Talanta 109 (2013) 203–208

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Application of quantum dots in clinical and alimentary fields using multicommutated flow injection analysis

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ARTICLE INFO

Article history:
Received 19 November 2012
Received in revised form
29 January 2013
Accepted 5 February 2013
Available online 13 February 2013

Keywords:
CdTe quantum dots
Multicommutation
Quenching
Food
Vitamin
Automation

ABSTRACT

In recent years, the number of scientific papers regarding the use of quantum dots (QDs) has increased almost exponentially, especially emphasizing their use for new applications and describing new approaches. One of the future trends in the development of new methods of analysis is the use of automated methodologies. Among them, Multicommutated Flow Injection Analysis has been here selected in order to show its potentiality in pharmaceutical and food analysis.

Using water-soluble CdTe QDs modified by mercaptopropionic acid, a flow system was developed for the determination of ascorbic acid. The system was based on the quenching effect produced by ascorbic acid on the fluorescence of QDs. Under the optimized conditions, the relationship between the fluorescence intensity of the QDs and ascorbic acid concentration was linear in the range of 12–250 μg mL^{-1}, obtaining a sample throughput of 68 determinations per hour. The proposed method was applied to the determination of ascorbic acid in pharmaceutical formulations, goji capsules and fruit juices. The results obtained were in good agreement with those showed by a reference method, so indicating the utility of the proposed method in the clinical and alimentary fields.

1. Introduction

Quantum dots (QDs) are colloidal semiconductor nanocrystals formed from group II–IV, III–V or IV–VI materials, such as those made of CdSe and CdTe. They have a narrow distribution density of energy states, strongly dependent on the dimensions of the confining potential with electronic confinement occurring in all spatial dimensions (3-D). These nanoparticles display superior luminescent properties, including high quantum yield of fluorescence, broad excitation spectrum, narrow/symmetric emission spectrum, size- and composition-tunable emission wavelength, high photobleaching threshold and excellent photostability. Therefore, thanks to recent advances in nanotechnology and nanomaterials, QDs are replacing conventional organic fluorophores for the design of fluorescence chemical and biological probes with different applications, such as the determination of biomolecules [1–4]. The scientific references found in the literature concerning QDs have increased throughout the years, with more than 4000 papers published each year over the last decade [5]. This productivity points out the wide acceptance by the scientific community of QDs for the development of new innovations and applications. In recent years several articles have been published regarding the use of QDs for the determination of contaminants in food samples [6–12]. Different analytical approaches have been used, such as immunosorbent assays [12] or the use of capillary chromatography [6] or capillary electrophoresis [7,11] as separation techniques. Other active field of research is the analysis of pharmaceutical formulations [13–16]. However, despite the great number of analytical applications making use of QDs nanotechnology, only a very restricted number of works are based on automated approaches [14,17–19], especially in food analysis.

The use of automated flow methodologies allows the development of environmental-friendly methods and to prevent operators to come into contact with toxic materials. The main goal of the present work is to combine Multicommutated Flow Injection Analysis (MCFIA) and QDs, showing its potentiality for the analysis of pharmaceutical and food samples. This coupling has not been described yet in scientific literature. In MCFIA, the employment of discrete commutation devices (solenoid valves) allows an easy reconfiguration of the manifold by means of the software procedure. Each analytical step can be independently implemented increasing the versatility of the flow system. This methodology combines the advantages of Flow Injection Analysis (FIA) such as high injection throughput, with those given by Sequential Injection Analysis (SIA), i.e. minimal reagent consumption and wastes generation [20,21], being this last characteristic necessary and very important that takes into account the presence of heavy metals in QDs structure.

Ascorbic acid (AA, vitamin C), an important water-soluble antioxidant in chemical and biological systems, has been selected as a model analyte. This nutrient, which can be supplied only by

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0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.02.019

the diet, is a natural compound that appears in fruits and vegetables, and it is also used as an essential additive in the food processing industry. Therefore simple, sensitive and selective methods, which can provide precise and accurate results, are required for its determination. To date, numerous methods have been developed for the analysis of AA in food (fruits and vegetables), pharmaceuticals and biological fluids including enzymatic [22,23], electrochemical [24,25], spectrophotometric [26,27], fluorimetric [28,29] and chromatographic [30,31] techniques. However, complicated extraction procedures, high cost, long operation time and lack of selectivity were sometimes found in their application.

Mercaptopropionic acid (MPA) capped CdTe QDs with different particle sizes were successfully synthesized in aqueous medium and applied to the quantitative determination of AA in different pharmaceuticals and food samples (goji capsules and cranberry, apple and orange juices). The developed approach was based on the monitoring of QDs' fluorescence quenching produced by AA, using MCFIA as the flow system. A reference method was also used in order to check the results obtained by the proposed method, observing no significant statistical differences between both methods.

