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Journal of Chromatography A, 787 (1997) 79–89

JOURNAL OF CHROMATOGRAPHY A

Liquid chromatography–atmospheric pressure ionization mass spectrometry for the determination of chloro- and nitrophenolic compounds in tap water and sea water

O. Jáuregui, E. Moyano, M.T. Galceran*

Departament de Química Analítica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

Received 14 October 1996; received in revised form 17 March 1997; accepted 9 June 1997

Abstract

Liquid chromatography coupled to atmospheric-pressure ionization mass spectrometry (LC–API-MS) with negative ion detection was studied for the determination of a variety of phenolic compounds in environmental waters. An isocratic mobile phase of 0.05% acetic acid–acetonitrile (50:50, v/v) was used. The influence of post-column addition of different bases on the sensitivity of the detection in electrospray (ES) was studied. The $[M-H]^-$ ion was the base peak for all the compounds using both ES and atmospheric-pressure chemical-ionization (APCI) ion sources. Moreover, abundant structural information was obtained by increasing the extraction voltage. Detection limits for standard solutions ranging from 2 to 13 ng injected for LC–ES-MS and from 0.02 to 20 ng for LC–APCI-MS were obtained. Good reproducibilities (day-to-day and run-to-run) were observed. The optimum LC–ES-MS and LC–APCI-MS conditions thus determined were used for a quantitative analysis of some phenolic compounds in spiked tap water and sea water samples. © 1997 Elsevier Science B.V.

Keywords: Water analysis; Environmental analysis; Phenols; Chlorophenols; Nitrophenols

1. Introduction

Phenols are present in the environment coming from different sources such as manufacturing processes used in the plastic, dye, drug, antioxidant and pesticide industries. Chloro- and nitrophenols are the main degradation products of many chlorinated phenoxy acid and organophosphorus pesticides, respectively [1,2]. These compounds are of particular interest and concern to the environment because they are toxic to most aquatic organisms [3,4]. Moreover, they affect the taste and odour of both water and fish even at very low concentrations (<1 μg l^{-1}) of phenolic compounds in water [5]. The US Environmental Protection Agency (EPA) has listed eleven phenols as priority pollutants [6]. European Community (EC) legislation states that the maximum admissible concentration of phenols in water intended for human consumption is less than 0.5 μg l^{-1} for the total content and 0.1 μg l^{-1} for the individual compounds [7], while in bathing water the maximum admissible value is 5 μg l^{-1} [8].

Gas chromatography (GC) has been widely used for the analysis of phenols in environmental samples usually with a derivatization step [9–11]. However, this increases the sample preparation time and introduces an additional source of error. Recently, some

*Corresponding author.

0021-9673/97/$17.00
PII S0021-9673(97)00653-5

authors have used GC without derivatization and mainly mass spectrometry (MS) as detection [12,13] but, phenols, and particularly nitrophenols, tended to tail even when highly deactivated columns were used [14–16]. For these reasons there is a general trend towards the use of liquid chromatography (LC) which can overcome these problems. LC with fluorescence [17,18] and electrochemical detection [19–25] would appear to be a good choice due to their high selectivity and sensitivity. However, fluorescence detection requires derivatization and electrochemical detection of the nitro compounds requires high (>1.0 V) working potentials [24,25]. Moreover, since environmental waters are very complex matrices, there is a need for reliable identification of sample constituents that only can be achieved by MS. This technique has the advantage that it can provide information for confirmation or identification. Thermospray mass spectrometry (TSP-MS) is widely used and some phenols have been identified in natural waters using this technique with negative ion detection [26–29], but in the field of LC–MS coupling, there is much current interest in the use of atmospheric pressure ionization (API) methods, i.e., electrospray (ES) and atmospheric pressure chemical ionization (APCI) [30]. Chloronitrophenols [31] and pentaclorophenol [32] have been analysed by ES-MS and recently, a paper appeared dealing with the determination of polyphenolic compounds using LC–APCI-MS [33]. The soft ionization in LC–API-MS techniques produces little structural information, but a proper adjustment of the extraction voltage readily produces this information from fragment ion signals. This mode of operation is termed pre-analyser collision induced dissociation (CID) or cone voltage fragmentation (CVF).

The purpose of this study was to investigate the use of high-flow LC–ES-MS and LC–APCI-MS for the determination of priority phenolic compounds in environmental waters. Post-column addition of different bases was performed to enhance the sensitivity in LC–ES-MS. Optimum conditions were obtained for both techniques. Detection limits, linearity and reproducibility were studied to determine the robustness of the method. The optimum conditions were used for a quantitative analysis of some phenolic compounds in tap and sea water.

