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Development of a photoinduced chemiluminescent method for the determination of the herbicide quinmerac in water

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Abstract

A new, simple and sensitive method, based on photoinduced chemiluminescence, was developed for the determination of quinmerac. The photoproduct, obtained after UV irradiation in basic medium, was mixed with sodium sulfite (sensitizer), and Ce(IV) (oxidant) in acid medium. A wide linear dynamic range (2-600 ng mL^{-1}) and a limit of detection of 0.6 ng mL^{-1} were obtained without any pretreatment (0.08 ng mL^{-1} after solid phase extraction). The determination was performed using a flow injection manifold, which allowed a high throughput (144 h^{-1}). The inter-day reproducibility was 5.6% (n=5), and the intra-day repeatability was 3.9 and 2.9% for 20 and 200 ng mL^{-1} of quinmerac, respectively (n=21). Finally, the method was applied to surface and ground waters with recoveries ranging from 78.1 to 94.5%.

Index Headings: Quinmerac; photoinduced chemiluminescence; pesticides; flow injection; water

INTRODUCTION

Substituted quinolinecarboxylic acids are highly selective auxin herbicides. Quinmerac, 7-chloro-3-methylquinoline-8-carboxylic acid (Fig. 1), is used for broad-leaved and grass weeds control in winter oilseed rape, but in sensitive dicots, auxins lead to tissue damage and cell death. On the other hand, it has been found that quinmerac can promote the cellular division and expansion allowing an increase of the proportion of fruits with adequate size for fresh market[1,2].

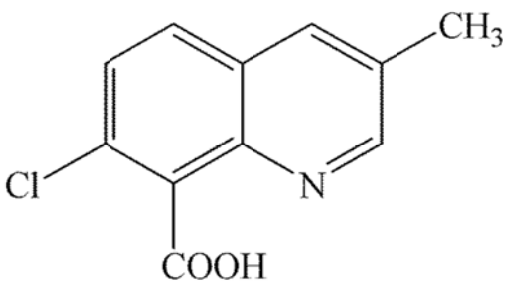

Figure 1. Molecular structure of quinmerac.

Quinmerac presents a low sorption by neutral or slightly acid agricultural soils, being the soil organic matter content the major factor determining its sorption. Consequently, soils with low and moderate organic carbon content are expected to show a low quinmerac adsorption[3]. In addition, this pesticide is quite stable in aqueous solutions at pHs ranging from 5 to 9; as a consequence it can be dragged by rain and irrigation water, contaminating ground and surface waters.

The occurrence of pesticides in water is a continuing regulatory concern and, to prevent health problem, low maximum residue levels have been fixed and therefore sensitive analytical methods are necessary for their determination[4]. Quinmerac is

included in the list of "Active substances authorized for incorporation in plant protection products; only for uses as herbicide" from the European Union[5]. However, there are very few papers devoted to the development of new analytical procedures for its determination and these are multi-residue methods. In all cases, liquid chromatography (LC) coupled to mass spectrometry (MS)[6-14] was used, except in the method proposed by Vandecasteele et al.[15]. In that case, a solid phase extraction (SPE) coupled to liquid-liquid microextraction and reversed-phase LC using diode array detection was proposed for quantification of 77 pesticides in groundwater, with a limit of detection of 175 ng mL^{-1}.

Most of existing LC-MS methods are applied to food samples, but some of them have been developed for the determination of quinmerac in water. E.g., tandem LC-MS/MS was used for the determination of 300 pesticides in drinking water by Greulich et al.[11.] That method allowed the determination of quinmerac residues down to 0.1 ng mL^{-1}, with a good precision (RSD<18%, n=15) and insignificant matrix effects (trueness between 101-107%, n=15) without need of sample enrichment and/or cleanup. On the other hand, Wode et al.[12] developed an ultra high performance liquid chromatography (UHPLC) – high resolution mass spectrometry (HRMS) for the determination of 72 contaminants, among them some acidic pesticides, as quinmerac. On-line SPE with C18 Hypersil Gold column led to limits of detection (LOD) of 8, 23 and 45 pg mL^{-1} in drinking, and diluted surface and waste waters, respectively. Mantzos et al.[14] determined quinmerac in runoff water within the range of 50-1000 ng L^{-1} (LOD 0.25 ng L^{-1}). A SPE (0.5 L) was performed before the separation with the above mentioned column, using a triple quadrupole MS with electrospray ionization for detection. Recoveries between 65.4 and 73.3% (RSD < 15.3%) were found for spiked samples.

