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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.

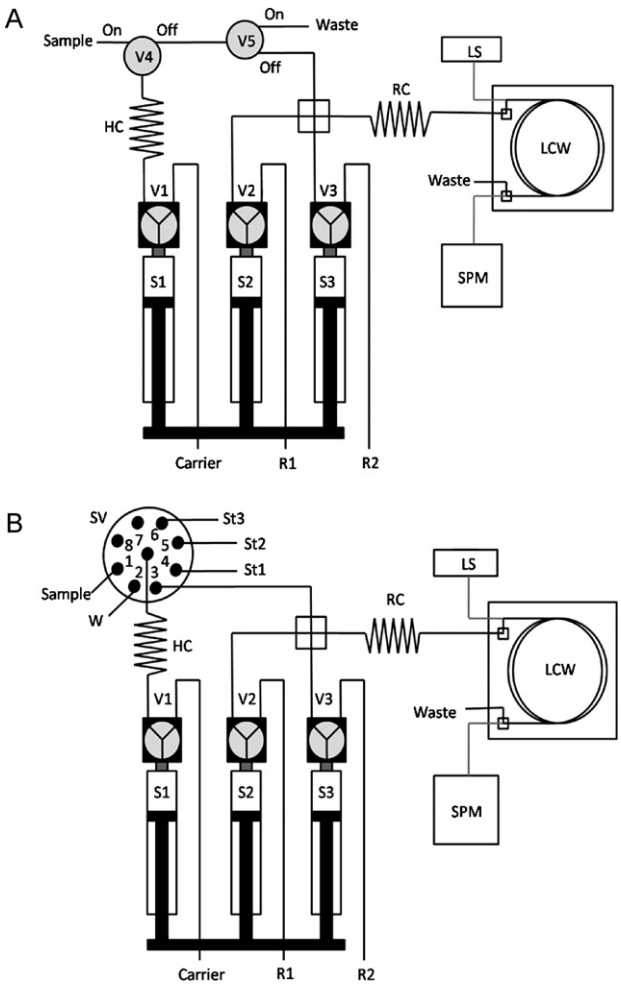

Fig. 1. Schematic depiction of the developed MSFIA systems for the determination of Pq^{2+}. (A) MSFIA system for the direct determination of Pq^{2+}. (B) MSFIA system for the sequential production of a sample-standard plug and subsequent forward flow determination of Pq^{2+} by the standard addition 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.

These steps are repeated 3 times in order to load a total volume of 1.2 mL.
3. The spectrophotometer starts the data acquisition each 0.4 s.
4. A volume of 3.5 mL of carrier containing the sample (or the sample-standards plug) is injected towards the detection system at a flow rate of 3 mL min^{-1} with valves 1, 2 and 3 in "On" position. In this step the sample is mixed with R1 and R2 at the confluence point. The reaction is developed in the knotted reactor and the reaction plug flows across the liquid core waveguide being finally deposited in a waste reservoir. In the system of Fig. 1B this step is identical and the SV is connected to position 3.
5. The data acquisition is stopped.
6. A volume of 1 mL of carrier (valve 1 "On") is dispensed at 5 mL min^{-1} towards de detector in order to avoid carry-over.
7. The syringes are re-filled at 15 mL min^{-1}.

5. Automation of a standard addition calibration procedure for the determination of Pq^{2+}

In order to solve the initial problem of the matrix effects, an automated procedure for the standard addition method was developed exploiting the versatility of the MSFIA technique (Fig. 1B). Flow techniques are useful tools for the automation of standard addition procedures [29,30]. Among them the MSFIA technique has also been used for the automation of standard addition calibration [31] where a peristaltic pump is used for sample propulsion and the Multisyringe burette for the addition of the standard solutions.

In this case the Multisyringe burette is used together with a selection valve, obtaining a new approach for the sequential loading of small plugs of sample and standards and the subsequent effective mixing of this plug with the colorimetric reagents in a forward-flow mode.

Instead to load 1.2 mL of sample, a sequential aspiration procedure facilitated by the selection valve is used to load 0.2 mL of sample followed by 0.2 mL of a standard solution of Pq^{2+} (located in ports 4, 5 and 6 of the SV). This action is repeated three times obtaining a sample-standards plug of 1.2 mL of volume. Immediately the plug is injected towards the reaction coil with the previous mixing with R1 and R2 facilitated by the additional syringes moved in parallel by the Multisyringe burette.

The maximum possible volume of the sample and the standard plugs was studied in order to obtain an effective mixing without compromise the analysis throughput of the developed method. Increasing the volume of the plugs up to 0.2 mL an effective mixing was obtained, so this volume was adopted for further experiments.

This alternative is a useful solution in order to increase the applicability of the developed method.

