

Paraquat quantification in deposits from drinking water networks

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Abstract

5 The aim of this work was to develop an expedite analytical methodology to evaluate the paraquat (PQ) contamination level in deposits proceeding from drinking water networks. To our knowledge, no other study has been focused on this matter, which is of crucial importance, for instance, to obtain a fast response after a suspicion of contamination (emergency situation). Three deposits representative of those typically found in drinking water networks were used: two iron-based – S2 and S3, and a calcium rich one – S4. The analytical method consists of an easy and fast extraction step, using a saturated ammonium chloride solution, followed by direct injection in a high
10 performance liquid chromatograph with diode array detector (HPLC-DAD). A matrix-matched calibration was performed for paraquat, in the range of 5 to 193 $\mu\text{gPQ g}^{-1}$ deposit, and a limit of detection of 0.1 $\mu\text{gPQ g}^{-1}$ deposit was reached. The good percentages of recovery (90-101% on average) and the low relative standard deviations observed for the PQ-S3 system (3, 4 and 2% for 20, 80 and 160 $\mu\text{gPQ g}^{-1}$ deposit, respectively) enable a reliable quantification of paraquat, even at the lowest contamination levels. The developed analytical methodology can also be extended for diquat and proved to be also suitable for paraquat quantification in other types of deposits.

15 Introduction

Paraquat (PQ) is a bipyridylum compound marketed since 1962 as a highly effective contact herbicide. Nowadays, PQ commercialization is forbidden in Europe, but it is still used in nearly 90 countries around the world, either for land preparation or for weed growth control [<http://paraquat.com/>] ¹. It has been reported that this herbicide is extremely toxic to humans ^{2,3} and, due to its low price and large accessibility, is often linked to suicide acts ^{3,4}.

20 The present work is part of a European project (SecurEau) whose main objective is to launch an appropriate response for rapidly restoring the use of the drinking water distribution system after a deliberate contamination event [<http://www.secureau.eu/>]. For that, SecurEau consortium selected representative contaminants based on several criteria for the definition of a general strategy envisaging the rehabilitation of the drinking water network. PQ is one of the representative chemical compounds studied and was selected because of being easily acquired and manipulated, despite of the effective control measures.

25 In case of chemical contamination of a drinking water distribution system, deposits formed in the pipe walls may represent crucial zones of contaminant accumulation. Although sorption studies of PQ on representative deposits from drinking water networks suggested that it is unlikely that this chemical compound may adsorb on such materials, at least during the normal water distribution ⁵, other situations should be taken into account. In fact, in case of a stagnancy of the fluid for a very long period of time (in tanks or pipes in case of a consumption break) or low water flow (e.g. during the night), these compounds may adsorb on such deposits. On the other hand,
30 adsorption on loose deposits that are transported with the flowing water is much more likely to occur ⁵. Therefore, beyond the PQ monitorization in water, it is imperative to develop an analytical methodology able to quantify this compound in deposits from drinking water networks. Ultimately, the quantification of PQ in such deposits may have particular impact and interest for society, since it may be used as an indirect measure of the water quality and degree of pollution. Indeed, whenever a cleaning or maintenance procedure is scheduled, the deposits may be considered for analyses with this purpose in mind.

35 Up to the author's knowledge, no studies exist in the literature about quantification of PQ, or even other chemical compounds, in deposits from drinking water networks. Due to the lack of information concerning this topic, it was decided to check which methodologies have been implemented for PQ quantification in soils. Even for soil samples, a relatively low number of studies was found in the open scientific literature (Table 1). Indeed, the analysis of paraquat in soils is a challenging task as a result of the strong affinity of this herbicide to such a matrix ^{4,6}. As evidenced in Table 1, the most reported methodologies for the extraction of PQ from soils involve
40 reflux or sample digestion procedures (in sulphuric or hydrochloric acids, or even under milder solvents such as an acidified mixture of MeOH/EDTA) ⁷⁻¹³. Such drastic extraction conditions with strong acids induces releasing of chemicals by matrix structure destruction ⁷. This extraction step is required due to the strong interaction between paraquat and soils, as referred before. Although digestion and refluxing extraction techniques do not demand sophisticated equipment, they demand time, large solvent quantities (25-100 mL) and high sample amounts (5-100 g) ^{7-11,13}. Pateiro-Moure et al. tested the ability of a mechanical shaking methodology to extract paraquat from a
45 contaminated soil and no recovery was attained under the conditions employed ¹¹. Microwave-assisted extraction (MAE) has the advantages over the other techniques of requiring shorter extraction times (10-50 min), less solvent quantities (10-20 mL) and lower sample amounts (1-3 g) ^{11,14,15}. Nonetheless, MAE involves sophisticated equipment, especially when *aqua regia* (nitro-hydrochloric acid) is employed as extraction solvent ¹¹ and, generally, leads to limits of detection comparable to the traditional refluxing or digestion techniques (0.008-0.1 $\mu\text{g g}^{-1}$).

Table 1. Studies found in the literature concerning the analytical methods for paraquat quantification in soils.

