by-pixel treatment of the image in which the RGB coordinates are loaded and processed to generate the hue component for the regions of the image corresponding to the metal sensitive membranes. A statistic of these pixels is carried out to determine the mode of the H data which is taken as the value for the whole membrane. After image processing to estimate the hue component, the concentration of copper and zinc can be calculated and shown in the micro-LCD screen.

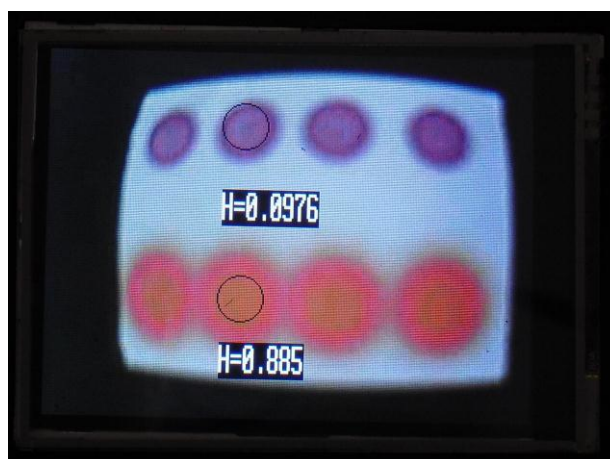


Figure 3: Micro-LCD screen showing obtained H components for two membranes.

4. Results

The characterization of the sensor array was performed using four replicates for each kind of membrane, PAN or ZINCON, using solutions containing the metals ions in a range from 0.06 to 65 mg/l for each metal. The reaction conditions (equilibration time, pH) were studied and optimized using single membranes against each metal ion. A comparison between the response of the prototype and a commercial scanner ScanMaker i900 (Microteck, Taiwan) is shown in Figure 4. The used scanner has a 6400 x 3200 dpi resolution and a maximum optical density of 4.2 and 24 to 48 bits of colour. The H parameter is calculated from the scanned image using the software Matlab r2007b (The MathWorks, Inc, Natick, MA, USA) [7].

As depicted in Figure 4, the response curves obtained with the scanner and the prototype for copper and zinc concentrations present the same behaviour and in both cases are obtained through image-processing of the captured image. Nevertheless, there are some discrepancies on the responses, caused by the different light sources and the lower resolution of colour in the micro-camera. The experimental curves for copper and zinc were modelled by splitting them into linear sections in order to obtain the metal concentration from the H parameter previously determined [9].

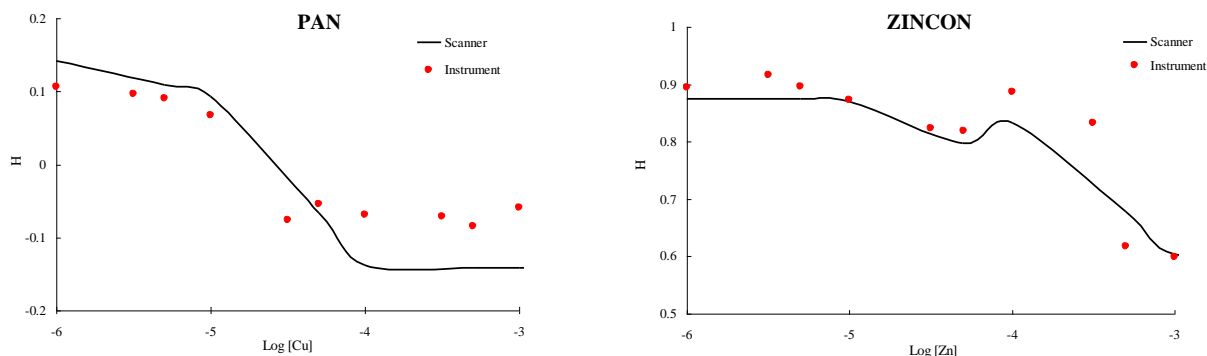


Figure 4: Response of the sensor array for copper and zinc.

5. Conclusions

A handheld colorimeter which uses the hue component of HSV colour space for a colorimetric sensor array to calculate the concentration of metals in solutions such as zinc and copper is presented. The analytical procedure consists of determining the colour changes in two different kind of sensing membranes, PAN or ZINCON, and relating them with variations of the metal concentration.

The H component of the colorimetric sensor is obtained from an image captured with an integrated micro-camera and displayed in a in a touch-micro LCD screen. The main advantage of the direct communication between the micro-camera and the LCD screen is to avoid the necessity of using an external memory to save the image, since the colour information of each pixel can be directly read from the screen. The prototype works in an ambient light environment; therefore there is no need of a specific light source integrated on the prototype. Because all of this, the result is a simple electronic design with a reduced number of electronic components.

A study of the membranes response in solutions with different metals concentration was carried out to obtain a complete characterization of the instrument. The obtained curves have a good agreement with the acquired models using a reference instrument, in this case, a commercial scanner. Although in this work the membranes response have been modelled only for a unique specific metal in a solution, future work will be focused in determine metals concentration in mixtures.

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