6. Experimental results

In this work is studied for the first time the determination of Pq^{2+} exploiting liquid core waveguides as detection cell. LCW's have been used previously in combination with the MSFIA technique for the development of a more environmentally friendly SPM determination of chloride [32] and for the SPM determination of uranium [33] and iron [34] with improved detection limits.

In R1, dehydroascorbic acid is produced by reaction of ascorbic acid with KIO_3. Dehydroascorbic acid reacts with Pq^{2+} in basic medium being developed a blue free radical. This radical is monitored at 610 nm. In order to avoid spectral interferences or changes in the refraction index caused by the use of a high concentration of NaOH as R2 a correction wavelength at 720 nm is used to compensate this effect. By this way, very low absorbance intensities are measured for the blank solutions. This is crucial if a long pathlength flow cell is used, due to the impossibility to work with this type of flow cell with chemical reactions that have a high blank absorbance.

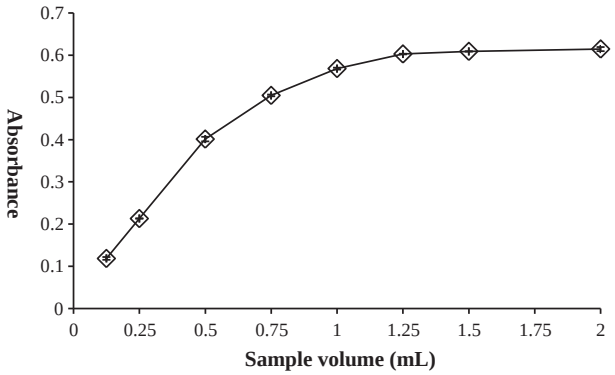

Fig. 2. Influence of the sample volume on the measured absorbance by using a 2 m long pathlength capillary flow cell. Pq^{2+} concentration is 250 μg L^{-1}.

Absorbance signal peak heights are used for the obtention of the analyte concentration. The baseline is stablished as the blank using distilled water.

7. Paraquat determination using a 1 cm optical pathlength conventional flow cell

As starting point we studied the initial features for the spectrophotometric detection of paraquat using a conventional 1 cm flow cell. S2 contained a 2.5 g L^{-1} ascorbic acid, 1 g L^{-1} KIO_3 and 1 g L^{-1} EDTA and S3 contained a 2.5 mol L^{-1} NaOH solution. For Pq^{2+} calibration graphs were performed between 0.5 and 5 mg L^{-1} (average slope = 0.0226, average R^2 = 0.9994). Using the calibrations and 10 consecutive injections of the blank, we calculated a limit of detection and limit of quantification of 180 and 240 μg L^{-1} Pq^{2+}, respectively.

8. Paraquat determination using a long pathlength liquid core waveguide

Changing the conventional flow cell for a 200 cm long LCW, the sensitivity of the method was enhanced by increasing the sample volume. In Fig. 2 we can observe the increasing trend of the measured absorbance by increasing the sample volume. This trend is stabilized for a sample volume of 1.25 mL, being the total volume of the reaction plug 2.5 mL.

The effect of the concentration of NaOH used in R2 over the performance of the proposed system was studied. Relatively strong concentrations of NaOH are required for the development of the reaction product. The concentration of NaOH was studied between 0.5 and 5 mol L^{-1}. An increase of the analytical signal was obtained while increasing the NaOH concentration reaching a plateau at a concentration of 2.5 mol L^{-1}. Higher NaOH concentrations do not produce any further increase of the analytical signal, however produces mixing problems in the reaction plug and a minor yield of production of the reaction product. The influence of the concentration of NaOH on the measured analytical signal is represented in Fig. 3A. A concentration of NaOH of 2.5 mol L^{-1} was adopted for further experiments.

The concentration of each one of the components of R1 was studied. The concentrations of ascorbic acid and EDTA were set at 5 g L^{-1} and 2 g L^{-1} respectively, being the concentration of KIO_3 studied in the range between 0 and 1.5 g L^{-1}. The trend of the increase of the absorbance with increasing the concentration of KIO_3 is shown in

