The hyphenated CSPT-potentiometric analytical system: An application for vegetable oil quality control

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ABSTRACT

The computer screen photo assisted technique (CSPT) has been used to develop a hyphenated optical-potentiometric sensing array, based on porphyrinoid materials dispersed into PVC membranes.

Sensing layers have been deposited onto indium tin oxide (ITO) glass slides, which were exploited as electrodes, for potentiometric measurements, and chromophore spots, to obtain CSPT data. Both measurements were contemporaneously carried out in the hyphenated sensing platform.

The performances of the hyphenated sensing array were first tested for the detection of model analytes, characteristics of vegetable oil matrices, and then evaluated in the discrimination of real samples of olive and seed oils. The results obtained demonstrated that the hyphenated system affords a significant improvement of information and oils classification with respect to the individual potentiometric and optical components.

1. Introduction

In the last few years the quest for devices able to monitor the chemical composition of different matrices has intensified for both environmental and security concerns [1,2]. The progress of analytical chemistry methods and the parallel development of scientific instrumentations has allowed the necessary performances for the detection of analytes with high selectivity and sensitivity in complex mixtures [3,4]. However in many cases both high costs and time-consuming protocols have hampered the exploitation of these methods in some practical applications. From this point of view chemical sensors seem to be the solution of such limitations, because they can conjugate both low cost with rapid response time. On the other hand, it should be considered that the low selectivity manifested by the majority of the developed solid-state chemical sensors is the related drawback that obstacle their successful application in many fields.

For this reason a great effort has been devoted to improve the performances of chemical sensors, particularly in the preparation of the sensing materials [5,6]. These sensor components are key subunits to determine the selectivity features of the resulting devices and the advance in nanoscience and nanotechnology has opened new promising perspectives in this field.

On the other hand, the hyphenation of two different techniques is a quite common and successful approach in analytical chemistry and gas chromatography–mass spectroscopy (GC–MS) is probably one of the most famous examples. Following this route, the development of sensing systems where two different transduction systems are used contemporaneously could represent an alternative and promising approach to develop high performance sensor systems [7]. In the case of chemical sensors this approach is, however, difficult, because it is necessary to ensure the compatibility of the sensing material with both of the transduction mechanisms exploited.

From this point of view porphyrins could represent a suitable solution, because the richness of properties of such compounds allows their exploitation with a wide range of sensors based on different transduction mechanisms [8,9]. We have been involved in this type of work and we have developed porphyrin based chemical sensors and sensor arrays, which have been exploited for applications in both gaseous and liquid phase [10,11].

In particular, since they have been called "the pigments of life", porphyrins are successful components for optical sensors and we have recently demonstrated their performances in a sensing platform constituted by low-cost advanced optical equipments, such as computer screens and webcams, whose properties can be usefully exploited in instrumentation for optical measurements. This technique is known as the computer screen photo assisted technique (CSPT) [12]; we demonstrated the development of a sensor array able to discriminate mixtures of gases and volatile compounds, by

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using different metalloporphyrin spots deposited on transparent glass or plastic slides [13–15]. The interaction with volatiles can lead to significant variations of absorbance and/or luminescence properties of the porphyrin complex that can be detected by CSPT.

On the other hand, porphyrins have been widely used as ionophores in potentiometric ion selective electrodes [16,17] and we have developed an electronic tongue based on such devices [18–20].

Considering the promising results showed by porphyrins in these sensors, we decided to explore the possibility to use the CSPT platform together with potentiometric measurement, in order to develop a combined optical and potentiometric system, with the hope to increase the sensing performances of the hybrid platform with respect to the results of the subunits. In this work we report the development of such a system and its exploitation in the analysis of vegetable oils, chosen as an example close to real applications.

2. Experimental

2.1. Reagents

Poly(vinyl chloride) (PVC), high molecular weight, bis(2-ethylhexyl) sebacate (DEHS), o-nitrophenyl octyl ether (o-NPOE) (plasticizers) and tridodecylmethyl ammonium chloride (TDMACl) (lipophilic cationic additive) were purchased from Fluka. Tetrahydrofurane (THF), ethanol and methanol were from Carlo Erba Reagents. Oleic, linolenic, linoleic, L-glutamic, L-ascorbic acids and L-leucine were from Sigma–Aldrich. All chemicals were of analytical grade and used without further purification, while THF was freshly distilled prior to use. Free base 5,10,15-triphenylcorrole (TPCorH$_3$) and 5,10,15-triphenylcorrolato Mn chloride (TPCorMnCl), 5,10,15-triphenylcorrolato Fe chloride (TPCorFeCl), 5,10,15-tris(4-tert-butylphenyl)corrolato Cu (TtButPCorCu), chloride salt of [5-(4-(3-trimethylammonium) propyloxy) phenyl)-10,15,20-triphenylporphyrinato] Co (AMTPPorCo), 2,3,7,8,12,13,17,18-octaethylporphyrinato Pt (OEPorPt) were prepared according to the literature methods [21,22]. All the solutions were prepared with distilled water.