Sample amount	Extraction/treatment	Clean-up	Instrumental technique	Analytical parameters	Year	Ref
10 g	Reflux with 18 N H ₂ SO ₄ ; 5 h	SP – Dowex 50 W-X8 (H ⁺ form) Eluent – Saturated ammonium chloride solution	Spectrophotometry	-----	1967	⁷
100 g	Reflux with H ₂ SO ₄	SP – Dowex 50-X8 (Na ⁺ form) Eluent – Ammonium chloride solution	Spectrophotometry	LR – 2.98-6.25 µg g ⁻¹ Rec – 95%	1988	⁸
10 g	freeze-dried; extracted with DCM	-----	LC-TSP-MS	LOD – 0.17 µg g ⁻¹	1993	¹⁶
10 g	Digestion with 6 M HCl; adjust to pH 9	SP – Adsorbex silica cartridges (400 mg) Eluent – 0.1 M HCl in MeOH	CZE-DAD	RSD – 4% LOD – 0.008 µg g ⁻¹ Rec – 92%	1996	¹²
5 mg	-----	-----	SIMS	LOD – 6 µg g ⁻¹	1997	¹⁷
50 g	Digestion with 25 mL H ₂ SO ₄ 5 M; adjust to pH 9	SP – silica gel column (25 cm × 1 cm i.d.); Conditioning – 2×20 mL H ₂ O Elution – 50 mL saturated ammonium chloride solution	Spectrofluorimetric	LR – 0.3-4.5 µg g ⁻¹ RSD – 1% LOD – 0.1 µg g ⁻¹ Rec – 101%	1998	¹³
3 g	MAE – 15 mL H ₂ SO ₄ 9 M; 1120 W; 15 cycles; 30 s/cycle	-----	-----	Rec – 22.1-105.3%	2001	¹⁴
1 g	Shaking with 10 mL of a 0.02 M EDTA/0.5 M ammonium acetate after acidification to a pH 4.7; adjust pH to 9-10	SP – silica cartridge	HPLC-UV	Not recovery	2008	¹¹
1 g	MAE – 200 µL benzalkonium chloride+8 mL HNO ₃ (65%)+ 2mL HCl (37%)+2 mL HF (48%); 30 min ramp time to reach 200 °C and hold there for 20 min; 800 W MAE – 20 mL 4% boric acid aqueous solution; 15 min ramp time to reach 180 °C and hold there for 15 min; 800 W; pH adjustment to 9-10	SP – silica cartridge	HPLC-UV	RSD – 10% LOD – 0.050 µg g ⁻¹ Rec – 102%	2008	¹¹
5 g	Digestion with 30 mL of a mixture 70:30 (v/v) MeOH:5%(w/v) EDTA acidified with 2% (v/v) formic acid ; 3 h; adjust to pH 9	SP – silica cartridge Elution – 10 mL 70:30 (v/v) MeOH; 6.5 M HCl	HPLC-UV	RSD – <15% LOD – 0.020 µg g ⁻¹ Rec – 98-102%	2009	⁹ ¹⁰ ¹¹

⁵ **Notes:** CZE-DAD – capillary zone electrophoresis-diode array detection; DAD – diode array detection; DCM – dichloromethane; EDTA – ethylenediaminetetraacetic acid; LC-TSP-MS – liquid chromatography-thermospray-mass spectrometry; LOD – limit of detection; LR – linearity range; MAE – microwave-assisted extraction; MeOH – methanol; Rec – recovery; RSD – relative standard deviation; SP – solid phase; HPLC-UV – high performance liquid chromatography with ultraviolet detector.

Despite of the differences observed on the extraction time for the different techniques and approaches referred above, generally the corresponding methods are globally time-consuming because they require clean-up steps after the extraction (see Table 1). A substantial reduction of the sample preparation time by extraction and clean-up steps elimination can be obtained by direct surface analysis¹⁷. Paraquat is easily detected by static secondary ion mass spectrometry (SIMS), which is a direct surface analysis technique, and offers fast analysis times, on the order of 10 min/sample¹⁷. However, it can be observed from Table 1 that the limit of detection obtained by SIMS (6 $\mu\text{g g}^{-1}$) is much higher than that achieved by the other methods (0.008-0.17 $\mu\text{g g}^{-1}$). Additionally, chromatographic methods allow obtaining higher quantitative information than surface analysis¹⁷.

In short, the search for an easy and fast extraction methodology for the extraction of PQ from deposits, but preserving matrix structure, justifies the procedure adopted in this work by using an aqueous saturated ammonium chloride solution. Indeed, the matrix structure destruction, as occurs in digestion and refluxing procedures, typically conducts to complex extracts that require clean-up procedures, which increase the time of analysis. On the other hand, the release of chemicals by matrix structure destruction provides little or no information about their adsorption status¹⁸. This can be a relevant aspect in the context herein addressed, once it is important to have an idea of the interaction between the chemical compounds and the deposits; in other words, whether the compounds have or not tendency to be released from the deposits by simple contact with "clean water".

This work intends therefore to diminish the great lack of information about analytical methodologies able to quantify compounds in deposits formed in pipe walls, developing a methodology for PQ as case-study. The simple and inexpensive method proposed here consists of a fast and easy extraction step, which uses small sample and solvent amounts. Furthermore, a complete set of validation parameters is presented, including the calculation of the global uncertainty associated to the results in the range of quantification. Moreover, the application of the developed analytical methodology in diquat (DQ) determination was also inspected. Diquat (DQ) was selected as a case study because it pertains to the quaternary ammonium compounds group like PQ; moreover, the analytical methods available in the literature are typically applicable for both PQ and DQ cations.

Materials and methods

Reagents and working solutions

Paraquat dichloride (PQ) PESTANAL® analytical standard 99.2% (Fluka) and Diquat dibromide (DQ) monohydrate PESTANAL® analytical standard were purchased from Sigma-Aldrich (St. Louis, USA). Heptafluorobutyric acid (HFBA) was from Sigma-Aldrich and acetonitrile (ACN) and methanol (MeOH), HPLC grade, were from VWR BDH Prolabo (Poole, UK). Syringe filters with 0.2 μm PTFE membrane were purchased from VWR (West Chester, USA), and granular anhydrous calcium chloride (93%) and ammonium chloride (99.9%) from Sigma-Aldrich.

Stock solutions (1 g L^{-1}) of PQ and DQ were prepared in distilled water by solubilizing a known amount of the correspondent dried salt. The saturated ammonium chloride solution was prepared by mixing 40 g of ammonium chloride salt with 100 mL of distilled water at 20 °C.

