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Time-of-flight high resolution versus triple quadrupole tandem mass spectrometry for the analysis of quaternary ammonium herbicides in drinking water

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Abstract

Conditions for the simultaneous determination of quaternary ammonium herbicides by liquid chromatography–electrospray–mass spectrometry were established. Two electrospray sources with different configurations and two mass analyzers were used: a Turbo Ionspray™ source with a triple quadrupole instrument and a Z-spray source with a time-of-flight (TOF) analyzer. The separation was performed using ion pair reversed phase chromatography. An on-line solid-phase extraction procedure with polydivinylbenzene cartridges was automatized by using a Prospekt device coupled to both LC–MS instruments. Good run-to-run precisions were obtained for both instruments, and the determination of quats in drinking water was evaluated using spiked samples. Better limits of detection were obtained using tandem mass spectrometry. The results obtained allowed the analysis of quats in drinking water samples below the legislated levels.

Keywords: Quaternary ammonium herbicides; Accurate mass measurement; Tandem mass spectrometry; Mass spectrometry; Time-of-flight

1. Introduction

Quaternary ammonium herbicides and plant growth regulators, commonly known as "quats", constitute a particularly difficult group of compounds to analyze. Included in this group are the three herbicides paraquat (PQ), diquat (DQ) and difenzoquat (DF), and the two plant-growth regulators chlormequat (CQ) and mepiquat (MQ). PQ and DQ are used as non-selective contact herbicides for the control of weeds and DF is a selective herbicide used for post-emergence control of wild oats in cereal crops. CQ is used to increase yield and to improve fruit setting in fruits and vegetables, while MQ is used on cotton to reduce vegetative growth and to inhibit sprouting [1]. On the basis of their toxicity, the World Health Organization (WHO) has classified PQ, DQ and DF as moderately hazardous and CQ and MQ as slightly hazardous [2]. Because of this, there is great concern about the presence of these compounds in different matrices such as fruits, soils and waters. For drinking waters, the US Environmental Protection Agency (EPA) has established a maximum contaminant level of 20 $\mu g\,l^{-1}$ for DQ and a maximum contaminant level goal of 3 $\mu g\,l^{-1}$ for PQ [3,4]. The European Union has not regulated the levels of these compounds in drinking water and continues to apply the values of 0.1 $\mu g\,l^{-1}$ for individual pesticides and 0.5 $\mu g\,l^{-1}$ for total pesticides [5].

The analysis of these compounds is difficult due to their cationic character and liquid chromatography (LC) with direct UV detection [6,7] and capillary electrophoresis (CE) with direct [8,9] or indirect [10] UV detection, are frequently applied. To overcome the problems of identification and quantitation of the methods mentioned above, mass spectrometry (MS) as a detection technique has been proposed. In addition, MS also permits the simultaneous analysis of the three herbicides and the two plant growth regulators. Thus, quats have been analyzed by LC–MS or LC–MS–MS using different MS spectrometers such as single quadrupoles [11–15], triple quadrupoles [16] and ion traps [14,17,18]. CE–MS has also been used for the determination of these

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compounds with these three previously mentioned analyzers [19–22]. Nevertheless, LODs achieved with the coupling of CE–MS for quats did not allow the analysis of these compounds in drinking water at the European Union legislated levels [5]. LC–MS has also been applied to the analysis of residues of chlormequat in fruits and fruit commodities such as purées and juice concentrates [23–27].

The use of LC–MS for confirmatory purposes is not always possible when working with quadrupole and ion trap mass analyzers in single MS mode due to their low mass resolution and the lack of structural information provided by the atmospheric pressure ionization techniques. To overcome this problem, tandem mass spectrometry is frequently used but, for confirmation purposes, at least two MS–MS transitions are needed [28]. However, this is only possible at low concentration levels when the MS–MS spectrum of the target compound has more than one abundant product ion.