In order to avoid sophisticated equipment, not always available for all laboratories, we selected chemiluminescence detection for the quinmerac determination, as it can provide the required selectivity and sensitivity. In addition, its combination with flow injection (FI) methodology allowed the automation of the procedure, and consequently, a low cost, highly reproducible and time saving alternative for the quinmerac determination.

To the best of the authors' knowledge, this is the first time that quinmerac has been determined by a luminescent technique. The developed method was based on the photoinduced chemiluminescence (PICL) of quinmerac performed in basic medium followed by oxidation of the photoproducts with Ce(IV) in sulfuric acid, using sulfite as sensitizer. The sensitivity and selectivity of the method was improved by means of SPE.

EXPERIMENTAL

Reagents

Milli-Q water and reagents of analytical grade were used to carry out the experiments. $Ce(NH_4)_2(NO_3)_6$, H_2SO_4 and Na_2SO_3 were supplied by Panreac; and NaOH was purchased from Scharlau. Quinmerac (99.2%), amitrole, metazachlor, metalaxyl, thiacloprid and cyromazine (99.9%); 2,4-D and pirimicarb (99.6%); diquat monohydrate (99.4%); glyphosate (99.2%); fenamiphos (97.7%); imazalil (99.8%); MCPA (98.7%) were supplied by Riedel-de Haën. Methomyl (99.5%) was purchased from Chem Service; while diphenamide, chloridazon (99.9%) and dimethoate (99.4%) were obtained from Fluka.

SPE of water samples was carried out using Chromabond HR-X 3 mL/200 mg from Macherey-Nagel.

Apparatus

The flow assembly used is depicted in Fig. 2 and consisted of PTFE coil of 0.8 mm i.d.; Gilson minipuls peristaltic pumps provided with pump tubing from Omnifit; and a Model V-450 (Upchurch Scientific) 6-port medium pressure valve. The flow cell was a flat-spiral glass tube of 1 mm i.d. and 3 cm total diameter. The photodetector package was a P30CWAD5 type 9125B photomultiplier tube supplied by Electron Tubes; in order to avoid the light input, it was located in a laboratory-made light-tight box. The output was fed to a computer equipped with a counter-timer, also supplied by Electron Tubes.

Photoreactor consisted of a 400 cm length and 0.8 mm i.d. PTFE tubing helically coiled around a 15 W low-pressure mercury lamp (Sylvania) for germicidal use.

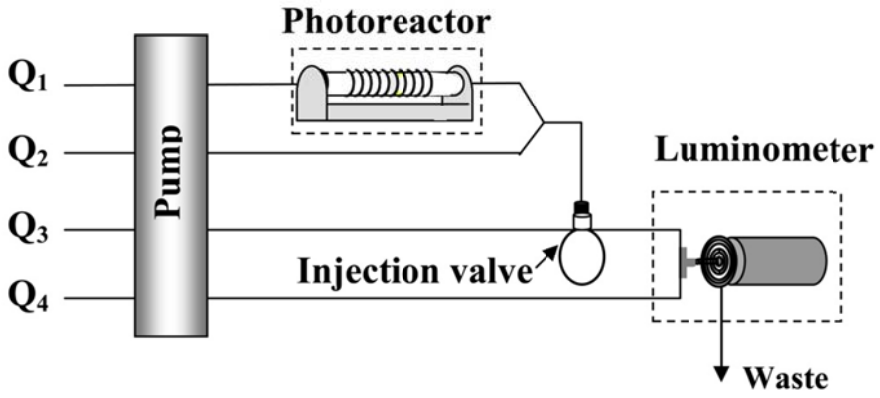

Figure 2. Flow assembly for the PICL determination of quinmerac. Q_1: quinmerac in NaOH 0.08 M at 2.0 mL min^{-1}; Q_2: sodium sulfite $9x10^{-4}$ M at 0.7 mL min^{-1}; Q_3: H_2O at 14.2 mL min^{-1}; Q_4: Ce(IV) $3x10^{-3}$ M in H_2SO_4 0.11 M at 5.2 mL min^{-1}. Injection volume: 508 μL.

