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Improved spectrophotometric determination of paraquat in drinking waters exploiting a Multisyringe liquid core waveguide system

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ABSTRACT

A novel Multisyringe flow injection analysis (MSFIA) system combined with a 200 cm long pathlength liquid core waveguide (LCW) has been developed enabling for the first time the sensitive spectrophotometric determination at $\mu g\,L^{-1}$ levels of the herbicide paraquat (Pq^{2+}) in drinking waters. The proposed system is a simple, economic and fast alternative for obtaining the first evidence of paraquat pollution prior the use of more complex instrumental techniques.

The proposed methodology is based on the production of a blue free radical by reaction of Pq^{2+} with ascorbic acid (partially oxidized with potassium iodate) in basic medium. Limits of detection and quantification as low as 0.7 and 2.3 $\mu g\,L^{-1}$, were obtained respectively. The working range is linear up to a concentration of 250 $\mu g\,L^{-1}$ of Pq^{2+}. The injection throughput of the proposed method is 34 h^{-1}. The results obtained with the LCW are compared with those using a conventional 1 cm flow cell. The automation of standard addition procedures has been studied and implemented for samples causing matrix effects. Finally the proposed system has been applied to the determination of paraquat in drinking water samples.

1. Introduction

Paraquat (Pq^{2+}, 1,1′-dimethyl-4,4′-bypiridilium) is a quaternary ammonium compound part of a group of herbicides known as "quats". Pq^{2+} is one of the most widely used "quats" and is a non-selective contact herbicide for crop desiccation, pasture renovation, crop production with limited or no tillage and selective weed control. Undesirable effects of Pq^{2+} are accidental toxicity for plants and aquatic organisms and toxicity in humans [1]. Cases of intoxication of Pq^{2+} in humans are often related to suicides [2]. Pq^{2+} is a banned substance in the European Union. Furthermore, the US environmental Protection Agency (EPA) has included Pq^{2+} in a priority list of hazardous chemicals and established a drinking water equivalent level of 200 $\mu g\,L^{-1}$ and a maximum contaminant level goal of 3 $\mu g\,L^{-1}$ for Pq^{2+} in drinking waters [3,4]. Pq^{2+} is polar, highly soluble in water and has a low volatility. According to its properties, this compound is usually determined by ion-pair HPLC with UV detection [5], being this one the method recommended by the EPA [6].

On the one hand, other separation techniques have been proposed for the determination of Pq^{2+} such as capillary electrophoresis [7], capillary electrophoresis-mass spectrometry [8] or liquid chromatography–mass spectrometry [9,10]. In these cases high selectivity and sensitivity are reached, but additional sample treatments are required, being methodologies with low analysis throughputs and high costs. On the other hand, several electrochemical methods have been proposed for the determination of Pq^{2+} [11,12]. These methods have the advantage of low cost and portability for field studies but their limited sensitivity also limits their direct applicability to the analysis of samples with a relatively high Pq^{2+} concentration.

Another alternative for the determination of Pq^{2+}, is its spectrophotometric (SPM) determination by reaction with sodium dithionite in alkaline medium. Pq^{2+} is reduced forming a blue free radical followed at 600 nm [13–15]. The main drawback of this methodology is the instability of the dithionite reagent, being replaced later by ascorbic acid (AA) [16]. The AA method was improved by oxidizing some of the AA with potassium iodate [17]. The subsequent automation of this method was performed using the flow injection analysis (FIA) technique [18]. Recently, Infante et al. [19] developed a multipumping flow system (MPFS) [20] providing an improved mixing achieved by using solenoid micropumps in combination with a homemade flow cell with an optical path of 10 cm for improved sensitivity.

A gradual improvement in the SPM determination of Pq^{2+} is observed, being these methodologies economic and high throughput alternatives prior a more accurate confirmation by using separation techniques, such as HPLC–MS. This fact was defined as Vanguard-Rearguard analytical strategies [21]. But at the moment,

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the SPM quantification of trace levels of Pq^{2+} according with the EPA goal (3 μg L^{-1}) is not a feasible task without utilizing additional sample treatments.

The aim of this work is the development of a fast and sensitive alternative for the determination of Pq^{2+} reaching the goal criteria established by the EPA. By this reason, a Multisyringe flow injection system [22–24] coupled to a 200 cm long pathlength liquid core waveguide (LCW) has been developed. The use of the LCW enables the possibility to increase the sensitivity of a SPM method due to the increase of the effective optical pathlength [25–28], but without require high sample volumes. The MSFIA manifold used as a front end of the LCW enables the robust automation of the reaction procedure for the development of the colored product.

We define the proposed methodology as a vanguard strategy prior to the use of the EPA method or other more sophisticated methods based on separation techniques.

2. Reagents

All chemicals used were of analytical-grade quality and were used without further purification. Millipore-quality water was used to prepare solutions.

The reagent R1 was prepared by dissolving 2 g of ascorbic acid (Fluka, http://www.sigmaaldrich.com), 0.5 g of potassium iodate (Sigma–Aldrich, http://www.sigmaaldrich.com) and 1 g of ethylenediaminetetraacetic acid (Panreac, http://www.panreac.es) in 1 L of water. The reagent R2 is a 3 mol L^{-1} sodium hydroxide solution (Panreac). A 1000 mg L^{-1} paraquat (Pq^{2+}) stock solution was prepared by dissolution of the dichloride salt (Riedel-de-Haen, http://www.sigmaaldrich.com) in water. Working solutions were prepared by dilution of the stock solution with distilled water. Different bottled drinking water samples were purchased from local supermarkets.