Time-of-flight (TOF) mass analyzers provide a high selectivity because of the high resolutions (∼10 000) now attainable without loss in sensitivity, and a high mass accuracy [29]. These characteristics make it possible to confirm the presence of the analytes in single MS mode. An internal standard reference mass was used to compensate the instrument drift and to perform the lock mass correction. Different approaches for the introduction of this lock mass reference compound are used, such as infusion in the same solution of the analytes [30], post-column addition [31,32], or switching between separate sample and reference sprays [33,34]. The lock mass correction can provide mass accuracy in the 5–10 ppm range [30,31,33].

Capillary electrophoresis-time-of-flight mass spectrometry has been used to analyze paraquat and diquat in drinking water [35] and matrix assisted laser desorption ionisation-time-of-flight mass spectrometry (MALDI-TOF) has also been applied to the analysis of quats in standard solutions [36,37]. However, none of these publications used a lock mass correction for the accurate mass determination of these compounds.

The aim of the present paper is to evaluate two LC–MS methods for the determination of quats in drinking water. A TOF analyzer with high resolution and mass accuracy in single MS mode and a triple quadrupole low resolution mass analyzer which provides high sensitivity in selected reaction monitoring (SRM) mode were used. The automatization of a previously established on-line preconcentracion method [17] by means of a Prospekt device was performed, and the procedure was applied to the analysis of spiked drinking water samples.

2. Experimental

2.1. Chemicals

Quats were obtained from the following sources: diquat (1,1′-diethylene-2,2′-bipyridinium ion, DQ), difenzoquat (1,2-dimethyl-3,5-diphenylpyrazolium ion, DF) and chlormequat (2-chloroethyltrimethylammonium ion, CQ) were purchased from Chemservice (West Chester, PA, USA), paraquat (1,1′-dimethyl-4,4′-bipyridinium ion, PQ) from Sigma (St. Louis, MO, USA) and mepiquat (1,1′-dimethylpyperidinium ion, MQ) from Riedel-de Haën (Seelze, Germany). Heptylviologen (1,1′-diheptyl-4,4′-bipyridinium ion, HV) purchased from TCI (Tokyo, Japan) was used as internal standard. The deuterated compounds paraquat-d_8 (1,1′-dimethyl-4,4′-bipyridinium-rings-d_8 ion, PQ-d_8), diquat-d_4 (1,1′-ethylene-d_4-2,2′-bipyridinium ion, DQ-d_4) and chlormequat-d_4 (2-chloroethyl-d_4-trimethylammonium ion, DQ-d_4, 100 mg l^{-1}) were obtained from Dr. Ehrenstorfer (Augsburg, Germany) and were also used as internal standards. Ethylviologen (1,1′-diethyl-4,4′-bipyridinium ion, EV) from Aldrich (Milwaukee, WI, USA) was used as internal standard reference mass for the lock mass correction with the Q–TOF instrument. The structures of all these compounds are shown in Fig. 1.

HPLC-gradient grade acetonitrile (ACN), sodium hydroxide, formic acid (98–100%), toluene and ammonia solution 25% (analytical grade) were purchased from Merck (Darmstadt, Germany). Heptafluorobutyric acid (HFBA) and hexamethyldisilazane (HMDS) were obtained from Sigma (Poole, UK).

Stock standard solutions of individual quats, internal standard and deuterated compounds, 1000 mg l^{-1}, were prepared in water and stored in plastic vials to prevent adsorption. Working solutions were obtained by mobile phase dilution and passed through a 0.45 μm nylon filter before use. All glass material in contact with quats, such as glass vials, were silanized for 24 h with a 10% HMDS solution in toluene in order to prevent the adsorption of these compounds.

