

Voltammetric determination of food colorants using a polyallylamine modified tubular electrode in a multicommutated flow system

M. Luísa S. Silva^a, M. Beatriz Q. Garcia^{a,*}, José L.F.C. Lima^a, E. Barrado^b

^a *Requimte, Departamento de Química-Física, Faculdade de Farmácia da Universidade do Porto, Rua Aníbal Cunha, 164, 4099-030 Porto, Portugal*

^b *Departamento de Química Analítica, Facultad de Ciencias de la Universidad de Valladolid, Prado de la Magdalena s/n, 47005 Valladolid, Spain*

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Abstract

This work describes the construction of a polyallylamine modified tubular glassy carbon electrode and its application in the electroreduction of food azo colorants (tartrazine, sunset yellow and allura red) by square wave voltammetry. The electrode modification prevented the surface fouling and, simultaneously, enhanced the analytical signal intensity. The developed unit was coupled to a multicommutated flow system which, given the complexity of samples, was designed to allow the implementation of the standard additions method in an automatic way, using only one standard solution.

The described method presented a linear range up to about $2.0 \times 10^{-4} \text{ mol l}^{-1}$ for the referred colorants, with a detection limit of $1.8 \times 10^{-6} \text{ mol l}^{-1}$ for tartrazine, $3.5 \times 10^{-6} \text{ mol l}^{-1}$ for sunset yellow and $1.4 \times 10^{-6} \text{ mol l}^{-1}$ for allura red. The method was applied in the analysis of these colorants in several food samples, and no statistically significant difference between the results obtained by the proposed and the comparative method (HPLC) was found, at a 95% confidence level. Repeatability in the analysis of samples (expressed in R.S.D.) was about 3% ($n = 10$).

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1. Introduction

The use of colorants as food additives has been exploited by food industry with the aim of enhancing the aesthetic appeal of foodstuffs to the consumer. Azo colorants, such as tartrazine (E102), sunset yellow (E110) and allura red (E129), constitute one of the major synthetic colorant groups, used commercially in food, drinks, medicines and cosmetics. Its vast application is due to an inexpensive production and to a large colour spectrum that can be obtained, when compared with natural colorants [1].

Some colorants can trigger adverse effects, namely tartrazine, which can cause the appearance of allergies and asthma [2] and childhood hyperactivity [3]. The colorants allowed to be used in food products and the authorized maximum levels are regulated by the Portuguese [4] and European [5] legislation.

Quantification of colorants in food products prompted the need for the development of analytical methodologies, namely

spectrophotometric [6–12] and chromatographic methods [13]. Voltammetric methods were also reported [1,2,14–19], presenting high sensitivity, simplicity and low cost. However, all of them use mercury electrodes, whose toxicity justifies the search for alternative electrode materials. Besides, the majority of the referred methodologies use the standard additions method for sample analysis, which is carried out in a non-automatic way, increasing the slowness of measurements and demanding specialized operators.

In this work, the construction, evaluation and application of a polyallylamine modified tubular glassy carbon electrode is proposed, as an alternative to the use of mercury electrode, for the determination of food colorants, which is based on the electroreduction of the azo dyes. For the first time, the modification of a tubular glassy carbon electrode with a polyelectrolyte coating is described, taking advantage of the ion-exchange and permselectivity characteristics of the polyallylamine film in relation to negatively charged species.

The developed unit was coupled to a multicommutated flow system [20], which was designed to enable the implementation, in an automatic way, of the standard additions method, considering the complexity of samples.

* Corresponding author. Tel.: +351 222078966; fax: +351 222004427.
E-mail address: bquinaz@ff.up.pt (M.B.Q. Garcia).

2. Experimental

2.1. Reagents and solutions

Reagents of p.a. quality were used, without having been subjected to any additional purification. In the preparation of solutions, water purified by the Millipore Milli Q system (conductivity $<0.1 \mu\text{S cm}^{-1}$) was used.

As supporting electrolyte and, simultaneously, carrier solution in the flow system, a hydrochloric acid solution 0.5 mol l^{-1} , prepared by dilution of concentrated HCl (Merck), was used.

Stock solutions of tartrazine (Sigma), sunset yellow (Aldrich) and allura red (Aldrich) $1.0 \times 10^{-3} \text{ mol l}^{-1}$ were prepared by weighing and dissolution of the solid colorants in HCl 0.5 mol l^{-1} . Working solutions were prepared by dilution of the respective stock solutions in HCl 0.5 mol l^{-1} .

For the working electrode surface coating, a polyallylamine hydrochloride solution 15.0 g l^{-1} , prepared by weighing and dissolution of the correspondent quantity of the polyelectrolyte (Aldrich), was used.

Solid samples were dissolved in HCl 0.5 mol l^{-1} warmed to about 70°C , centrifuged for 10 min at 3000 rpm and filtered. Liquid samples were diluted in HCl 0.5 mol l^{-1} and filtered.