2. Experimental

2.1. Chemicals

Phenols were obtained from the following sources: phenol (P) and 2,4,6-tribromophenol (246TBP) from Carlo Erba (Milan, Italy); 4-nitrophenol (4NP), 2,4-dimethylphenol (24DMP), 4-chloro-3-methylphenol (4C3MP) and 2-methyl-4,6-dinitrophenol (2M46DNP) from Scharlau (Barcelona, Spain); 2-chlorophenol (2CP), 2,4-dichlorophenol (24DCP) and 2,4,6-trichlorophenol (246TCP) from Aldrich (Milwaukee, WI, USA); 2-nitrophenol (2NP) from Fluka (Buchs, Switzerland), 2,4-dinitrophenol (24DNP) from Merck (Darmstadt, Germany) and pentachlorophenol (PCP) from Chem Service (West Chester, PA, USA). Stock standard solutions of phenols, 500 mg l^{-1}, were prepared in acetonitrile; aliquots of the standard solutions were further diluted with mobile phase to prepare the working solutions.

HPLC-grade acetonitrile was purchased from J.T. Baker (Deventer, Netherlands). Water was purified using a Culligan system (Barcelona, Spain). Dimethylamine was from Carlo Erba and acetic acid from Merck. Poly(styrene–divinylbenzene) (PS–DVB) membrane extraction disks were obtained from J.T. Baker; the disks used in this work were 47 mm in diameter and 0.5 mm thick; each disk contained about 500 mg of adsorbent. All the other reagents were of analytical-grade.

2.2. Chromatographic conditions

For optimization of mobile phase, LC with UV detection was carried out on a Hewlett-Packard (Waldbronn, Germany) Series 1050 liquid chromatograph with an isocratic pump, an automatic injector and a UV detector. The optimum mobile phase composition, acetonitrile–0.05% acetic acid (50:50), was used for the chromatographic separation at a flow-rate of 1 ml min^{-1}. A Shandon Hypersil Green ENV C_8 (5 μm particle size, 250×4.6 mm I.D.) reversed-phase column (Shandon Scientific, Cheshire, UK) with a Pelliguard LC-18 (20 μm) precolumn (2 cm×4 mm I.D.) from Supelco (Gland,

Switzerland) was used for the LC separation of the phenols.

LC coupled to MS was carried out using a LKB-HPLC pump 2248 from Pharmacia (Bromma, Sweden). In LC–ES-MS, post-column addition of 100 m*M* dimethylamine in acetonitrile–water (50:50) at 400 ml min^{-1} was carried out using a Phoenix 20 (Carlo Erba) syringe pump and a Rheodyne (Cotati, CA, USA) two-position six-port switching valve, Model 7000. Mobile phase and dimethylamine were mixed in a tee (Valco) and a split system (LC Packings, Amsterdam, Netherlands) 1/50 was used to introduce the effluent into the ES.

MS was performed using a VG Platform II (Fisons Instruments, VG Biotech, Altrincham, UK) quadrupole mass spectrometer equipped with both a standard pneumatically assisted ES (nitrogen flow-rate 20 l h^{-1}) and an APCI (nitrogen flow-rate 100 l h^{-1}) ion sources.

The working conditions for ES were the following: drying nitrogen was heated to 80°C and introduced into the capillary region at a flow-rate of 400 l h^{-1}. The capillary was held at a potential of −4.2 kV relative to the counter electrode for the negative-ion mode. The extraction voltage was varied between −20 and −80 V. The working conditions for the APCI were the following: drying nitrogen heated to 80°C and introduced into the capillary region at a flow-rate of 200 l h^{-1}. The capillary was heated to 200°C, and the corona voltage held at −1.5 kV. Calibration was performed using a standard solution of phenols.

Full scan data acquisition was performed scanning from *m/z* 80 to 300 in centroid mode and using a cycle time of 1 s and an inter-scan time of 0.1 s. In selected-ion monitoring (SIM) mode, the $[M-H]^-$ ion for each phenol was used and for chlorophenols the isotope ion signals were also used, with a dwell time of 100 ms and an inter-channel time of 1 ms. The ions used in the SIM mode for both techniques are given in Table 1.

In order to optimize the API-MS parameters, a standard solution of phenols was introduced (100 μl) in flow injection analysis (FIA).