2.2. Instrumentation

A quaternary pump system from Agilent Technologies (USA) model Series 1100 was coupled to an API 3000™ (Perkin Elmer Sciex, Canada) equipped with a Turbo Ionspray™ ionization source working in positive mode and a triple quadrupole analyzer. Mass spectrometry data were processed with Analyst v1.1 software. Optimal ionization source working parameters were: electrospray voltage 1.5 kV; nebulizer gas flow-rate 11 arbitrary units (a.u.); curtain gas flow-rate 13 a.u.; turbo ionspray gas flow-rate 4000 cm^3/min; turbo ionspray gas temperature 550 °C; declustering potential 38 V. For LC–MS selected ion monitoring (SIM) using the *m*/*z* corresponding to the ions $[M]^+$ (CQ, CQ-d_4, MQ and DF) or $[M–H]^+$ (PQ, PQ-d_8, DQ, DQ-d_4 and HV) are used (Table 1). For LC–MS–MS, SRM mode was used selecting as precursor ions the $[M]^+$ and $[M–H]^+$ mentioned above, and the *m*/*z* corresponding to the most abundant product ion was monitored. The collision cell offset voltage was between 33 and 45 V and the collision gas pressure (N_2) was 5 a.u. The chromatogram was segmented into three windows and only three or four transitions were monitored simultaneously for each

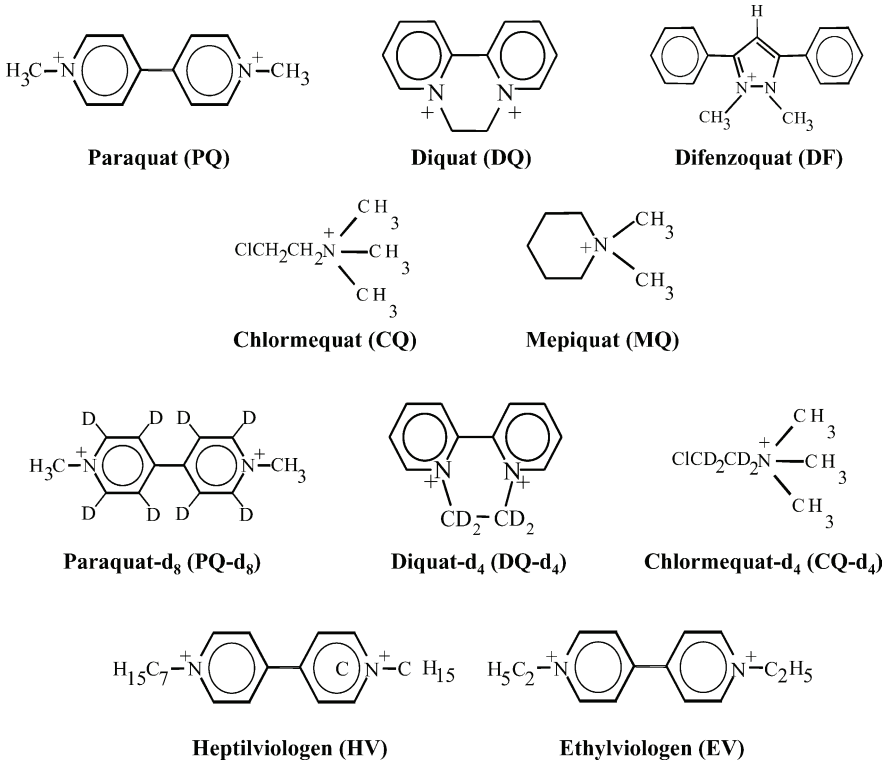

Fig. 1. Structures of quats, internal standards, and lock mass reference.

one (Table 1). Both SIM and SRM acquisitions were performed in centroide mode.

A quaternary pump system from Waters (Milford, MA, USA) model Alliance 2690 was coupled to a quadrupole–time-of-flight (Q–TOF Ultima) mass spectrometer (Micromass, Manchester, UK) equipped with a Z-spray ESI source working in positive mode and V-Optics configuration. Data acquisition was carried out with MassLynx v4.0 software. Optimal ionization source working parameters were: capillary voltage 4.0 kV; cone voltage 60 V; source temperature 150 °C; desolvation temperature 150 °C; cone gas flow-rate 100 l h^{-1}; desolvation gas flow-rate 900 l h^{-1}. The scan time for the Q–TOF instrument was 1 s monitoring *m*/*z* values ranging from 50 to 400 (interscan time 0.1 s). Post-column addition by means of a zero-dead volume Valco T-piece (1 μl min^{-1}) of a 15 mg l^{-1} solution of EV (*m*/*z* = 214.1470) in mobile phase was used as lock mass for accurate mass measurement. Acquisition was performed in profile mode. Moreover, to improve quantitative results PQ-d_8, DQ-d_4 and HV were used as internal standards for PQ, DQ and DF, respectively, and CQ-d_4 as internal standard for CQ and MQ and a mass window of ±0.01 Da was used for quantitation purposes.