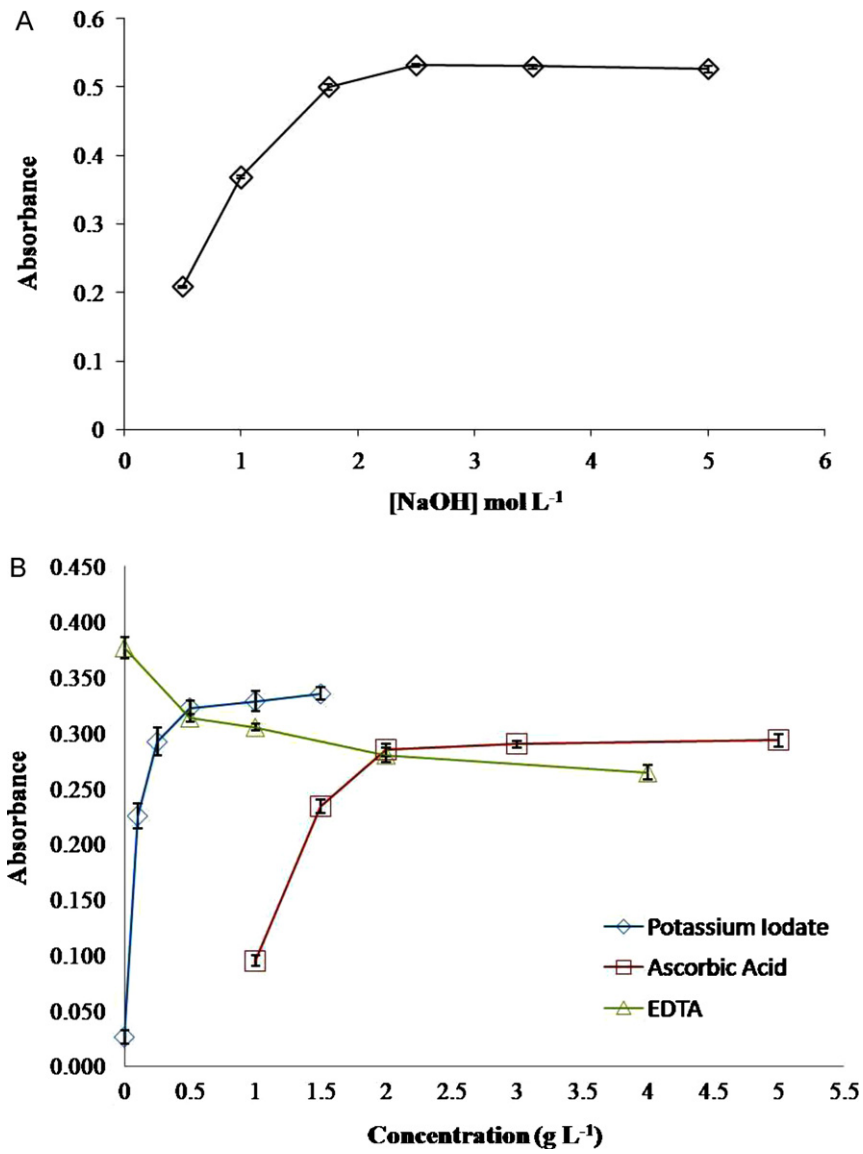

Fig. 3. (A) Influence of the concentration of NaOH in R2 on the measured absorbance. (B) Influence of the concentration of potassium iodate, ascorbic acid and EDTA contained in R1 on the obtained absorbance.

Fig. 3B. A concentration of 0.5 g L^{-1} KIO_3 was adopted for further experiments.

Once adopted the new concentration of KIO_3, the concentration of ascorbic acid was studied in a range of 1–5 g L^{-1}. As is shown in Fig. 3B, a plateau in absorbance is reached for a concentration of 2 g L^{-1} of ascorbic acid, being this concentration selected for further experiments. Finally, the effect of the concentration of EDTA contained in R1 was studied in a range of 0–4 g L^{-1} (Fig. 3B). The addition of EDTA is necessary for the minimization of potential interferences caused by metallic cations. In a compromise between signal peak height and adopting the highest concentration of EDTA possible, a concentration of EDTA of 1 g L^{-1} was selected for further experiments.

9. Reaction coil and reaction flow rate

The MSFIA set-up comprises the simultaneous use of three syringes of volumes of 10, 5 and 2.5 mL. The motor of the Multisyringe module has 5000 steps, which corresponds to a minimum flow rate of 2 mL min^{-1} for a 10 mL syringe. In order to develop the reaction product, the three syringes are connected in "On" position being the minimum reaction total flow rate of 3.5 mL min^{-1}. A factor to have in mind in that point is the relatively high back-pressure that the Multisyringe suffers due to the 200 cm long pathlength flow cell, in comparison with working with a conventional 1 cm flow cell. Working under the minimum reaction flow rate the length of the reaction coil was studied, being a minimum length of 150 cm required for the complete development of the reaction product.