Sample preparation

Water samples from different origins, namely: ground, spring, mineral and tap waters, were collected in plastic flaks at 4 ºC and analysed before 48 h. In order to remove sand and other suspended solid matters, the samples were filtered over a 0.45 μm membrane filter (Sartorius). After that, the pH of samples was adjusted to 2 using HCl 2 M.

SPE of 100 mL of the spiked samples (0.5, 2.0, 3.5, 5.0 and 6.5 ng mL^{-1}) was performed at a flow-rate of 5 mL min^{-1} using a vacuum system and cartridges Chromabond HR-X. Preconditioning of cartridges was performed with 6.0 mL of methanol followed by 6.0 mL of water and 2 mL of HCl 0.01 M. After the sample went through, 2 mL of HCl 0.01 M and 6 mL of water was used for washing, next, air was passed 15 min for drying. Quinmerac was eluted by gravity with 3.0 mL of methanol and finally under vacuum. Finally, the solvent was evaporated to dryness, using a water bath at 30ºC, under a gentle stream of nitrogen. The residue was dissolved with 4.8 ml of water and 0.2 mL of NaOH 2.0 M. As a result, a 20-fold pre-concentration was achieved.

RESULTS AND DISCUSSION

Preliminary studies

Chemiluminescent (CL) response from quinmerac and its photoproducts was tested with different oxidant systems, namely $KMnO_4$, Ce(IV), KIO_4, $K_2S_2O_8$, $K_3Fe(CN)_6$, N-bromosuccinimide, H_2O_2 and $NaClO_4$ using a FI assembly. To this aim, a quinmerac solution flowing at 1.9 mL min^{-1} and different photodegradation media (water, H_2SO_4 0.1 M or NaOH 0.1 M) at 0.65 mL min^{-1} were mixed just before the

photoreactor. After that, 508 μL of the photodegraded mixture were inserted in a carrier of water at 7.9 mL min^{-1}, and mixed with different oxidant systems (obtained by mixing oxidants and media both at 1.35 mL min^{-1}). Fig. 3 shows the obtained results after irradiation (in all cases negligible signals were obtained without photodegradation). As can be seen, Ce(IV) in sulfuric acid provided the highest outputs, when using NaOH as irradiation medium. Consequently, those conditions were selected for further work.

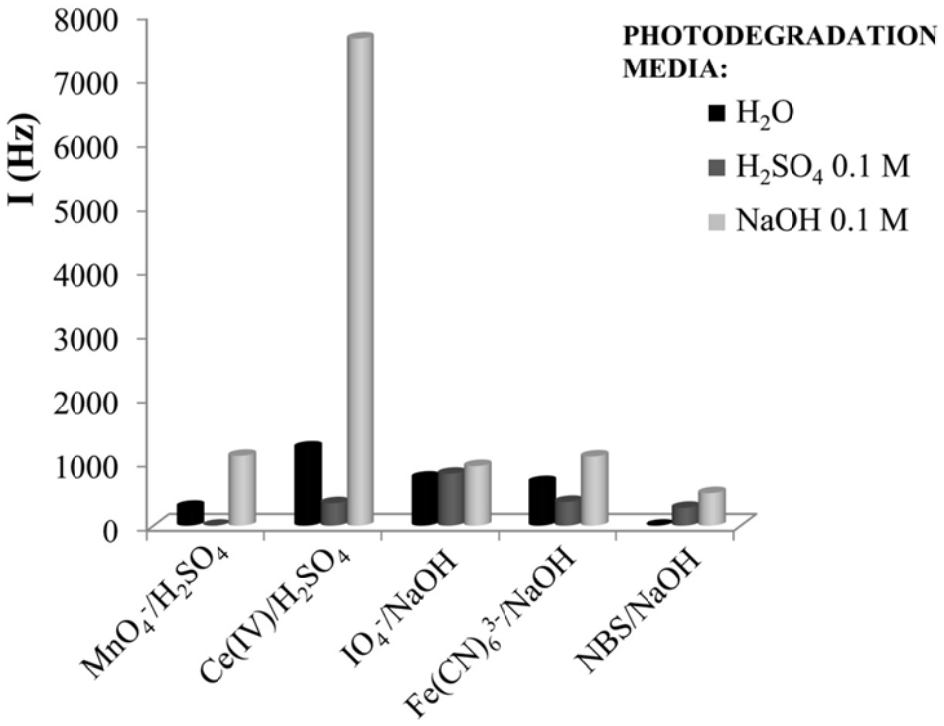

Figure 3. Chemiluminescent signal (I) from photoproducts of 100 μg mL^{-1} of quinmerac, obtained using different oxidant systems and photodegradation media. [$KMnO_4$] = $1.2x10^{-3}$ M; [Ce(IV)]= [KIO_4]= [$K_3Fe(CN)_6$]= $8x10^{-3}$ M; [N-bromosuccinimide (NBS)]= $2x10^{-2}$ M. Oxidation media: [H_2SO_4]= 2 M; [NaOH]= 2 M.