Deposits

The analytical methodology developed in this work was applied to three deposits representative of those typically found in drinking water distribution systems^{19, 20}. Deposits (S2, S3 and S4) from drinking water networks in Germany and The Netherlands were kindly supplied by the IWW Water Centre (Mülheim an der Ruhr, Germany) and were already well characterized in previous published works^{5, 20}. For simplicity, the nomenclature used before was kept here: S2 and S3 are iron-rich materials and S4 is a calcium-rich deposit. Those deposits were collected from old cast iron pipes that needed to be replaced. They were dried in an oven before being sieved and kept dry until the experiments. Only particles sized between 38 and 64 μm were used in this work.

Equipment and operating conditions

The amounts of PQ and DQ extracted from deposits were measured by direct injection of 99 μL of the liquid phase in a Hitachi Elite LaChrom HPLC (Darmstadt, Germany) equipped with a L-2130 pump, a L-2200 autosampler and a L-2455 diode array detector (DAD). The chromatographic separation was achieved by a Purospher® STAR LiChroCART® RP-18 endcapped (240×4 mm, 5 μm) reversed phase column, supplied by VWR (West Chester, USA), using gradient elution. The mobile phase was composed by a 10 mM HFBA aqueous solution and ACN. Initial gradient conditions were set at 100% 10 mM HFBA for 5 min, and then the organic phase was increased to 20% v/v during 5 min and kept for 15 min. Finally, it was returned to 100% 10 mM HFBA after 5 min and kept for 10 min. The spectra were recorded from 220 to 400 nm, but PQ and DQ quantifications, with retention times of 16.2 and 16.0 min, were performed at 259 and 310 nm, respectively.

Spiking of deposits with PQ/DQ

In order to have samples contaminated with different PQ/DQ concentrations, 0.5 g of deposit was put in contact with 10 mL of a PQ/DQ aqueous solution of known concentration. After 24 h of agitation at 20 °C, the liquid and solid phases were separated by centrifugation in

a Hettich Rotofix 32A Centrifuge – Kirchlengern, Germany (10 min, 4000 rpm). The PQ or DQ amount remaining in the liquid phase was measured by HPLC-DAD and the difference between the amounts at the beginning and at the end of the contamination/adsorption experiment allowed the calculation of the amount transferred to the solid phase (i.e., amount of pesticide adsorbed on the deposit and, consequently, the degree of contamination).

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Extraction procedure for the analytical determination

After PQ or DQ spiking, the deposit was freeze-dried for 12 h. After that, different amounts of extraction solvent were added to the contaminated deposit and the mixture kept under agitation during a given period, at 20 °C. A parametric study was performed in order to improve the extraction efficiency. The parameters considered in this study were: the type/nature of extraction solvent, the volume of extraction solvent and the extraction time. The extraction percentage was determined based on the comparison of the analytical response obtained when a S3 sample was extracted after being contaminated with a known amount of PQ with the analytical response obtained when a “clean” S3 sample was submitted to the same extraction procedure and was contaminated only at the end of such procedure (with the same amount of PQ).

15 Validation

The validation of the analytical method, including the uncertainty measurement, followed the *bottom-up* approach described in the EURACHEM CITAC Guide ²¹, and also elsewhere ^{22,23}. It comprised a first step of in-house validation, where the main parameters were obtained – linearity of the response, limit of detection (LOD) and limit of quantification (LOQ), precision and accuracy. The precision of the method was evaluated extracting independent contaminated deposits at different contamination levels. Results were expressed as the coefficient of variation (%CV) of different replicate measurements. Accuracy was evaluated comparing the contamination level obtained by the calibration curve and the real amount of PQ/DQ adsorbed on the deposits. This parameter was evaluated at different degrees of contamination and for different systems.

The uncertainty of the results was then estimated assuming that the above mentioned parameters represent the main source of uncertainty of the final result.

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Results and Discussion

This work comprised a previous optimization of the extraction technique for S3 deposit contaminated with PQ, followed by the validation of the analytical methodology; special attention was given to the estimation of the global uncertainty associated to the results. S3 was selected for the method development given its higher PQ adsorption capacity, as demonstrated in a previous study ⁵. Even so, the method response was also evaluated for the other two deposits (S2 and S4). Additionally, the analytical methodology developed for PQ was extended to the quantification of DQ, using S3 deposit as a case-study.

Optimization of the extraction technique

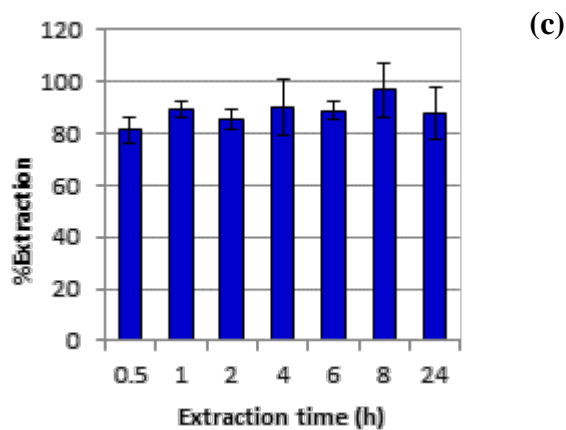
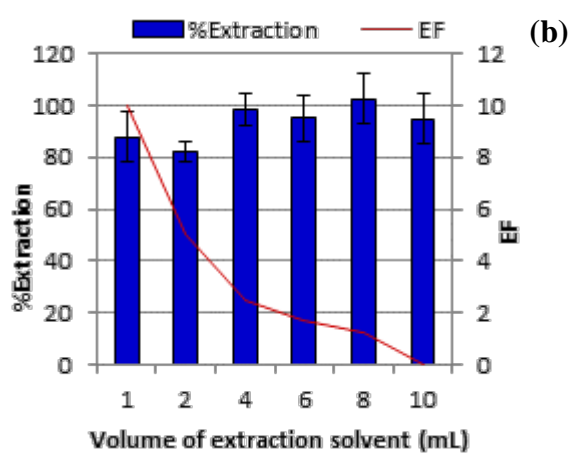
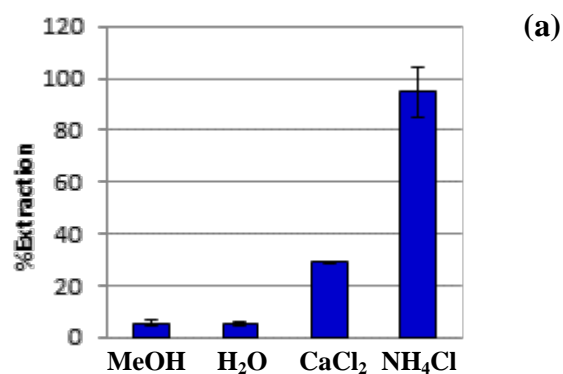
Effect of extraction solvent type