Back-pressure measurements were accomplished in order to know the maximum flow rate able to work with. The maximum pressure enabled by the valves (V1–V5) is equal to 2 bar. The obtained back-pressures for S1 were of 0.8, 1.2, 1.6 and 3 bar, working at flow rates of 2, 2.5, 3 and 3.5 mL min^{-1}, respectively. A flow rate of 3 mL min^{-1} for S1 is selected for further experiments, avoiding by this way the premature damage of the solenoid valves caused by overpressures. The resultant reaction flow rate will be 5.25 mL min^{-1}. Working with this higher flow rate and the reaction coil of 150 cm, a small decrease on the reaction yield was observed. This drawback was overcome increasing the reaction coil length to 250 cm.

10. Effect of the reaction matrix

According to Infante et al. [19] the spectrophotometric method for the determination of Pq^{2+} exploiting the AA–KIO_3 method does not suffer significant interferences from any of the major components of drinking and river waters, not being observer effects of the reaction matrix.

In this work, the use of a 200 cm LCW instead a conventional 1 cm optical pathlength flow cell provided significant differences on depending of the sample matrix studied. Calibration graphs were performed with Pq^{2+} standards added to distilled or drinking water. The distilled water blank was 0.015 a.u. and the blank for a drinking water with a high saline content 0.095 a.u.

Comparing drinking waters from different sources: Mallorca water (high content in salts, total Water A 240 mg L^{-1}, Water B 350 mg L^{-1}) and Segovia (low content in salts, total 26 mg L^{-1}). Spikings of 0.2 mg L^{-1} of Pq^{2+} were done in each of the previous samples and in distilled water. On the one hand, the results obtained analyzing Segovia water were only a 3.5% higher than the obtained analyzing standards in distilled water. On the other hand, analyzing drinking water samples from Mallorca (with one order of magnitude higher mineral content) a 44.5% increase in the obtained signals was observed for Water A, and a 45.2% for Water B.

For the Segovia water a calibration graph was performed. This water was spiked with an adequate amount of stock solution of Pq^{2+}. The slope of this calibration graph was only a 1.1% higher than the calibration graph performed by using standard solutions.

As a conclusion, for the useful determination of Pq^{2+} with the proposed method, a dedicated calibration graph is required on depending of the source of the sample. For samples with low mineral content, the results can be interpolated to the calibration graph performed with the standards. Another option is the use of a standard addition calibration procedure, which was described previously. Furthermore the individual matrix effects caused by several major components of drinking waters are studied in a later section.

11. Analytical figures of merit

Working under the final defined operating conditions for the proposed MSFIA–LCW system, its performance was evaluated. This evaluation was carried out using Pq^{2+} standards prepared in distilled water.

For the direct determination of Pq^{2+}, a linear dynamic range between 5 and 250 μg L^{-1} was obtained. The limits of detection (LOD) and quantification (LOQ) were estimated from 3 to 10 times the standard deviation of the absorbance measured in 10 consecutive injections of a 5 μg L^{-1} Pq^{2+} standard divided by the calibration slope and found to be 0.7 and 2.3 μg L^{-1}, respectively. The LOD and LOQ were calculated by this way because the blanks obtained were essentially zero with a very low standard deviation [35].

The slope and the regression coefficient of the calibration graphs were calculated from 5 day-to-day calibration curves and found to be 4.7454 ± 0.0628 L mg^{-1} and 0.9995 ± 0.0003, respectively. The reproducibility was calculated from the RSD of the slopes of 5 day-to-day calibration curves and found to be 1.3%.

The repeatability of the obtained analytical signals was evaluated as the relative standard deviation (RSD) for 10 consecutive measurements, and it was done at four different concentration levels. The RSD's obtained were 3.3, 2.5, 1.3% and 1.1 for 12.5, 25, 50 and 125 μg L^{-1} Pq^{2+}, respectively.

The injection throughput (IT) of the proposed method is 34 h^{-1} being the back-pressure from the liquid core waveguide and the high sample volumes used the main factors that limit this feature. Using the standard addition calibration procedure, the IT is 25 h^{-1}.

Table 1
Effect of major saline components and other "quat" herbicides on the determination of 0.2 mg L^{-1} of Pq^{2+} by the developed method.

Added specie	Amount (mg L^{-1})	Signal variation (%)
Sulphate	10	+1.0
	30	+6.3
	100	+46.9
Nitrate	10	+2.9
	30	+19.9
	100	+29.4
Chloride	10	+3.8
	30	+24.5
	100	+34.8
Carbonate	5	−3.9
	10	−9.1
	100	−51.3
Difenzoquat	0.2	+1.5
	100	+18.0
Diquat	0.2	−1.7
	2	–