Optimization

Chemical and hydrodynamic parameters were optimized using the univariate method. The effect of the Ce (IV) concentration on quinmerac 50 μg mL^{-1} was studied within the 10^{-3} – $1.5x10^{-2}$ M range. A maximum signal was achieved for Ce (IV) $6x10^{-3}$ M; accordingly, that value was selected. Then, H_2SO_4, HCl, $HClO_4$, HNO_3, H_3PO_4 and CH_3COOH, all of them at 2 M, were tested as oxidation media. As sulfuric and nitric acids provided the best results, the effect of their concentration on the CL signal was further studied. As a result, nitric acid was discarded because of its negative effect on the baseline. On the other hand, the optimal concentration found for sulfuric acid was 0.22 M (studied range: 0.05-2.0 M).

As oxidation time is dependent on carrier and oxidant system flow rates, the effect on the CL signal of global flow rates within the 10.8-24.6 mL min^{-1} range was studied using quinmerac 15 μg mL^{-1}. The signal remained constant from 19.6 mL min^{-1} (14.3 and 5.3 mL min^{-1} for carrier and oxidant system respectively) onwards; consequently this value was chosen for further work.

NaOH concentrations in the 0.04 - 0.12 M range were tested as irradiation medium using quinmerac 10 μg mL^{-1}. A maximum signal was found for NaOH 0.09 M. After that, different irradiation times were assayed using this medium. Outputs increased with irradiation time, but from 67 s onwards only small increases were observed. Therefore, quinmerac was irradiated for 67 s (flow rates of 1.35 and 0.45 mL min^{-1}, for sample and NaOH respectively) in order to avoid a throughput decrease.

The effect of potential CL enhancers and photosentizers[16], was assayed, namely: ethanol 10%, acetone 1%, acetonitrile 30%, a mixture of acetonitrile 30% and acetone 1%, 2-propanol 25%, 1,4-dioxane 10%, formic acid 1%, sodium sulfite 10^{-4} M,

quinine 10^{-4} M, 8-hydroxyquinoline 10^{-4} M, fluorescein 10^{-4} M, eosin yellowish 10^{-4} M and rhodamine B 10^{-6} M, riboflavin 10^{-4} M, H_2O_2 0.05%, β-cyclodextrin 0.17 and 0.5%, sodium dodecyl sulfate 0.05 and 0.15%, hexadecyltrimethylammonium bromide 0.07 and 0.22%, Triton X-100 0.05 and 0.15% and hexadecylpyridinium chloride (HPC) 0.08 and 0.25%. To this aim, quinmerac 5 μg mL^{-1} in NaOH 0.09 M. was mixed with the sensitizer after or before the photoreactor, depending on whether the sensitizing effect was studied, both on the oxidation and photodegradation or only on the oxidation step.

As a result, it was found that eosin yellowish (+290% increase, when introduced before irradiation) and sulfite (+320%, introduced after irradiation; +108% introduced before irradiation) provided the highest outputs. Further study with different concentrations of these substances demonstrated that sulfite $1.5x10^{-3}$ M, mixed with quinmerac 2 μg mL^{-1} after the lamp, provided the best results, with a 73-fold increase in sensitivity. Consequently, despite the blank signals obtained from the excited state of sulfur dioxide produced together with Ce(III) [17], the use of sulfite as a sensitizer was advantageous. To avoid dilution of samples, sulfite was introduced by an additional channel that merged with the oxidant stream. As a result, the baseline was negatively affected, and smaller signals were found. Consequently, the configuration of the FIA manifold finally selected was that depicted in Fig. 2.

In order to study the effect of the temperature, the sample loop and two 1.5 m sections of teflon tube (0.8 mm i.d.) corresponding to the carrier (located immediately prior to the injection valve to minimize sample dispersion) and oxidant, were submerged in a water bath at temperatures within the 21-80ºC range. No improvements were achieved; consequently, room temperature was chosen for further work.