2.3. Sample treatment

Tap water samples from Barcelona and sea water samples from Castelldefels beach (Barcelona, Spain) were treated, prior to the analysis, following a method described previously [34]. Aliquots of each sample, which were specified in Section 3.3, were acidified to pH 2 with sulfuric acid and then extracted using two PS–DVB membrane extraction disks. The extraction steps were: (i) conditioning of the disks with methanol and HPLC-grade water at pH 2; (ii) extraction of water samples at a flow-rate of 20–25 ml min^{-1}; (iii) elution with acetonitrile and iv) evaporation of the extracts. The final volume

Table 1
Time-scheduled in SIM conditions for the analysis of water samples using the LC–ES-MS and the LC–APCI-MS conditions described in Section 2.2

Compound	*m/z*			
	ES		APCI	
	−30 V	−50 V	−20 V	−50 V
2CP	127, 129	127, 129	127, 129	127, 129
4NP	138	108, 138	138	108, 138
2NP	138	108, 138	138, 122	92, 122
4C3MP	141, 143	141, 143	141, 143	141, 143
24DCP	161, 163, 165	125, 161, 163, 165	161, 163, 165	125, 161, 163, 165
24DNP	183	123, 153, 183	183, 167	109, 137
246TCP	195, 197, 199	195, 197, 199	195, 197, 199	123, 159, 195, 197, 199
2M46DNP	197	137, 197	197, 181	123, 151
PCP	263, 265, 267	263, 265, 267	263, 265, 267	263, 265, 267

was made up to 1 ml with the LC mobile phase after the addition of the internal standard, 246TBP.

3. Results and discussion

3.1. Optimization of LC–MS

Different mobile phases were tested in order to optimize the separation and the peak shape for all the phenolic compounds studied. The best separation was obtained with an isocratic mobile phase of 0.1% acetic acid–acetonitrile (50:50, v/v) although this mobile phase resulted in poor resolution of 2CP and 24DNP and of 24DCP and 2M46DNP. As the mass spectra of these two pairs of compounds are different, selectivity is easily introduced in the detection step by using specific m/z values.

In LC–MS, post-column addition of base has been proposed to enhance the sensitivity for acidic compounds [35–37]. In this work, different bases which promoted deprotonation of phenolic compounds, using LC–API-MS were studied. No improvement in the responses were observed for the APCI experiments. In contrast, an increase was observed for ES. Ammonia (pK_a=9.3), triethylamine (pK_a=9.8) or dimethylamine (pK_a=10.7), 100 mM and at a flow-rate of 200 μl min^{-1}, were used in comparative experiments in LC–ES-MS. Injection of 50 μl of a 10 mg l^{-1} standard solution of phenols was performed and mass spectra in full scan mode were obtained. Higher responses were observed when dimethylamine (100 mM) was used as can be expected because it is the strongest base. Different flow-rates of dimethylamine dissolved in water and in water–acetonitrile (1:1) were tested in order to find the optimal conditions for MS detection of phenols. Normalized absolute abundance at different conditions are shown in Fig. 1. Dimethylamine 100 mM in water–acetonitrile (1:1) at 400 μl min^{-1} was found to be optimal for enhancement of the response of phenolic compounds using LC–ES-MS.

The specific behaviour of phenolic compounds could be related to their differences in pK_a. Therefore, the addition of dimethylamine (pK_a 10.7) allowed the detection of 2CP (pK_a 8.1) and 2NP (pK_a 7.2) which, without base, gave no response and low response, respectively. An increase in peak height

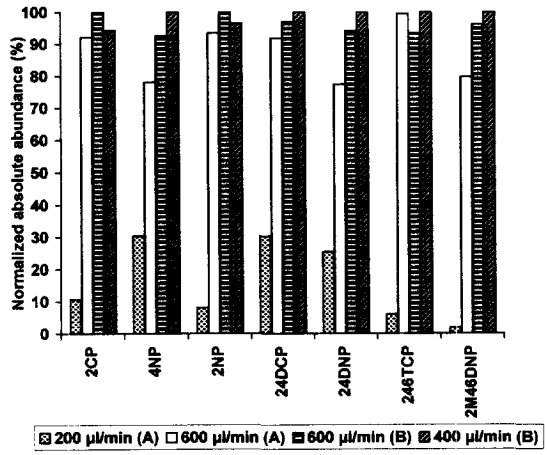

Fig. 1. Variation of the normalized absolute abundance (%) of the $[M-H]^-$ ion for some phenolic compounds using different conditions of post-column addition of base in LC–ES-MS. (A) Water, (B) water–acetonitrile (1:1).