3. Materials

Fig. 1 depicts schematically the proposed set-ups. A multisyringe burette (Crison, http://www.crison.es) was equipped with three glass syringes (S1–S3, Hamilton, http://www.hamiltoncompany.com), which were all mounted onto a common metallic bar and every one of them was provided with a solenoid valve (V1–V3, N-Research, http://www.nresearch.com). As a result, all syringes were operated simultaneously. Depending on the position of the solenoid valves, the fluids contained in the syringes were loaded (PK, pickup) or dispensed (DP, dispense) towards the flow network (on) or towards the reservoirs (off).

Syringe S1 (10 mL) contains the carrier (distilled water) and performs sample loading into the flow network and its subsequent injection towards the detector. S2 and S3 are of 5 and 2.5 mL respectively, and are used for the injection of R1 and R2 in a forward flow mode.

For sample introduction were used two additional solenoid valves (Fig. 1A, V4–V5, Takasago, http://www.takasago-elec.com) connected to a peripheral port of the Multisyringe module. In some experiments an eight-port selection valve (Fig. 1B), Crison was used instead of V4–V5.

All the tubing of the system was made of polytetrafluoroethylene (PTFE) 0.8 mm i.d. including a 6 m holding coil (3 mL volume) and various knotted reaction coils of different length were used.

The detection system is composed of a deuterium–halogen light source (Ocean Optics, http://www.oceanoptics.com), two optical fibers 400 μm in diameter (Ocean Optics), a flow cell composed by a 200 cm Type II Teflon AF liquid core waveguide (World Precision Instruments, http://www.wpiinc.com; internal diameter 550 μm, effective pathlength 200.0 ± 0.5 cm, internal volume 480 μL), and a USB2000 miniaturized fiber-optic spectrophotometer (Ocean Optics), connected to a computer via a USB interface. Dual-wavelength spectrophotometry (610 and 720 nm) was used to compensate possible errors caused by changes of the refractive index.

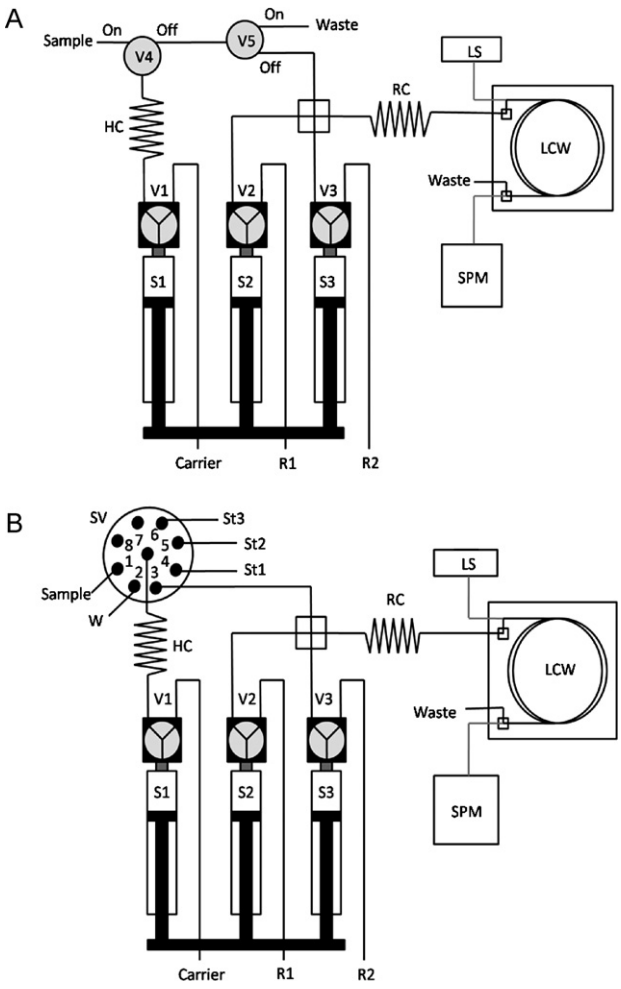

Fig. 1. Schematic depiction of the developed MSFIA systems for the determination of Pq^{2+}. (A) MSFIA system for the direct determination of Pq^{2+}. (B) MSFIA system for the sequential production of a sample-standard plug and subsequent forward flow determination of Pq^{2+} by the standard addition method. S1–S3, syringes; V1–V5, solenoid valves; R1–R2, reagents; W, waste; HC, holding coil; RC, reaction coil; SPM, spectrophotometer; LS, light source; SV, selection valve; St1–St3, Pq^{2+} standards.

Instrumental control and data acquisition were performed by using the AutoAnalysis 5.0 software package (Sciware, http://www.sciware-sl.com).

4. Analytical procedure

The main procedure developed for the determination of Pq^{2+} in waters using the systems depicted in Fig. 1 is based on the next steps:

1. The volume of the syringes is adjusted by dispensing 1.2 mL at 10 mL min^{-1} with all valves in "Off" position.
2. Using the system depicted in Fig. 1A, a volume of 1.2 mL of sample is loaded in the holding coil at 5 mL min^{-1} with valves 1 and 4 in "On" position. Using the system depicted in Fig. 1B, 0.2 mL of sample (SV pos. 1) followed by 0.2 mL of a standard solution (located in positions 4, 5 and 6 of the SV) are loaded into the HC.