The initial results obtained using a conventional 1 cm flow cell have been improved by using the 200 cm long pathlength capillary cell, obtaining a 210-fold improvement on the slope of the calibration curves, thus a 257-fold improvement in the LOD. In Fig. 4, the signals obtained measuring 50 mg L^{-1} of Pq^{2+} with a 1 cm flow cell and 0.25 mg L^{-1} of Pq^{2+} with the 200 cm LCW are compared. We can appreciate that for a 200-fold higher concentration of Pq^{2+} a slightly higher than 200-fold in signal is observed using the LCW. Increasing the concentration of the analyte 200-fold using the 1 cm cuvette, an exact signal increase of 200-fold is obtained. Comparing both flow cells using the same sample volume and flow rate, for the 200 cm LCW an improvement of 217-fold on peak height is obtained. This slightly higher than the 200-fold ideal increase (as obtained with the conventional flow cell) can be attributed to the different morphology of these two flow cells, being the conventional one like a small deposit and the LCW a capillary, obtaining with the last one thinner and higher peaks.

12. Interference studies

The spectrophotometric method based on the use of the AA–KIO_3 reaction system for the determination of Pq^{2+} in waters is influenced on depending of the matrix of the sample and different responses were obtained for different types of water samples. In this section is studied the effect of the major saline components commonly presented in waters and the effect of similar compounds to Pq^{2+} have over the measured signals. The obtained results are shown in Table 1.

Chloride, sulphate and nitrate do not produce any signal change bigger than a 5% at a concentration level of 10 mg L^{-1}. Higher concentrations produce a signal increase on depending of the concentration of this species. The presence of carbonate has the opposite effect, decreasing the obtained signal while increasing its concentration. The increase of the obtained absorbance for drinking waters with a high saline content can be attributed to this fact.

The potential interference of other "quat" herbicides was also evaluated. At the same concentration level than Pq^{2+} no significant interference was observed for diquat and difenzoquat. The concentration of these foreign species was increased in order to observe some effect. A 18% signal increase was obtained by increasing the concentration of Difenzoquat from 1-fold to 500-fold. Increasing the concentration of Diquat from 1-fold to 10-fold the signal is almost completely inhibited due to the decomposition of Diquat in basic medium, producing spectral interferences, and not being able to measure the signal of Pq^{2+} properly. Anyway, the presence of Diquat at mg L^{-1} levels is not common in drinking waters.

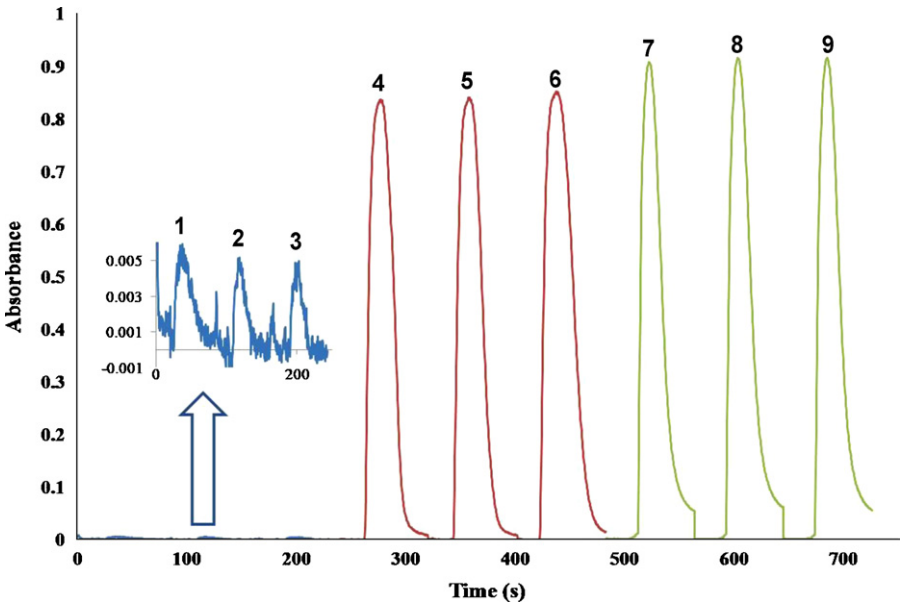

Fig. 4. Different signals obtained in the spectrophotometric detection of Pq^{2+} using a conventional 1 cm flow cell and a 200 cm LCW. Blue (peaks 1–3); 0.25 mg L^{-1} Pq^{2+} with 1 cm flow cell. Red (peaks 4–6); 50 mg L^{-1} Pq^{2+} with 1 cm flow cell. Green (peaks 7–9); 0.25 mg L^{-1} Pq^{2+} with a 200 cm LCW. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

13. Application of the developed systems to the determination of paraquat in drinking water samples

The developed MSFIA–LCW systems were applied to the determination of Pq^{2+} in drinking waters from different sources.