was also observed for 24DCP (pK_a 7.7) and 246TCP (pK_a 7.4) that can be explained by the increase of deprotonation due to the basicity of the mobile phase after the addition of dimethylamine. As phenolate ions are needed in ES negative ion detection, compounds with higher pK_a gave lower responses; for instance, P (pK_a 9.9) and 24DMP (pK_a 10.5) gave responses 100-times lower than the other compounds. Also, no increase in the responses was observed for these compounds when dimethylamine was added and only a slight increased occurred for 4C3MP which has a pK_a 9.6. Compounds with low pK_a values (24DNP, pK_a 4.1; PCP, pK_a 4.9 and 2M46DNP, pK_a 4.3), were probably dissociated in the original (acetonitrile–0.05% acetic acid, 50:50) mobile phase and, as expected, no improvement was observed by adding dimethylamine. The no increase in the 4NP (pK_a 7.2) response cannot be explained by its pK_a value. As the addition of dimethylamine (100 mM, 400 μl min^{-1}) generally increased the responses, post-column addition was performed throughout further LC–ES-MS studies.

In order to identify the main ions for every analyte under the LC conditions described, FIA was used to introduce the analytes (100 μl of a 50 mg l^{-1} individual standard solution) and the mass spectra were obtained in full scan mode for both ion sources. Extraction voltages from −10 to −80 V were applied

Table 2
Mass spectral fragments, relative intensities of phenols using acetonitrile–0.05% acetic acid (50:50) as LC eluent and different extraction voltages under the ES-MS (with post-column addition of dimethylamine 100 m*M*) and APCI-MS conditions described in Section 2.2

Abbreviations	M_r	m/z[a]	Tentative assignation	Relative intensity (%)			
				ES		APCI	
				−30 V	−50 V	−20 V	−50 V
2CP	128	127	$[M-H]^-$	100	100	100	100
		91	$[M-H-HCl]^-$	–	10	–	20
4NP	139	138	$[M-H]^-$	100	100	100	45
		122	$[M-OH]^-$	–	–	3	–
		108	$[M-H-NO]^{-\cdot}$	2	100	–	100
		92	$[M-H-NO_2]^{-\cdot}$	–	5	–	5
2NP	139	138	$[M-H]^-$	100	95	100	10
		122	$[M-OH]^-$	–	–	100	50
		108	$[M-H-NO]^{-\cdot}$	36	100	20	25
		92	$[M-H-NO_2]^{-\cdot}$	–	8	–	100
4C3MP	142	141	$[M-H]^-$	100	100	100	100
		105	$[M-H-HCl]^-$	–	–	–	12
24DCP	162	161	$[M-H]^-$	100	100	100	100
		125	$[M-H-HCl]^-$	–	35	–	75
		89	$[M-H-HCl-HCl]^-$	–	5	–	45
24DNP	184	183	$[M-H]^-$	100	100	100	25
		167	$[M-OH]^-$	–	–	45	20
		153	$[M-H-NO]^{-\cdot}$	1	30	–	15
		137	$[M-H-NO_2]^{-\cdot}$	–	25	–	70
		123	$[M-H-NO-NO]^-$	–	40	–	30
		109	$[M-H-NO_2-CO]^{-\cdot}$	–	20	–	100
		95	$[M-H-NO-NO-CO]^-$	–	12	–	30
246TCP	196	195	$[M-H]^-$	100	100	100	100
		159	$[M-H-HCl]^-$	–	–	–	10
		123	$[M-H-HCl-HCl]^-$	–	–	–	10
2M46DNP	198	197	$[M-H]^-$	100	100	100	30
		181	$[M-OH]^-$	–	–	80	42
		167	$[M-H-NO]^{-\cdot}$	–	20	–	13
		151	$[M-H-NO_2]^{-\cdot}$	–	8	–	100
		150	$[M-H-NO_2-H]^-$	–	2	–	15
		137	$[M-H-NO-NO]^-$	–	30	–	38
		123	$[M-H-NO_2-CO]^{-\cdot}$	–	–	–	80
		121	$[M-H-NO_2-NO]^{-\cdot}$	–	–	–	81
		109	$[M-H-NO-NO-CO]^-$	–	12	–	47
		93	$[M-H-NO-NO_2-CO]^-$	–	–	–	12
PCP	264	265	$[M-H]^-$	100	100	100	100

[a] Only the most abundant isotope peaks are given.

and the main ions obtained at two extraction voltages for both techniques are given in Table 2.