The Q–TOF instrument was calibrated daily using quats as calibrating standards. Moreover, to extend the mass range, diethylamine (M_r 74 Da), EV (M_r 214 Da) and HV (M_r 354 Da) were added to the calibration standard mixture.

Table 1
SIM and SRM parameters used with triple quadrupole instrument

Segment	Time (min)	Analyte	SIM (*m*/*z*)	Assignment	SRM (precursor → product ion *m*/*z*)	Collision offset voltage (V)	Dwell time[a] (ms)
1	0–12	CQ	122	$[M]^+$	122 → 58	38	400
		CQ-d_4	126	$[M]^+$	126 → 58	38	400
		MQ	114	$[M]^+$	114 → 98	45	400
2	12–17	PQ	185	$[M–H]^+$	185 → 170	35	300
		PQ-d_8	193	$[M–H]^+$	193 → 178	35	300
		DQ	183	$[M–H]^+$	183 → 157	33	300
		DQ-d_4	186	$[M–D]^+$	186 → 158	33	300
3	17–25	DF	249	$[M]^+$	249 → 193	45	500
		HV	353	$[M]^+$	353 → 282	35	500

[a] Interchannel time delay: 5 ms.

2.3. Chromatographic conditions

The chromatographic separation was carried out in a Kromasil C_8 column (200 mm × 21 mm, 5 μm; Tracer Analitica, Spain). Gradient elution was used for optimal separation of quats; solvent A was 20 mM HFBA aqueous solution in 100 mM formic acid/ammonium formate buffer (pH 3.3) and solvent B was acetonitrile. The elution program consisted in an isocratic step of 2 min at 10% of solvent B, a linear gradient from 10 to 40% in 7.5 min, an isocratic step of 4 min at 40% and a stepwise elution from 40 to 70% in 11.5 min. The flow rate was 200 μl min^{-1}. The temperature of the column was maintained at 50 °C using a CH-30 Column Heater (Eppendorf, Hamburg, Germany). The injection volume was 20 μl.

2.4. Sample treatment and on-line trace enrichment

On-line trace enrichment was carried out with an automated SPE Prospekt device from Spark Holland (Emmen, The Netherlands) consisting of a high pressure dispenser and an automated cartridge exchange unit and following the procedure established by Castro et al. [17]. HySphere-Resin GP Prospekt SPE (5–15 μm polydivinylbenzene particles) cartridges were used and they were pre-conditioned with 10 ml of methanol, 10 ml of water and 10 ml of 20 mM HFBA adjusted to pH 7 with ammonium hydroxide. Water samples were then passed through the cartridges at a flow rate of 2.0 ml min^{-1}. Analytes were desorbed in backflush mode to the analytical column. In order to avoid the passage of HV and the labeled compounds used as internal standards through the cartridge, these compounds were injected (20 μl, 250 μg l^{-1}) via the LC autosampler at the beginning of the elution program (Prospekt valve on Purge position). One minute later, analytes were desorbed in the backflush mode to the analytical column (Prospekt valve on Elute position). This valve was returned to the Purge position within 30 s to avoid band broadening. Between runs, 30 ml of a solution ACN:water:formic acid (80:18:2) was passed through the Prospekt system to prevent memory effects and cross contamination between samples.

Before the analysis, drinking water samples were filtered through a 0.45 μm nylon membrane. HFBA was added to water samples to obtain a 20 mM solution and the pH was adjusted to 9 using a 10% sodium hydroxide solution.