The effect of the injection volume was studied in the 407 – 608 μL range. Signals rose until a value of 508 μL and then levelled off, thus this value was selected.

Finally, a re-optimization of the most important parameters was performed. The ranges studied were as following (selected values in brackets): [Ce(IV)]: 10^{-3} – $4x10^{-3}$ M ($3x10^{-3}$ M); [sulfuric acid]: 0.10 – 0.13 M (0.11 M); carrier+oxidant system flow rates: 17.7 – 22.9 mL min^{-1} (19.4 mL min^{-1}, corresponding to 14.2 and 5.2 mL min^{-1} for carrier and oxidant, respectively); [NaOH]: 0.02 – 0.12 M (0.08 M); [sulfite]: $6x10^{-4}$ – 1.5 10^{-3} M ($9x10^{-4}$ M); and, irradiation times 54 – 80 s (60 s, corresponding to a flow rate of 2 mL min^{-1}).

Possible mechanism for the PICL reaction

M.V. Pinna et al.[18] reported that quinmerac, when exposed to UV irradiation from low-pressure mercury lamps (maximum irradiation at 254 nm), is degraded rapidly in water through a decarboxylation reaction, resulting in 7-chloro-3-methylquinoline as the only product. On the other hand, sulfite can be oxidized by Ce(IV) to produce excited SO_2*. Bearing in mind the low luminescence efficiency exhibited by that specie within the 300-450 nm range[19], the possible enhancenment mechanism would involve energy transfer processes between SO_2* and the photoproduct of quinmerac, which would yield an excited specie responsible of the light emission. That CL mechanism has been already reported for many organic compounds from different chemical families[20-25].

In addition, the proposed mechanism is in agreement with previous studies dealing with the CL mechanism for other quinoline derivatives as lomefloxacin in the presence of a Ce(IV)-Na_2SO_3-Tb^{3+} system[26,27]. According to those studies, SO_2*

transfers its energy to a complex between the lomefloxacin[27] (or its photoproduct[26]) and Tb(III). Then an intramolecular energy transfer from lomefloxacin (or its photoproduct) in the excited-state complex to Tb^{3+} yields the excited Tb^{3+*} which is proposed as the CL emitter[27]. In our case no lanthanide ion was present, consequently as above-mentioned, energy transfer from SO_2* to the photoproduct should be the responsible of the enhanced CL.

Analytical performance

A wide linear dynamic range was found between 2 and 600 ng mL^{-1}, fitting the equation I = (0.268±0.015) C + (0.6±0.2), r^2=0.9990 (n=5), where I is the intensity after subtracting the blank signal in kHz, and C is the concentration of quinmerac in ng mL^{-1}. The limit of detection (LOD), defined as the lowest quinmerac concentration giving a signal equal to or greater than the blank peak plus three times its standard deviation (SD), was found to be 0.6 ng mL^{-1}. The inter-day reproducibility was determined from the above-mentioned series of 5 calibrations and the relative SD was 5.6%. The intra-day repeatability was investigated using two series of 21 injections of quinmerac 20 and 200 ng mL^{-1}; the relative standard deviations (RSD) were 3.9 and 2.9%, respectively. The throughput, calculated from both series, was 144 h^{-1}.

Interferences

In order to assess the tolerance of the proposed method, the interfering effect of the ions commonly present in natural waters was investigated (Table I). The effect of 17 pesticides from different chemical groups[28] was also studied (Table II). Diphenamid, diquat and metazachlor exhibited the strongest interfering effect. Chloridazon,

formulated together with quinmerac at a ratio of 8:1 in some formulations[29], at a 20-fold higher concentration than that from quinmerac, did not interfere significantly. The other pesticides tested did not show a significant interfering effect, despite some of them, or photoproducts thereof, have chemiluminescent properties.[30-33]

Table I. Interfering effect of ionic species on quinmerac 20 ng mL^{-1}.

Interferent	Concentration ($\mu g\ mL^{-1}$)	Error (%)
Na^+	600	-4.0
K^+	70	+4.7
Ca^{2+}	60	-4.9
Mg^{2+}	100[a]	+1.3
NH_4^+	40	-3.5
Cl^-	926	-4.0
SO_4^{2-}	1000[a]	-3.4
CH_3COO^-	6	+4.9
$H_2PO_4^-$	20	-4.6
HCO_3^-	1000[a]	+0.9
NO_3^-	10	-4.0
Urea	1.5	-3.7

[a] Maximum concentration assayed

Table II. Interfering effect of pesticides on quinmerac 20 ng mL^{-1}.