2.2. Sensor preparation and evaluation

Membranes of 100 mg weight consisted of 1% (wt.) of ionophore, PVC/plasticizer (1:2) polymeric matrix and varying amounts of lipophilic additive. All components were dissolved in 1 mL of THF and the mixture was casted on transparent indium tin oxide modified glass slide (ITO, Sigma–Aldrich, conductive layer 300 Å, surface resistivity 30–60 Ω/sq). Solvent was allowed to evaporate overnight. Potentiometric and optical properties of sensors were evaluated one day after preparation. The compositions of the PVC plasticized membranes are given in Table 1.

Table 1
Composition of polymeric membrane sensors utilized in CSPT-potentiometric analytical system.

| No.	Membrane components		
	Ionophore, 1 wt%	Plasticizer	Lipophilic additive[a]
1	TPCorFeCl	DEHS	–
2	TtButPCorCu	DEHS	–
3	TtButPCorCu	DEHS	TDACl, 40 mol%
4	OEPorPt	DEHS	–
5	OEPorPt	oNPOE	TDACl, 10 mol%
6	TPCorMnCl	oNPOE	–
7	AMTPPorCo	oNPOE	–
8	TPCorH$_3$	DEHS	–

[a] mol% relative to the ionophore content.

Sensors were soaked in 0.01 M KCl at least for 12 h before testing.

The sensor array was composed of 7 or 8 potentiometric solvent polymeric membranes deposited on an ITO modified glass slide. Separate electrical channels were realized by cutting the conductive ITO layer, and they were connected to a high-impedance analog-to-digital potentiometer (Smartronix srl, Italy). The potential changes of sensors were measured versus a Saturated Calomel reference Electrode (SCE, AMEL, Italy), immersed in the outlet chamber. All measurements were performed at room temperature (∼22 °C), carried out with the following type of potentiometric cell: SCE; KCl sat/sample solution//membrane//ITO WE.

2.3. CSPT-potentiometric flow-through measurement set-up

The flow-through cell had an internal volume of 90 μL and permitted an easy integration of the potentiometric sensor array within the cell, as well as a simple replacement of individual sensors. A photograph of the developed flow-through cell with the size of 5 cm × 3 cm × 0.7 cm and flow channel of 3 cm length is shown in Fig. 1. The cell was made from two separate blocks of transparent polymer (plexiglass), a rectangular 3.5 cm × 1.5 cm, 1.5 mm thick silicone spacer with 3 cm × 0.1 cm cut out flow channel, was placed between two cellblocks. In order to register the optical response, the sensor array was placed in the transparent flow-through cell illuminated from the backside by 2.5″ color TFT-LCD panel (Prime View International Co.). A webcam (Logitech Quickcam® for Notebook), with a detector operating at a resolution of 352 × 288 pixels
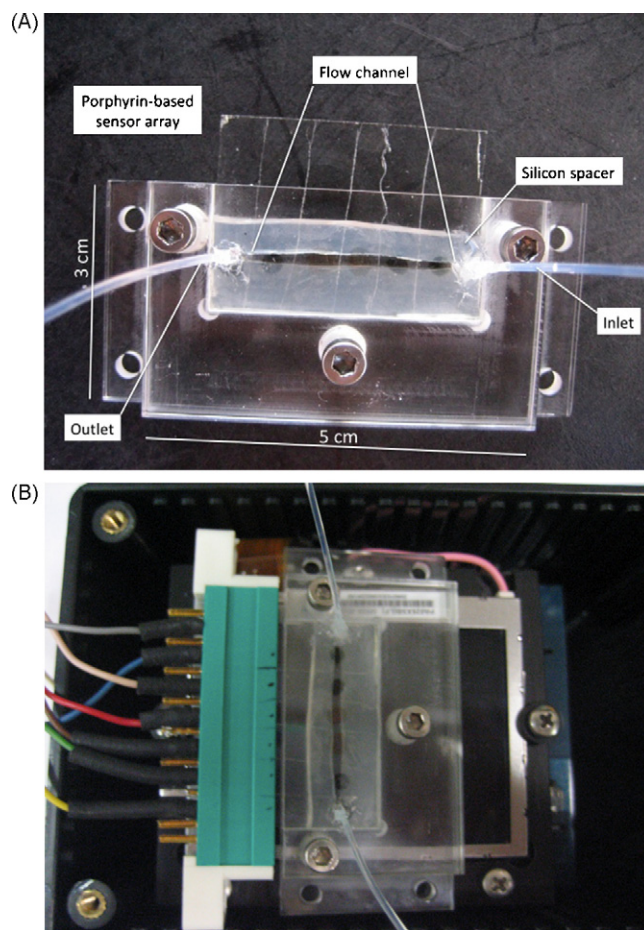
Fig. 1. Picture of the designed flow-through cell containing sensor array (A), cell assembled with its backside-placed on a TFT-LCD screen and connections to potentiometer (B).