3. Results and discussion

The cationic character of quaternary ammonium herbicides makes liquid chromatography separation difficult and ion-pair liquid chromatography coupled to mass spectrometry is the method of choice for these ionic species. Nevertheless, this type of coupling presents some problems due to the requirement of high concentrations of non-volatile conventional ion-pair reagents. In a previous paper, where an on-axis ESI source was used, these problems have been overcome [11]. A relatively volatile ion-pair reagent, such as heptafluorobutiric acid at a relatively low concentration (15 mM), was used in combination with a post-column addition of acetonitrile to improve the ionic evaporation and consequently to increase the response of these compounds. Nevertheless, an important ionic suppression effect between quats was observed. For instance, DQ showed a 30% decrease in its response when coelution with PQ occurred, and the signal of CQ decreased 70% when coeluted with MQ. For these reasons, in the present work, both ionic suppression effect and post-column addition were evaluated in the two ESI configurations, Turbo Ionspray™ source and Z-spray source. Both ESI sources showed a similar behavior, post-column addition of acetonitrile was not needed and ionic suppression was not observed when the coelution of quats occurred. For this reason a high resolution LC separation is not imperative. Even though Turbo Ionspray™ and Z-spray sources have high ionization efficiency, working conditions must be energetic enough to enhance ionic evaporation. So, relatively high gas flow-rates and high temperatures were applied to obtain maximal responses. Moreover, to enable an efficient declustering but preventing fragmentation in the source, both the declustering potential (Turbo Ionspray™ source) and the cone voltage (Z-spray source) were optimized and values of 38 and 60 V, respectively, were chosen.

3.1. Instrumental quality parameters

Instrumental quality parameters in both triple quadrupole and TOF instruments were obtained using standards in Milli-

Table 2
Quality parameters (standards in Milli-Q water)

Compound	LC-MS-MS			LC-MS		SPE-LC-MS-MS			SPE-LC-MS	
	Triple quadrupole			TOF		Triple quadrupole			TOF	
	LODs (μg l^{-1})		Run-to-run[a] (% RSD, n = 5)	LODs (μg l^{-1})	Run-to-run (% RSD, n = 5)	LODs (μg l^{-1})		Run-to-run[a] (% RSD, n = 5)	LODs (μg l^{-1})	Run-to-run (% RSD, n = 5)
	SIM	SRM				SIM	SRM			
PQ	7	0.2	7	8.6	7	0.04	0.002	7	0.02	8
DQ	3	0.3	7	3.4	8	0.01	0.001	8	0.01	9
CQ	0.3	0.05	4	2.6	4	0.003	8×10^{-4}	6	0.01	8
MQ	0.3	0.05	3	9.0	5	0.002	$7 \times 10\text{-}^{4}$	7	0.02	5
DF	0.1	0.02	5	0.2	5	0.001	1×10^{-4}	8	0.003	7

[a] In SRM mode.

Q water and the figures of merit are given in Table 2. The LODs based on a signal-to-noise ratio of 3:1 were in the range 0.1–7 $\mu g\,l^{-1}$ when the triple quadrupole instrument equipped with the Turbo Ionspray^{TM} source was used in SIM mode and decreased to 0.02–0.3 $\mu g\,l^{-1}$ with SRM mode. In both cases, PQ and DQ showed higher LODs than the other compounds, in agreement with the results previously observed working with other ionization techniques and mass analyzers [11,17]. Nevertheless, for CQ, MQ and DF the LODs were about 10 times lower with the triple quadrupole instrument than with the ion trap mass analyzer. With the TOF instrument in single MS acquisition mode, LODs in the range of 0.2–9.0 $\mu g\,l^{-1}$ were obtained (Table 2). These values are similar or slightly higher than those obtained with the SIM mode in the triple quadrupole instrument.