2.2. Equipment

In the developed multicommutated flow system (Fig. 1A) solutions and samples were aspirated by an automatic burette (Crison model Micro BU 2031) equipped with a 10 ml syringe. To control the selection and direction of solutions and samples inside the manifold four 3-way solenoid valves (161 T031, NRResearch) were used. A homemade power driver, based on an

integrated ULN 2003 circuit, was used to operate solenoid valves [21]. Control of the analytical system was made through an interface card (PC-LABCard model PCL-711B, Advantech) and a microcomputer. The software was developed in QuickBasic Version 4.5 (Microsoft) and allowed to control the functioning of the burette and the solenoid valves. Connection between the components of the flow system was made with Teflon tubes (Omnifit), of 0.8 mm inner diameter. Voltammetric measurements were carried out in an Autolab electrochemical system (Eco Chemie model PGSTAT 10) and data acquisition was accomplished through GPES software (Version 4.6).

Scanning electron microscopy (SEM) micrographs were obtained using an electron microscope JEOL, model JSM-35C.

To perform sample analysis by the comparative method, a chromatograph Varian, model 9012, with UV-Vis detector, model 9050, was used. The HPLC system was equipped with a column C18 ($150 \text{ mm} \times 4.6 \text{ mm i.d.}$ and particle size $5 \mu\text{m}$) Waters Spherisorb ODS2.

2.3. Voltammetric detector with a polyallylamine modified tubular electrode

Usually, in multicommutated flow systems, solutions are aspirated instead of being propelled, which simplifies the flow manifolds since, in this case, only one propulsion device is needed for the driving of all solutions. As a consequence, flow systems present an inner pressure lower than the atmospheric pressure, demanding that all manifold components, including the detector, are tightly fixed, in order to avoid air entrance. The construction of the voltammetric detector was based in a tubular detector with modified electrodes recently described [22], which demonstrated to have the required robustness to be used in flow systems in which solutions are aspirated.

The detector, of tubular configuration (Fig. 1B), was constituted by a central Perspex support, which encased the working and auxiliary electrodes, both of glassy carbon, with 2.0 mm thickness and a central orifice of 0.8 mm diameter (this value was diminished after the surface coating with polyallylamine solution), being firmly fixed to the central support by two rubber disks, also perforated in the centre. A Metrohm (Ag/AgCl-KCl 3.0 mol l^{-1} , model 6.0727.000) electrode was used as the reference electrode, fixed by a threaded screw to the Perspex support. Electric contact with working and auxiliary electrodes was established through two metallic contacts threaded into the Perspex support. The tubular detector had an inner volume of $15.0 \mu\text{l}$ (volume between working and auxiliary electrodes).

For cleaning and modification (coating of the active surface) of the working electrode, this was withdrawn from the tubular detector and was firstly polished, using a cotton thread soaked in alumina aqueous slurry of $0.075 \mu\text{m}$ and washed with deionised water. The surface coating, by droplet evaporation method, consisted in the deposition of $20 \mu\text{l}$ of polyallylamine hydrochloride solution 15.0 g l^{-1} directly into the central orifice of the electrode. It was kept at 70°C , and was overturned several times until the complete evaporation of the solvent (about 15 min), as a way to assure uniformity of the deposit on the cylindrical wall of the electrode.

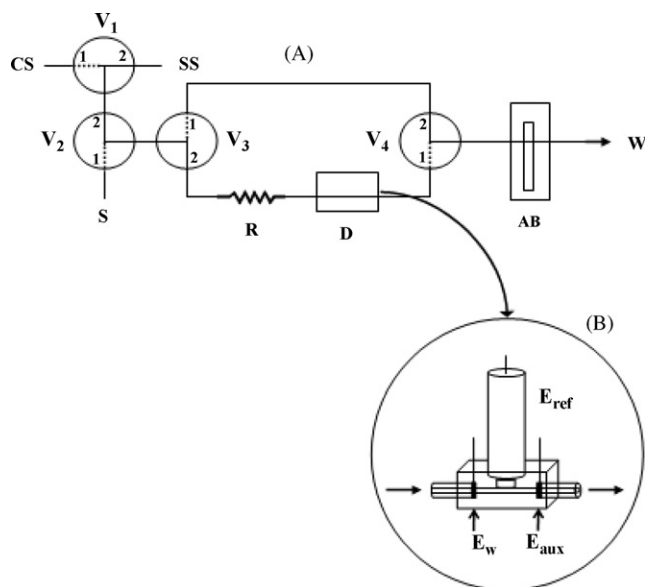


Fig. 1. (A) Multicommutated flow system for food colorants determination: V_1 , V_2 , V_3 and V_4 , three-way solenoid valves; CS, carrier solution ($\text{HCl } 0.5 \text{ mol l}^{-1}$); SS, standard solution $1 \times 10^{-4} \text{ mol l}^{-1}$; S, sample; R, reactor; D, tubular voltammetric detector; AB, automatic burette equipped with a 10 ml syringe; W, waste. (B) Schematic representation of the tubular detector: E_{ref} , reference electrode; E_w , polyallylamine modified working electrode; E_{aux} , auxiliary electrode.

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