35 The selection of the extraction solvents used to remove PQ from the deposits was based on the available information for soil matrices, which may however have a higher load of organic constituents. Additionally, a detailed study previously performed by our research group, about PQ adsorption on typical deposits, was taken into consideration ⁵. In such a work it was demonstrated that, although morphologically similar, soils and deposits could behave very differently in terms of PQ adsorption. It was concluded that the interactions between PQ and the deposits are extremely weak when compared to those established in most of the PQ-clay and PQ-soil systems found in the literature ⁵. Two major factors were pointed out as the main contributors for such observation: the lower organic fraction exhibited by pipe deposits (around 1 wt.% or less) and their lower clay mineral content. Therefore, water and a saturated ammonium chloride solution were selected as extraction solvent because, according to Tucker and co-workers ⁷, these solvents are able to remove the unbound and the loosely bound PQ from a soil, respectively. Methanol is sometimes also applied to extract PQ from soils ^{11,24} and, for that reason, was included in the list of solvents tested. The calcium chloride solution (0.01 M) was also selected since it is often chosen to remove PQ from soils, although to an extremely low extent due to the strong interactions established between them ^{9,10,25}.

An S3 deposit (0.5 g) was spiked with PQ and was extracted with 10 mL of extraction solvent for 24 h at 20 °C. Then, a “clean” S3 deposit was extracted under the same conditions and the final extract was spiked with the same amount of PQ. The analytical responses for both were compared to calculate the extraction percentage.

50 Water and MeOH exhibited very low extraction percentages when compared to the other solvents (Figure 1a). These results indicated that, according to Tucker and co-workers⁷, PQ is loosely bound to S3 because a simple ion exchange process is sufficient to remove almost all the analyte. On the other hand, it is important to highlight that it is unlikely that PQ may desorb from S3 deposit by a simple contact with “clean” water, as occurs in a normal drinking water flow after the contamination front has passed through.

Therefore, the following experiments were carried out using saturated ammonium chloride solution as extraction solvent.



5 Figure 1. Effect of some parameters on the percentage of PQ extraction from S3 deposit and on the enrichment factor (EF): (a) Effect of extraction solvent type – 0.5 g S3, 10 mL of extraction solvent, 24 h, 20 °C; (b) Effect of extraction solvent volume – 0.5 g S3, saturated ammonium chloride solution, 24 h, 20 °C and (c) effect of extraction time – 0.5 g S3, 1 mL saturated ammonium chloride solution, 20 °C. Error bars correspond to standard deviation.

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Effect of extraction solvent volume

Once the extraction consists in the replacement of paraquat molecules adsorbed on S3 deposit by ammonium chloride ones, the objective here was to select the lowest extraction volume possible, without compromising the extraction efficiency. Indeed, the lower the extraction solvent volume, the higher the PQ concentration in the final extracts and, consequently, the lower is the limit of detection reached. The volumes tested were 1, 2, 4, 6, 8 and 10 mL of saturated ammonium chloride solution. Volumes below 1 mL were not considered because there was not enough extract for subsequent HPLC analysis. As can be seen in Figure 1b, the extraction percentage is almost not affected by the solvent volume (in the range studied), meaning that the lowest volume tested (1 mL) is enough to displace

almost all PQ molecules. Thus, the solvent volume used in the following experiments was set at 1 mL.

Effect of the extraction time

The time of analysis is an important aspect if the analytical method is designed to be applied either for environment monitoring or degradation/sorption studies. Additionally, this is a crucial point, for instance, to obtain a fast response after a suspicion of contamination of water networks. Thus, extraction times of 0.5, 1, 2, 4, 6, 8 and 24 h were tested. According to the results shown in Figure 1c, $82\pm 5\%$ of PQ is extracted from the deposit after 30 min of contact. An increase of the time of contact apparently does not lead to an increase on the PQ extraction percentage, or is marginal. This indicates that this simple and fast extraction process has a great advantage over other time-consuming processes in use and mentioned in the introduction section.

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Quantitative analysis

Matrix interference

The matrix interference studies were performed to evaluate the effect of the presence of other species in the solution, resulting from the contact between the extraction solvent and the deposit, on the analytical response for PQ and DQ. With this purpose, S3 deposit was put in contact with water (to simulate the contamination step, but without PQ or DQ). Afterwards, it was submitted to the extraction step, in the same conditions as described previously in the Materials and methods section. This final solution was designated as blank. It is expected that it contains the species that may (or not) interfere in the analyses. After that, spiked tests were carried out, corresponding to the addition of known amounts of analyte to this blank (spiked blanks). The analytical response obtained for each spiked blank was compared with the correspondent standard prepared in distilled water. The tests were carried out at different concentration levels and the results are presented in Figure 2. The blank was also injected directly into the HPLC-DAD and neither PQ nor DQ were detected in the original matrices. As can be checked from Figure 2, the analytical responses achieved for all spiked blanks (experiments denoted as PQ-S2, PQ-S3, PQ-S4 and DQ-S3) are statistically equivalent to those obtained for standards prepared in water (experiments denoted as PQ-water and DQ-water in Figure 2). It was concluded that the analytical response is not affected by the presence of other species in solution.