Calibration curves based on the peak area ratio ($A_{compound}/A_{internal\ standard}$) for the five herbicides at concentrations between 1 and 400 $\mu g\,l^{-1}$ (triple quadrupole instrument in SRM mode) and between 15 and 800 $\mu g\,l^{-1}$ (TOF instrument in single MS acquisition mode) were obtained showing acceptable linearities ($r^2 > 0.991$). Five replicate determinations of a standard solution of 7.5 $\mu g\,l^{-1}$ for PQ and 1 $\mu g\,l^{-1}$ for the other quats (triple quadrupole instrument, SRM mode) and about 70 $\mu g\,l^{-1}$ for all quats (TOF analyzer) were carried out under optimum conditions to determine run-to-run reproducibility. The relative standard deviations (RSDs) based on concentrations were lower than 8% for both MS instruments.

3.2. On-line trace enrichment

Although the detection limits obtained with the triple quadrupole instrument in SRM conditions using only one transition for each compound (Table 1) ranged between 0.2 and 0.5 $\mu g\,l^{-1}$, the method would not permit the analysis of some of these compounds below the maximum contaminant level for drinking water legislated by the European Union (0.1 $\mu g\,l^{-1}$). Moreover, for a more accurate confirmation in a triple quadrupole instrument, at least two transitions are necessary for each compound. In addition, for PQ and DQ at the conditions used in this work only one product ion is obtained in the MS–MS spectrum and to have a second transition for confirmation higher collision energies are needed. As a consequence, an increase in the detection limits occurred.

In order to improve limits of detection, preconcentration methods are required. Castro et al. [17] have proposed a manual on-line trace enrichment procedure for quats using polydivinylbenzene cartridges and a LC–MS system equipped with an ion trap analyzer that provided good results. We applied this preconcentration method using an automated system (SPE Prospekt device). Breakthrough volume and recoveries, calculated by dividing peak areas obtained when percolating a given volume by those obtained for the smallest volume at which breakthrough did not occur (10 ml), were similar to those of Castro et al. [17]. A volume of 30 ml was chosen for the on-line sample enrichment as a compromise

Table 3
Analysis of spiked water samples

Compound (I.S.)	LODs[a]					Sample quantitation (n = 2)															
	Triple quadrupole (SRM) ($\mu g\,l^{-1}$)			TOF ($\mu g\,l^{-1}$)			TOF ($\mu g\,l^{-1}$)					Triple quadrupole ($ng\,l^{-1}$)									
	Tap water	Mineral water	Groundwater	Tap water	Mineral water	Groundwater	Target value	Calculated value (tap water)			Target value	Calculated value									
								Mean value	σ	Ac[b]		Tap water			Mineral water			Groundwater		
												Mean value	σ	Ac[b]	Mean value	σ	Ac[b]	Mean value	σ	Ac[b]
PQ (PQ-d_6)	0.06 (0.2)	0.03 (0.1)	0.04 (0.1)	0.5 (1.7)	0.07 (0.2)	0.2 (0.7)	5.1	5.3	0.5	4	74	77	4	4	76	6	3	69	6	7
DQ (DQ-d_4)	0.003 (0.01)	0.001 (0.003)	0.001 (0.003)	0.8 (2.6)	0.3 (1.0)	0.3 (1.0)	3.5	3.6	0.4	3	56	52	6	7	51	5	9	59	5	5
CQ (CQ-d_4)	0.004 (0.01)	0.002 (0.007)	0.003 (0.01)	0.7 (2.3)	0.3 (1.0)	0.3 (1.0)	5.2	5.3	0.4	2	78	80	5	3	73	5	6	83	6	6
MQ (CQ-d_4)	0.002 (0.07)	0.001 (0.003)	0.002 (0.07)	0.6 (2.0)	0.4 (1.3)	0.3 (1.0)	4.9	5.1	0.3	4	69	73	3	6	72	5	4	75	7	9
DF (HV)	7×10^{-4} (0.002)	3×10^{-4} (0.001)	5×10^{-4} (0.002)	0.07 (0.2)	0.008 (0.03)	0.01 (0.03)	4.6	4.7	0.5	2	71	72	4	2	74	5	4	73	4	3

[a] The LOQs are indicated between parenthesis.
[b] Accuracy as % relative error.

between the recovery and the amount of compound available for detection. At this volume, the recoveries were 50% for CQ and MQ, 70% for PQ and DQ and 90% for DF.