Drinking waters with a matrix of low mineral content (drinking water; Segovia (Spain); total saline content 26 mg L^{-1}) were analyzed with the direct method using the system depicted in Fig. 1A. Samples were spiked with 5, 10, 25 and 50 μg L^{-1} of Pq^{2+} and analyzed. The results obtained were interpolated to a calibration graph performed with distilled water standards of Pq^{2+}. The obtained results are shown in Table 2. Standard deviations between 1.3 and 4.1% and recoveries between 102 and 108% were obtained.

Drinking water samples with a saline matrix were spiked with Pq^{2+}. Drinking water A (spiked with 10, 20, 30 and 50 μg L^{-1} of Pq^{2+}); Mallorca (Spain) total saline content 240 mg L^{-1}. Drinking water B (spiked with 10, 25 and 50 μg L^{-1} of Pq^{2+}); Mallorca (Spain); total saline content 351 mg L^{-1}. These samples were analyzed with the automated standard addition method using the system depicted in Fig. 1B. The concentration of the sample was estimated from the injection of three different standard additions using different standard solutions (located at the ports 4, 5 and 6 of the SV) with a concentration of 25, 50 and 75 μg L^{-1} of Pq^{2+}. The results reported in Table 2 are the mean of the results obtained accomplishing the standard addition procedure per triplicate. For Mallorca Water A, relative standard deviation ranging between 1.8 and 4.8% and recoveries of 98 and 107% were obtained. In the case of Mallorca Water B, for higher concentration spiking levels (25–50 μg L^{-1} of Pq^{2+}) acceptable standard deviations and recoveries were obtained. Spiking this sample at a level of 10 μg L^{-1} of Pq^{2+}, both standard deviation and recovery were slightly higher. However, if we represent the mean of three replicates for each standard addition instead the accomplishment of three different runs of standard addition with three standards and analyzing one point each, the results of the recovery of this sample can be improved. Obtaining as is shown in Fig. 5 a concentration of Pq^{2+} of 10.2 μg L^{-1} for an initial spiking of 10 μg L^{-1}.

Table 2
Paraquat determination in spiked drinking water samples. Each sample was analyzed per triplicate.

Drinking water	Added Pq^{2+} (μg L^{-1})	Measured Pq^{2+} (μg L^{-1})	RSD (%)	Recovery (%)
Segovia	5.0	5.1 ± 0.1	2.9	102
	10.0	10.8 ± 0.3	2.8	108
	25.0	26.3 ± 0.3	1.3	105
	50.0	53.9 ± 2.2	4.1	108
Mallorca A	10.0	10.1 ± 0.5	4.8	101
	20.0	21.4 ± 0.6	3.0	107
	30.0	30.5 ± 0.9	3.0	102
	50.0	49.0 ± 0.9	1.8	98
Mallorca B	10.0	11.4 ± 1.0	8.5	114
	25.0	26.9 ± 0.8	2.9	108
	50.0	47.3 ± 1.2	2.4	95

14. Comparison with previously described methods and their real utility in the determination of paraquat in water samples

In Table 3 is presented a comparison of flow-based analytical methodologies for the determination of Pq^{2+} in waters. The chemistry of these systems is based on the reaction of Pq^{2+} with sodium dithionite [14,15] or with ascorbic acid–potassium iodate (AA–KIO_3) [17,19]. The automated fluidic handling is performed using Flow Injection Analysis [15,17], Sequential Injection Analysis [14] or Multi-pumping Flow Systems [19]. These methods generally present high injection throughputs and good precision in the measurement of Pq^{2+}. On the contrary, these methods often present a low sensitivity obtaining limits of detection of tens of μg L^{-1}, being the sensitivity non sufficient for the direct determination of Pq^{2+} in waters requiring additional sample treatments such as solid phase extraction. A solid phase extraction procedure was implemented inside the flow cell developing a spectrophotometric sensor [15] for the determination of Pq^{2+}. Using this sensor a high improvement on the sensitivity and LOD are obtained, but a drastic decrease in the injection throughput is also obtained, thus and a concomitant diminution in the precision of the method. The proposed MSFIA–LCW system due to its inherent characteristics provides the advantage of obtain a sensitivity and LOD in a similar range than the