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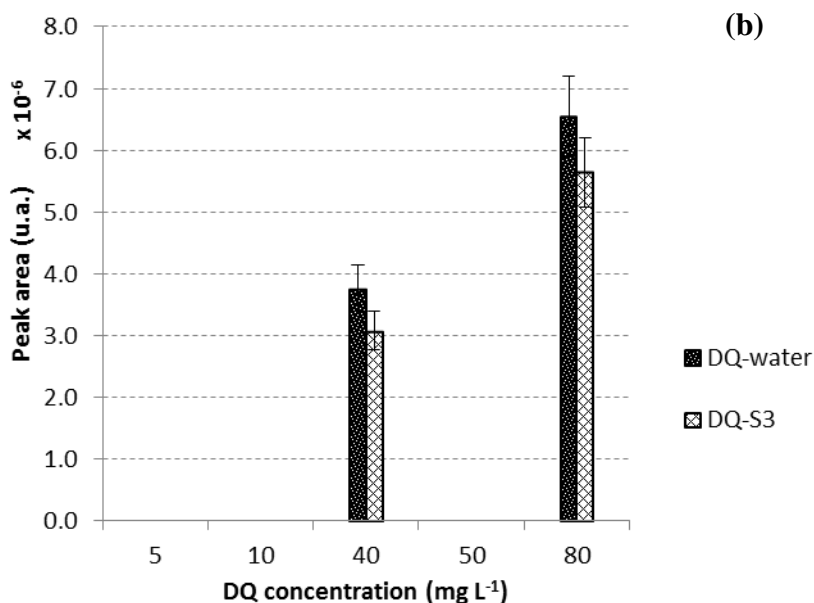
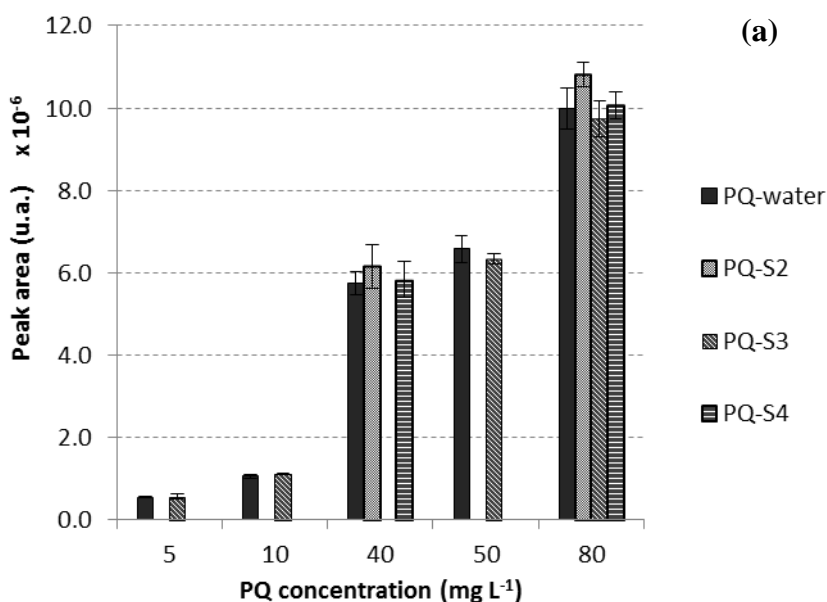


Figure 2. Interference studies in the paraquat (a) and diquat (b) quantification by the proposed method.

Linearity and limits of detection and quantification

Calibration was performed for PQ by HPLC-DAD using S3 deposit contaminated at 7 PQ concentration levels, from 5 to 193 $\mu\text{gPQ gS3}^{-1}$, and submitted to extraction as described in the Materials and methods part (sections “Spiking of deposits with PQ/DQ” and “Extraction procedure for the analytical determination”, respectively) – (Figure 3). The correlation coefficient of 0.996 revealed a linear relationship between the analytical signal and the PQ contamination degree. The limit of detection (LOD) and limit of quantification (LOQ) calculated based on a signal-to-noise-ratio of 3 and 10 were 0.1 and 0.4 $\mu\text{gPQ gS3}^{-1}$, respectively. Figure S1 of the supporting information shows an example of a chromatogram obtained for the PQ-S3 system, where it can be observed a high resolution.

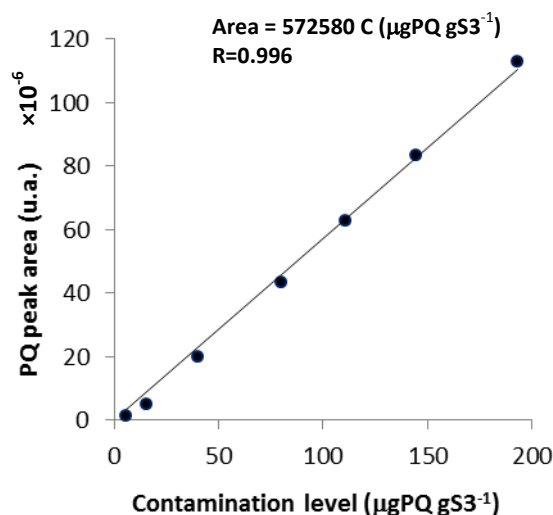


Figure 3. Calibration curve obtained for PQ-S3 system by HPLC-DAD.