Quality parameters of the automated on-line SPE–LC–MS methods using both the triple quadrupole and the TOF instruments were obtained and the results for standards in Milli-Q water are given in Table 2. As can be seen, the on-line preconcentration gave LODs for all the compounds lower than the legislated levels in drinking water. All compounds showed a decrease in limits of detection around two orders of magnitude. The on-line SPE–LC–MS–MS method (triple quadrupole in SRM mode) gave the lowest LODs, with values between 0.1 and 2 ng l^{-1}. As stated above, the LODs using the TOF instrument in single MS acquisition mode are similar to those obtained with the triple quadrupole in SIM mode. The three acquisition modes studied gave similar or better LODs than those previously reported with the same preconcentration method and working with an on-axis ESI source in a Classic LCQ ion-trap instrument [17].

Calibration curves based on the peak area ratio ($A_{\text{compound}}/A_{\text{internal standard}}$) for the five herbicides at concentrations between 0.005 and 1 μg l^{-1} (triple quadrupole instrument in SRM mode) and between 0.05 and 20 μg l^{-1} (TOF instrument) were established, showing acceptable linearities ($r^2 > 0.990$). To determine run-to-run reproducibility, five replicate determinations of a standard solution of the five herbicides of ~0.05 μg l^{-1} were carried out under optimum conditions with the triple quadrupole instrument in SRM mode and ~2.5 μg l^{-1} with the TOF instrument in single MS acquisition mode. Relative standard deviations (RSDs) based on concentrations were lower than 9% for both MS instruments.

3.3. Application

To study the applicability of the on-line preconcentration method for the analysis of quats in water at low levels, spiked tap water, mineral water and groundwater samples were analyzed using both MS instruments. LODs based on a signal-to-noise ratio of 3:1 were estimated by spiking water samples at very low levels and the results are given in Table 3. For both instruments, the values are higher than those obtained for standards in Milli-Q water due to the ion suppression caused by the matrix and the possible increase in the breakthrough that can occur when real water samples are preconcentrated. The on-line preconcentration method with the triple quadrupole instrument in SRM mode gave LODs in drinking water samples below the maximum contaminant levels legislated by both the US EPA [3,4] and the European Union [5]. When using the TOF instrument, only DF gave detection limits below the levels legislated by the European Union, although for the other herbicides the values are only slightly higher.

Since the on-line preconcentration method with the triple quadrupole instrument in SRM mode enabled the analysis of drinking water samples at European Union legislation levels [5], three spiked water samples of different origin (tap water, mineral water and groundwater) were analyzed at a level below 100 ng l^{-1} (target values indicated in Table 3). Fig. 2b