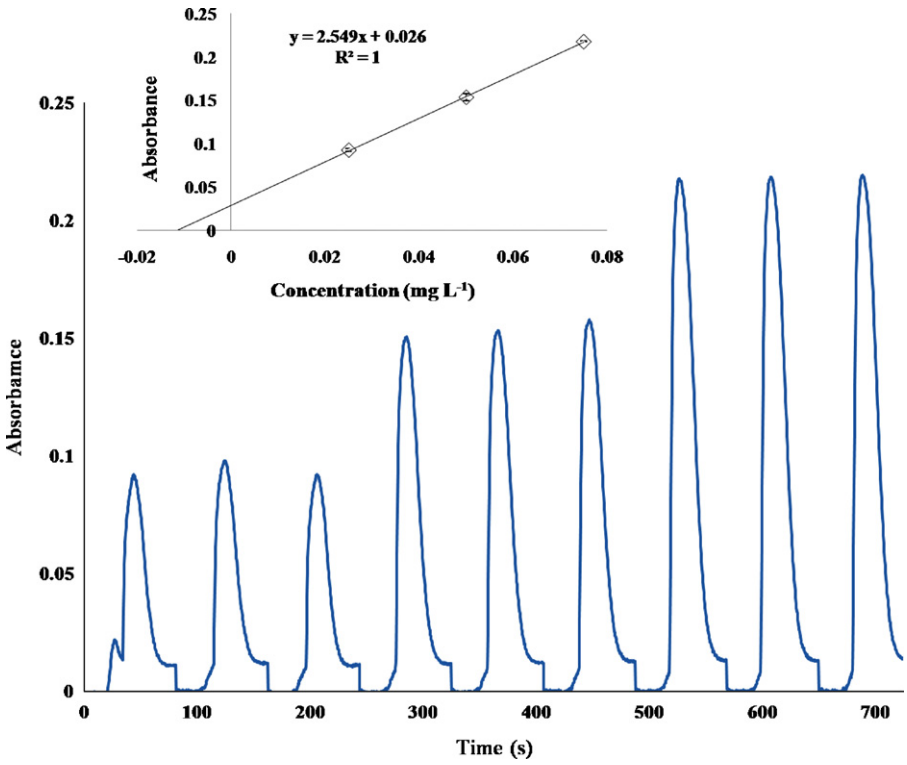

Fig. 5. Analytical signals obtained for a drinking water sample Mallorca Water B, corresponding to the addition of three Pq^{2+} standards (3 replicates for each standard) and a calibration curve obtained with this data. Standard 1, 25 μg L^{-1}; Standard 2, 50 μg L^{-1}; Standard 3, 75 μg L^{-1}.

Table 3
Comparison of flow-based methodologies for the spectrophotometric determination of Pq^{2+} in waters.

	Flow systems for the spectrophotometric determination of Pq^{2+}					
	FIA[a]	FIA-sensor[b]		SIA[c]	MPFS[d]	MSFIA[e]
Reaction	AA–KIO_3	5 mL sample Dithionite	250 mL sample Dithionite	Dithionite	AA–KIO_3	AA–KIO_3
LOD (μg L^{-1})	20	–	0.11	39	22[f]	0.7
Working range (μg L^{-1})	100–10^5	80–200	0.4–5.5	100–20,000	100–5000[f]	2.3–250
IT (h^{-1})	–	15	0.9	102	63	34
Repeatability (%)	2.5 (100 μg L^{-1}) 1.0 (5000 μg L^{-1})	4.8	7.9	2.9	1.0	3.3 (12.5 μg L^{-1}) 1.1 (125 μg L^{-1})

[a] Flow Injection Analysis system including temperature control of the reaction at 60 °C [17].
[b] Flow Injection Analysis flow-through spectrophotometric sensor [15].
[c] Sequential Injection Analysis [14].
[d] Multi-pumping Flow System [19].
[e] System developed in this work.
[f] Obtained using a 10 cm optical pathlength flow cell. Using a 1 cm flow cell the LOD is 57 μg L^{-1}.

spectrophotometric FIA sensor [15] and a concomitant high injection throughput and precision than the other flow-based systems for the determination of Pq^{2+} [14,17,19].

15. Conclusions

In this work, a new application of long pathlength spectrophotometry based on long liquid core waveguides has been developed and focused to the improved determination of paraquat in drinking waters. A 200 cm liquid core waveguide has been combined with the Multisyringe flow injection analysis technique in order to obtain a high level of automation being able to accomplish completely automated determinations of paraquat, plus the automation of standard addition procedures for the measurement of paraquat in samples presenting matrix effects.

The developed methodology is focused as a fast, economic, completely automated and highly sensitive alternative to separation techniques like liquid chromatography–mass spectrometry for the determination of paraquat, in order to obtain fast information about the possible presence of paraquat in a sample prior confirmation by means of a more precise but also more complex and expensive instrumental technique.

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References

[1] M.E. DeLorenzo, G.I. Scott, P.E. Ross, Environ. Toxicol. Chem. 20 (2001) 84–98.
[2] C. Bismut, A.H. Hall (Eds.), Paraquat Poisoning, Prevention, Treatment, Marcel Dekker, New York, 1995, pp. 1–16.