Precision and Accuracy

The intermediate precision was evaluated at three PQ spiking levels – 20, 80 and 160 $\mu\text{gPQ gS3}^{-1}$. Intermediate precision, as expressed here, corresponds to the relative standard deviation (RSD%) observed when six independent samples, for each contamination level, were extracted and injected in the same day under the same conditions. Average precision was respectively 3, 4 and 2% for 20, 80 and 160 $\mu\text{gPQ gS3}^{-1}$ (Table 2).

Accuracy was assessed comparing the contamination level obtained from the calibration curve and the real amount of PQ adsorbed on the deposit. Average recoveries ranging from 90 to 101% were reached (Table 2).

The good recovery results and the low RSDs observed enable a reliable quantification of PQ in the tested samples, even at the lowest contamination level assessed.

Table 2. Precision and Accuracy for PQ-S3 system by HPLC-DAD

Contamination level ($\mu\text{gPQ gS3}^{-1}$)	Precision (RSD%)	Recovery (%)
20	3	90 \pm 1
80	4	97 \pm 2
160	2	101 \pm 1

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Estimation of the global uncertainty associated to the results

It was assumed that there are four main sources responsible for the overall uncertainty of the results²¹: uncertainty associated with the preparation of the standards (U1), uncertainty associated with the calibration curve (U2), uncertainty associated to the precision of the extraction and to the chromatographic method (U3), and uncertainty associated to the accuracy (U4). The contribution of each source is depicted in Figure 4a. As observed, the most significant uncertainty source at low contamination levels corresponds to the uncertainty associated with the calibration curve (U2). On the other hand, an increase on the weight of the uncertainty of precision (U3) is evident for the highest contamination levels.

Both combined and expanded uncertainties were determined for each point of the calibration curve (Figure 4b). The combined uncertainty corresponds to the standard uncertainty and, as the name implies, was calculated from the combination of the overall uncertainty sources, as described in the *bottom-up* approach of the EURACHEM CITAC Guide²¹. The expanded one was obtained multiplying the combined uncertainty by a coverage factor of two, which provides a level of confidence of approximately 95%²³. The values for the expanded uncertainty are between 10 and 54%, when the concentration ranges from 193 to 5 $\mu\text{gPQ gS3}^{-1}$. It is clearly evident that the uncertainty increases significantly when approaching the LODs (lower contamination levels), being around 10% for PQ concentrations above 40 $\mu\text{gPQ gS3}^{-1}$.

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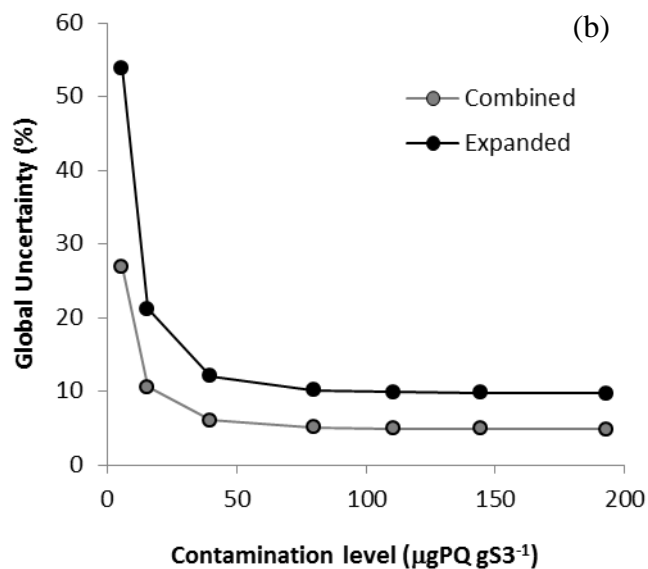
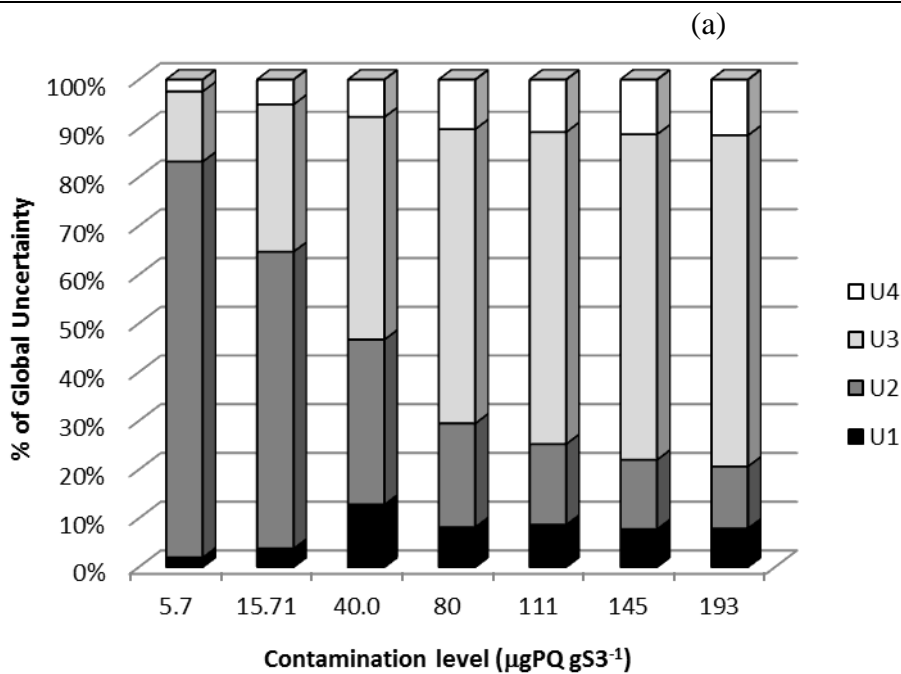


Figure 4. (a) Contribution of each source of uncertainty to the global uncertainty for different PQ contamination levels and (b) combined and expanded global uncertainty for PQ analysis in the S3 deposit.