2. Materials and methods

2.1. Reagents and solutions

CdTe QDs were synthetized using tellurium powder (200 mesh, 99.8%), sodium borohydride ($NaBH_4$, 99%), cadmium chloride hemi (pentahydrate) ($CdCl_2 \cdot 2.5H_2O$, 99%) purchased from Sigma-Aldrich (St. Louis, MO, USA); and 3-mercaptopropionic acid (MPA, 99%) and absolute ethanol (99.5%) obtained from Fluka (St. Louis MO, USA) and Panreac (Barcelona, Spain), respectively. For adjusting the alkalinity of the reaction medium, a 1.0 mol L^{-1} NaOH solution was used. QDs solutions were prepared by dissolving a certain amount of the dried nanocrystals in ultrapure water and used directly.

AA ($\geq$ 99%), sodium hydroxyde (NaOH, 98%), disodium hydrogen phosphate 2-hydrate ($Na_2HPO_4 \cdot 2H_2O$, 99%) and the excipients used in the interference study were obtained from Sigma (Madrid, Spain). AA standard solutions of 500 mg L^{-1} were prepared daily and were protected from light using aluminum foil.

2.2. Instrumentation

For the characterization of the synthesized QDs, absorbance and fluorescence spectra were recorded using a Jasco V-660 spectrophotometer and a PerkinElmer LS-50B luminescence spectrometer, respectively. QDs centrifugation was performed with a ThermoElectron Jouan BR4I refrigerated centrifuge.

The flow system (Fig. 1) was built with: one four-channel Gilson Minipuls-3 peristaltic pump (Villiers le Bel, France), fitted with a rate selector and pump tubing type Solvflex (Elkay Products, Shrewsbury, MA, USA); three 161T031 NResearch three-way solenoid valves (Neptune Research, MA, USA); and an electronic interface, based on ULN 2803 integrate circuits, to generate the electric potential (12 V) and current (100 mA) required to control the valves. PTFE tubing (0.8 mm i.d.) and methacrylate connections were also used. The software for controlling the system was developed by our research group using Visual Basic 6.0.

Luminescence measurements in the flow system were performed with a Cary-Eclipse Luminescence Spectrometer (Varian Inc., Mulgrave, Australia) controlled by a computer equipped with a Cary-Eclipse (Varian) software package for data collection and treatment. Instrument excitation and emission slit widths were set at 5 and 10 nm, respectively. The detector voltage was 670 V and the excitacion and emission wavelengths were 285 and 628 nm, respectively. A Hellma flow cell 176.752-QS (25 µl of inner volume and a light path length of 1.5 mm) was used too. All experiments were carried out at room temperature.

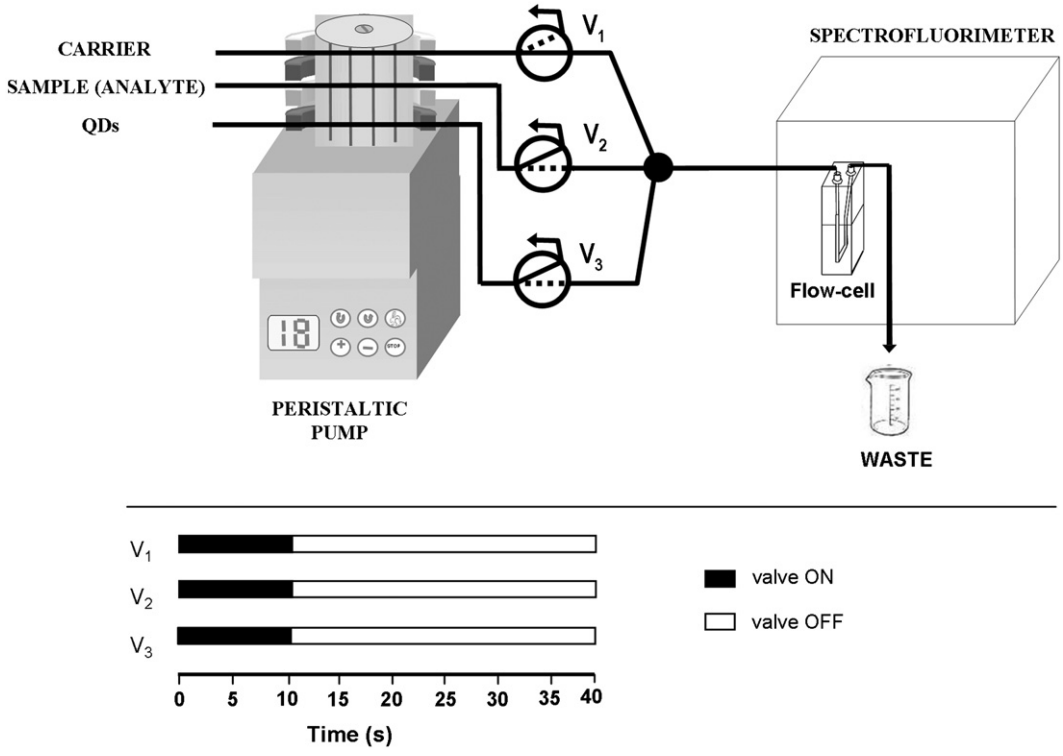

Fig. 1. MCFIA manifold. Scheme of the solenoid valves (V_1, V_2 and V_3) procedure is shown.