[3] Drinking Water Health Advisory: Pesticides, Lewis, Chelsea, MI, US Environmental Protection Agency, 1989.
[4] Code of Federal Regulations, Title 40, Part 141, US Government Printing Office, Rev. July 1, 1997.
[5] M.C. Carneiro, L. Puignou, M.T. Galcerán, J. Chromatogr. A 669 (1994) 217–224.
[6] J.W. Hodgeson, W.J. Bashe, J.W. Eichelberger, Method 549.1, Revision 1.0, Environmental Monitoring Systems Laboratory, Office of Research And Development, US Environmental Protection Agency, 1992.
[7] Q.X. Zhou, J.L.L. Mao, J.P. Xiao, G.H. Xie, Anal. Methods 2 (2010) 1063–1068.
[8] E. Moyano, D.E. Games, M.T. Galceran, Rapid Commun. Mass Spectrom. 10 (1996) 1379–1385.
[9] R. Castro, E. Moyano, M.T. Galceran, J. Chromatogr. A 830 (1999) 145–154.
[10] R. Castro, E. Moyano, M.T. Galceran, J. Chromatogr. A 914 (2001) 111–121.
[11] L.C.S. de Figuereido, V.B. dos Santos, B.C. Janegitz, T.B. Guerreiro, O. Fatibello, R.C. Faria, L.H. Marcolino, Electroanalysis 22 (2010) 1260–1266.
[12] L.B.O. dos Santos, C.M.C. Infante, J.C. Masini, Anal. Bioanal. Chem. 396 (2010) 1897–1903.
[13] S.H. Yuen, J.E. Bagness, D. Myles, Analyst 92 (1967) 375–381.
[14] C.M.C. Infante, J.C. Masini, Spectrosc. Lett. 40 (2007) 3–14.
[15] M. Agudo, A. Ríos, M. Valcárcel, Anal. Chim. Acta 281 (1993) 103–109.
[16] P. Shivhare, V.K. Gupta, Analyst 116 (1991) 391–393.
[17] A. Jain, K.K. Verma, A. Townshend, Anal. Chim. Acta 284 (1993) 275–279.
[18] M. Trojanowicz, Advances in Flow Analysis, Wiley-VCH, Weinheim, 2008.
[19] C.M.C. Infante, A. Morales-Rubio, M. de la Guardia, F.R.P. Rocha, Talanta 75 (2008) 1376–1381.
[20] R.A.S. Lapa, J.L.F.C. Lima, B.F. Reis, J.L.M. Santos, E.A.G. Zagatto, Anal. Chim. Acta 466 (2002) 125–132.
[21] M. Valcarcel, S. Cardenas, Trends Anal. Chem. 24 (2005) 67–74.
[22] V. Cerdà, J.M. Estela, R. Forteza, A. Cladera, E. Becerra, P. Altimira, P. Sitjar, Talanta 50 (1999) 695–705.
[23] M.A. Segundo, L.M. Magalhaes, Anal. Sci. 22 (2006) 3–8.
[24] F. Maya, J.M. Estela, V. Cerdà, Spectrosc. Lett. 42 (2009) 312–319.
[25] R.D. Waterbury, W.S. Yao, R.H. Byrne, Anal. Chim. Acta 357 (1997) 99–102.
[26] J.Z. Zhang, J. Chi, Environ. Sci. Technol. 36 (2002) 1048–1053.
[27] Q.Y. Li, K.J. Morris, P.K. Dasgupta, I.M. Raimundo, H. Temkin, Anal. Chim. Acta 479 (2003) 151–165.
[28] L.J. Gimbert, P.J. Worsfold, Trends Anal. Chem. 26 (2007) 914–930.
[29] E.C. Silva, M.C.U. Araujo, R.S. Honorato, J.L.F.C. Lima, E.A.G. Zagatto, S.M.B. Brienza, Anal. Chim. Acta 319 (1996) 153–158.
[30] O. Elsholz, C. Frank, B. Stachel, H. Reincke, R. Ebinghaus, Anal. Chim. Acta 438 (2001) 251–258.
[31] J.R. Santos, M.A. Segundo, J.L.F.C. Lima, M. Korn, Microchem. J. 92 (2009) 180–185.
[32] F. Maya, J.M. Estela, V. Cerdà, Anal. Bioanal. Chem. 394 (2009) 1577–1583.
[33] J. Avivar, L. Ferrer, M. Casas, V. Cerdà, Anal. Bioanal. Chem. 397 (2010) 871–878.
[34] R.N.M.J. Páscoa, I.V. Tóth, A.O.S.S. Rangel, Microchem. J. 93 (2009) 153–158.
[35] J. Ma, P.K. Dasgupta, W. Blackledge, G.R. Boss, Anal. Chem. 82 (2010) 6244–6250.