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Paraquat quantification in different deposits

The analytical method response was also evaluated when different types of deposits spiked with PQ were used. For that, two other deposits were also considered (S2 and S4). The tests with S2 were made in triplicate at three PQ contamination levels (40, 80 and 160 $\mu\text{gPQ gS2}^{-1}$ – Figure S2 of the supporting information). As can be seen from Table 3, although the method remains precise, the extraction percentages obtained for S2 (around 30%) were much lower than those achieved for S3 (Figure 1). A limit of detection of 0.6 $\mu\text{gPQ gS2}^{-1}$ was estimated for the PQ-S2 system. In this case a matrix-matched calibration is recommended for PQ quantification.

Table 3. Extraction percentages, precision and recovery for PQ-S2 and PQ-S4 systems.

System	Contamination level ($\mu\text{g g}^{-1}$)	%Extraction	Precision (RSD%)
PQ-S2 (n=3)	40	31 \pm 5	16
	80	27 \pm 3	10
	160	32 \pm 2	7
PQ-S4 (n=3)	80	32 \pm 3	9
	120	50 \pm 4	9
	160	66 \pm 3	5
	200	72 \pm 4	6

For S4, four PQ contamination levels were considered (80, 120, 160 and 200 $\mu\text{gPQ gS4}^{-1}$). The experiments were also carried out in triplicate and the results were compiled in Table 3. In this case, it can be observed that the extraction percentage is dependent on the degree of contamination (ranged from 32 to 72%). Actually, by plotting the four points it can be observed that the representation follows a linear tendency but, the trendline crosses the x-axis at $59\pm 4 \mu\text{gPQ gS4}^{-1}$ (Figure S3 of the supporting information). This means that the extraction methodology used herein is not suitable for the PQ-S4 system at levels below $59\pm 4 \mu\text{gPQ gS4}^{-1}$. Such observation may be related to the kind of sorption isotherm obtained when S4 deposit is put in contact with a saturated ammonium chloride solution contaminated with increasing amounts of PQ until equilibrium is established (Figure S4 of the supporting information), for which the fitted Langmuir isotherm provided a calculated PQ maximum adsorption capacity of $60 \mu\text{gPQ gS4}^{-1}$. Nevertheless, this analytical method is still very useful for calcium rich deposits (like S4 sample) because, in case of a deliberate or accidental contamination, much higher PQ contamination levels are plausible ($400 \mu\text{gPQ gS4}^{-1}$ at 20°C and $550 \mu\text{gPQ gS4}^{-1}$ at 4°C)⁵. Additionally, the method proved to be very precise (Table 3). Again, a matrix-matched calibration will have to be performed to quantify PQ.

Generally, this simple analytical methodology proved to be suitable for the quantification of PQ in different kinds of deposits whenever the extraction percentages are taken into account.

Suitability of the extraction methodology for Diquat

The applicability of the developed analytical methodology for DQ quantification in S3 contaminated deposits was also evaluated. For that, S3 samples were contaminated with DQ and then submitted to the same extraction procedure developed previously for PQ. This study was performed at three different contamination levels (9, 76 and $154 \mu\text{gDQ gS3}^{-1}$) and in triplicate. The extraction percentages were, on average, $82\pm 15\%$. Mean precision was 5, 3 and 2% for 9, 76 and $154 \mu\text{gDQ gS3}^{-1}$, respectively. The accuracy was again assigned to the difference observed between real contamination and that determined from the calibration curve. Recoveries were 95%, 114% and 107% for 9, 76 and $154 \mu\text{gDQ gS3}^{-1}$ contamination degrees, respectively.

Being simple and fast, this method constitutes an excellent approach for PQ/DQ quantification in deposits, for instance, to obtain a fast response after a suspicion of contamination of a water network (emergency situation).

Conclusions

An analytical methodology able to quantify PQ and DQ in deposits from drinking water networks was developed. This simple and inexpensive method consists in a fast and easy extraction step that requires small sample and solvent amounts. Concerning the optimization of the extraction procedure, the best conditions found correspond to add 1 mL of a saturated ammonium chloride solution to 0.5 g of deposit for 30 min. A limit of detection of $0.1 \mu\text{gPQ gS3}^{-1}$ was obtained for the PQ-S3 system with the expanded uncertainty ranging from 10-54% for concentrations between 193 and $5 \mu\text{gPQ gS3}^{-1}$, respectively. The method was also successfully applied to the DQ quantification in the S3 deposit. Additionally, precision and accuracy was verified when applied to different kinds of deposits (S2 and S4), but the correspondent extraction percentages must be taken into account to obtain the PQ/DQ contamination level.

This methodology can be easily implemented in a quality control laboratory and, due to its simple and expedite nature, proves to be a good approach for the quantification of PQ and DQ in deposits from drinking water distribution systems.