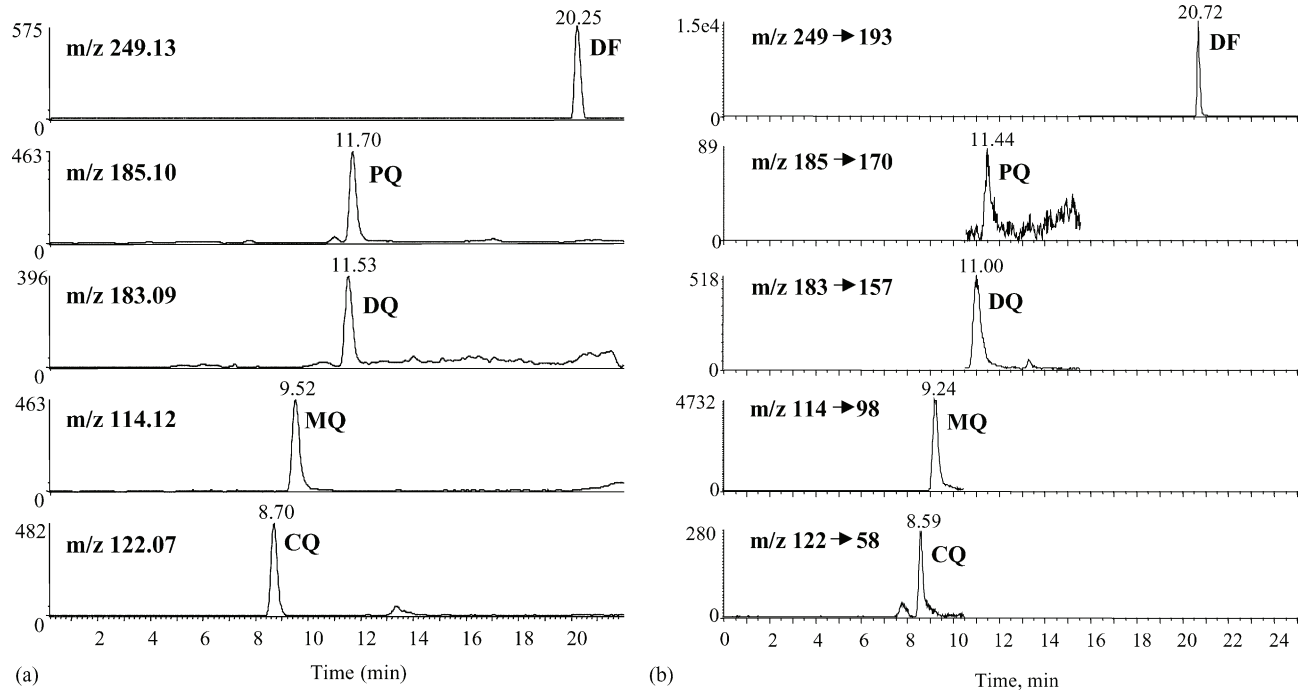

Fig. 2. Chromatograms of spiked water samples obtained by automated on-line SPE–LC–MS: (a) tap water spiked at ~5 μg l^{-1} for PQ, CQ, MQ and DF, and at ~3.5 μg l^{-1} for DQ in a TOF instrument; (b) groundwater spiked at ~0.07 μg l^{-1} for PQ, CQ, MQ and DF, and at ~0.05 μg l^{-1} for DQ in a triple quadrupole instrument acquiring in SRM mode.

shows, as an example, the chromatogram of a spiked groundwater sample obtained with the triple quadrupole instrument. The quantitation of these samples was also carried out by duplicate and external calibration with internal standards, and the results are given in Table 3. As can be seen, good results were obtained with the triple quadrupole instrument, with relative errors lower than 9% (calculated with reference to the target value). These samples could not be analysed with the TOF instrument since LODs are generally higher than the spiked level. For this reason, a tap water sample spiked at a level below the US EPA legislation (∼3–5 $\mu g\,l^{-1}$, see Table 3) was analyzed with the TOF instrument. Fig. 2a shows the obtained chromatogram. Two replicate analyses of this sample were performed by external calibration using internal standards, and the results are given in Table 3. As can be seen, the TOF instrument showed good results for quantitation at these levels with relative errors lower than 4%.

4. Conclusions

Two LC–MS systems, one using a Z-spray ionization source and a TOF analyzer in single MS acquisition mode, the other using a Turbo Ionspray™ source in a triple quadrupole instrument (SRM mode), were compared for the analysis of quats in water samples. An on-line SPE preconcentration method was automatized by using a Prospekt device, showing a good run-to-run reproducibility. The low LODs and good precision of SRM mode led us to propose on-line SPE–LC–MS–MS with a triple quadrupole instrument for quantitation of quats in drinking water samples below the European Union legislated levels ($0.1\ \mu g\,l^{-1}$), although the TOF analyzer can be proposed for the analysis of relatively contaminated samples, since LODs are only slightly higher than this level. Moreover, the accurate mass measurement with the TOF instrument can be used as a complementary confirmation tool, mainly for PQ and DQ since these compounds only give one product ion in the triple quadrupole instrument.

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