Common name	Chemical group	[pesticide] ($ng\ mL^{-1}$)	[pesticide] / [quinmerac]	Error (%)
Amitrole	Triazole	400	20	-4.8
Chloridazon	Pyridazinone	400	20	-4.9
Cyromazine	Triazine	40	2	+4.9
2,4-D	Alkylchlorophenoxy	160	8	+2.7
Dimethoate	Organophosphate	400	20	+1.1
Diphenamid	Alkanamide	20	1	+2.4
Diquat monohydrate	Bipyridylium	20	1	+3.9
Fenamiphos	Organophosphate	400	20	+2.9
Glyphosate	Phosphonoglycine	400	20	-1.6
Imazalil	Imidazole	100	5	+1.9
MCPA	Aryloxyalkanoic acid	100	5	+3.8
Metalaxyl	Phenylamide	240	12	+0.5
Metazachlor	Chloroacetamide	20	1	+3.6
Methomyl	Carbamate	400	20	-1.6
Pirimicarb	Carbamate	140	7	+2.2
Thiacloprid	Neonicotinoid	240	12	-0.4

Analytical applications

In order to increase the selectivity and sensitivity of the method, a SPE strategy was applied as described in Section 2.3 to mineral, tap, ground and spring water samples. A mixture of methanol:tetrahydrofuran (1:1, v/v) was also considered as eluent, instead of methanol. However, lower recoveries were found and consequently its use was discarded.

SPE of 100 mL allowed a LOD of 0.08 ng mL^{-1} to be achieved, which is under the maximum permitted concentrations, established by European Community: 0.1 ng mL^{-1} for individual pesticides and 0.5 ng mL^{-1} for total pesticides in drinking water[34] and 1–3 ng mL^{-1} in surface water. [35]

As can be seen in Table III, recovery factors ranging from 78.1 to 94.5% (RSD < 17%) for samples spiked at five levels (between 0.5 and 6.5 ng mL^{-1}) were obtained. Bearing in mind that the acceptable range for recoveries in water samples is usually set between 70 and 110%, with a maximum permitted RSD of 20% [36], it can be considered that the analytical performance of the proposed PICL method was successful.

Table III. Accuracy of the method.

Sample	Added (ng mL^{-1})	Found (ng mL^{-1})	Average recovery (%) (RSD, %)
Mineral water	0.500	0.461	94.1 (9.1)
	2.000	2.147	
	3.500	3.410	
	5.000	4.330	
	6.500	5.660	
Tap water	0.500	0.462	94.5 (7.6)
	2.000	2.060	
	3.500	3.518	
	5.000	4.273	
	6.500	5.922	
Ground water	0.500	0.453	78.1 (17.0)
	2.000	1.873	
	3.500	2.464	
	5.000	3.174	
	6.500	4.712	
Spring water	0.500	0.453	88.3 (17.0)
	2.000	2.228	
	3.500	2.582	
	5.000	4.475	
	6.500	4.949	

CONCLUSIONS

It can be concluded that the proposed method is satisfactory for the analysis of quinmerac in water samples, as FI methodology provide a high sample throughput (144 h^{-1}) and reproducibility (RSD of 3.9 and 2.9% for 20 and 200 ng mL^{-1} of quinmerac, respectively). On the other hand, the use of CL detection led to wide linear dynamic ranges (2-600 ng mL^{-1}) and low LODs (0.08 ng mL^{-1} and 0.6 ng mL^{-1} with and without SPE respectively). Those values are under the maximum permitted concentrations established by the European Community for drinking water, and they are much better than those obtained using LC and diode array detection (LOD: 175 ng mL-ng mL^{-1})[15] and competitive with some of the reported LODs of LC-MS methods (0.1 ng mL^{-1},[11] 0.008-0.045 ng mL^{-1}, [14]). On the other hand, the low cost and simplicity of the

developed method makes it highly suitable for routine analysis of quinmerac. Its applicability was tested in water collected from different sources with recoveries between 78.1 and 94.5% for samples spiked at five concentrations.

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