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Notes and references

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Supporting Information

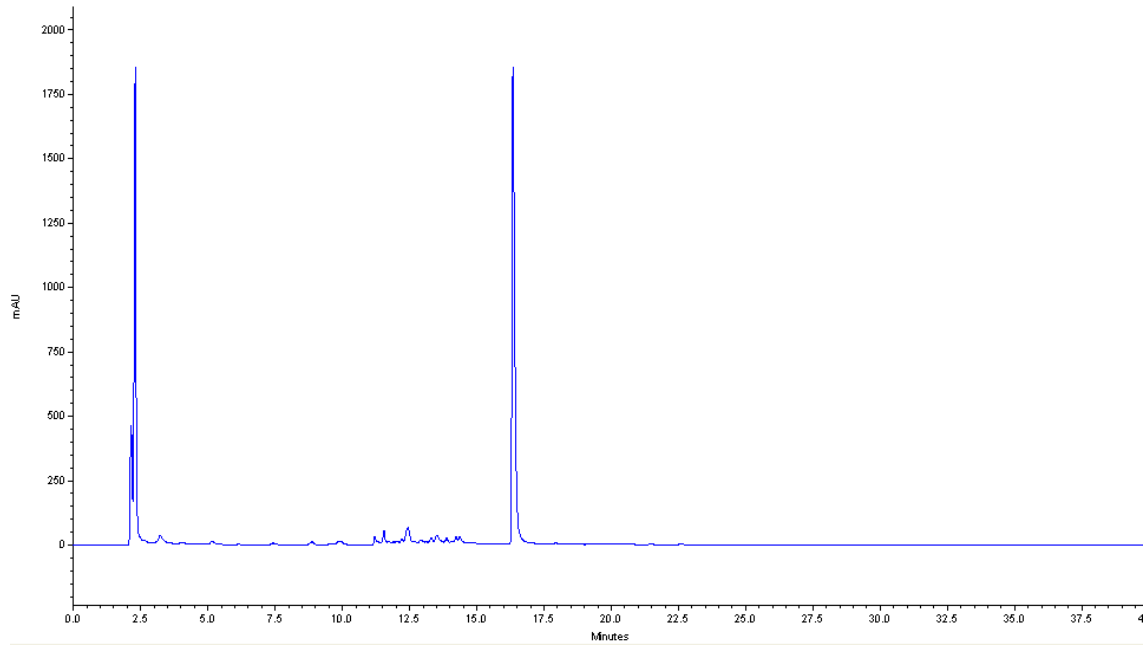


Figure S1. Example of a chromatogram for PQ-S3 system (80 $\mu\text{gPQ/gS3}$).

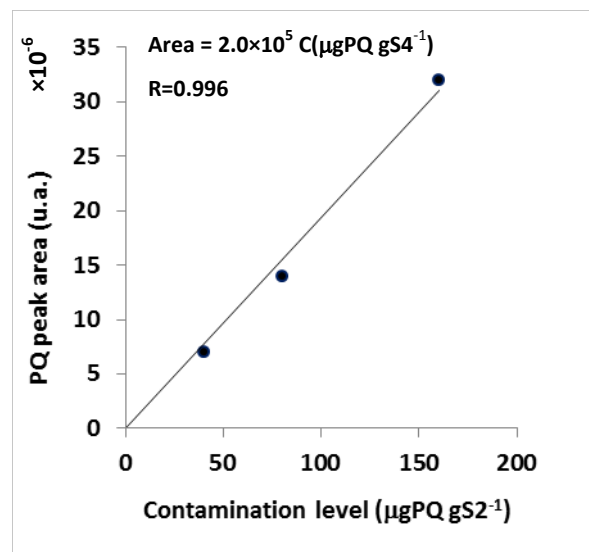


Figure S2. Linear relationship obtained for PQ-S2 system by HPLC-DAD.

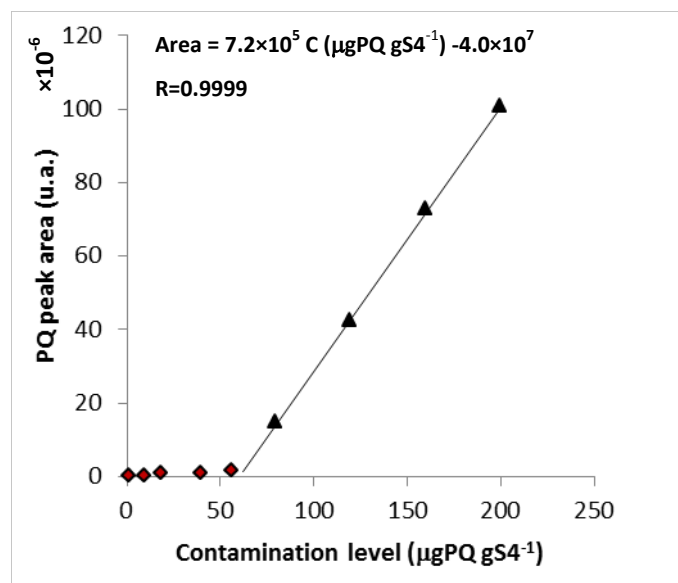


Figure S3. Linear relationship obtained for PQ-S4 system by HPLC-DAD (results out of linearity are signaled with different symbols)

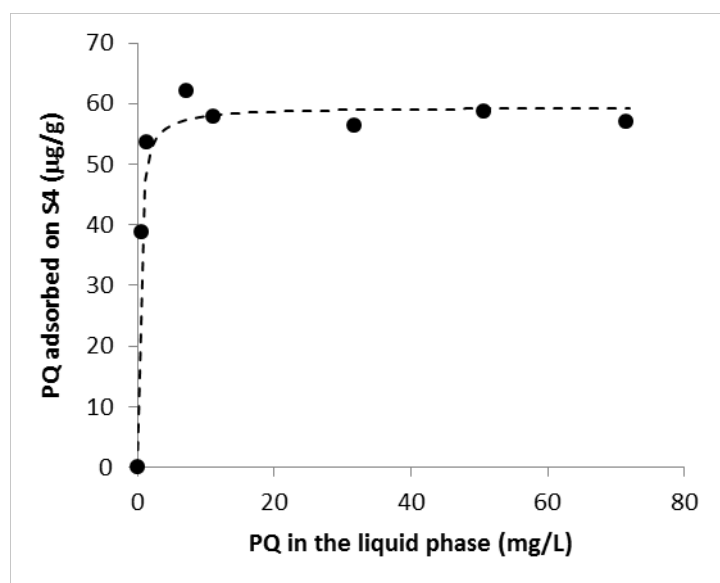


Figure S4. Adsorption isotherm for PQ-S4 system.