The spectra generated by ES at extraction voltages below −40 V and by APCI below −20 V, gave only the $[M-H]^-$ ion except for the *o*-nitrophenolic compounds in APCI which showed some fragments even at −20 V with a relative intensity of 45–100% (Table 2). When higher extraction voltages were used, more fragmentation was observed and a decrease in the intensity of $[M-H]^-$ occurred. In order to establish the optimum extraction voltage for the analysis of all the compounds, normalized absolute abundances of $[M-H]^-$ ions vs. extraction voltage for each compound were studied. Most of the compounds showed a maximum between −30 and −40 V for ES and between −20 and −30 V for APCI as can be seen in Fig. 2A,B where, as an example, the behaviour of 24DNP is given. The optimum extraction voltages were −30 V for ES and −20 V for APCI.

The loss and multiple loss of HCl were the only fragmentations for chlorophenols in both ion sources. More fragmentation was observed for nitrophenols which typical displayed signals for $[M-H-NO]^{-\cdot}$ and $[M-H-NO_2]^{-\cdot}$. Moreover, losses of CO from these ions also occurred for dinitrophenols at high extraction voltages (−50 V) giving high relative intensities in both ionization modes. With APCI, the *o*-nitro compounds specifically favour the loss of OH over that of NO or NO_2. In practice, the dominant OH loss in 2NP as compared to that in 4NP, allowed a sufficiently specific detection of the first compound in the chromatographic tail of the second. Fig. 3 gives the reconstructed ion chromatogram at *m/z* 138 and at *m/z* 122 for a standard solution of phenols (1 mg l^{-1}, 50 μl injected). As can be seen, 2NP can be detected using *m/z* 122 whereas the signal for the 4NP is near 1/30 the corresponding value at *m/z* 138. This is an example that demonstrates compensation of poor LC separation by MS.

3.2. Quality parameters

Calibration graphs (8 points) were constructed for standard solutions (between 0.1 and 1.5 mg l^{-1} for ES and between 0.5 μg l^{-1} and 2 mg l^{-1} for APCI) and good linearity was observed (r^2>0.99) for all the compounds using both techniques. Limits of

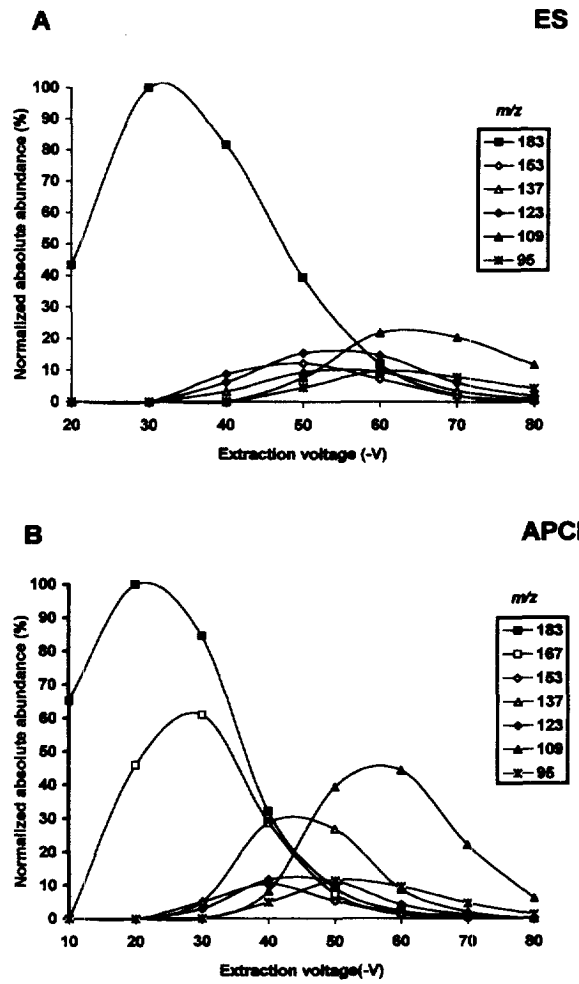

Fig. 2. Variation of the normalized absolute abundance (%) of some fragment ions vs. the extraction voltage (−V) for 24DNP using (A) LC–ES-MS with post-column addition of dimethylamine (100 m*M*, 400 μl min^{-1}) and (B) LC–APCI-MS. For identification see Table 2.

detection (LODs) were determined using standard solutions, SIM detection and a signal-to-noise ratio of 3:1; these limits ranged from 2 to 13 ng injected in ES ionization and from 0.02 to 20 ng injected in APCI ionization (Table 3). The LODs in tap water and seawater were determined in samples spiked at low μg l^{-1} level, taking the preconcentration into account. In ES, detection limits for tap water between 0.02 and 0.5 μg l^{-1} were obtained whereas in APCI the LODs ranged from 0.002 to 1 μg l^{-1} showing that using APCI higher sensitivity can be

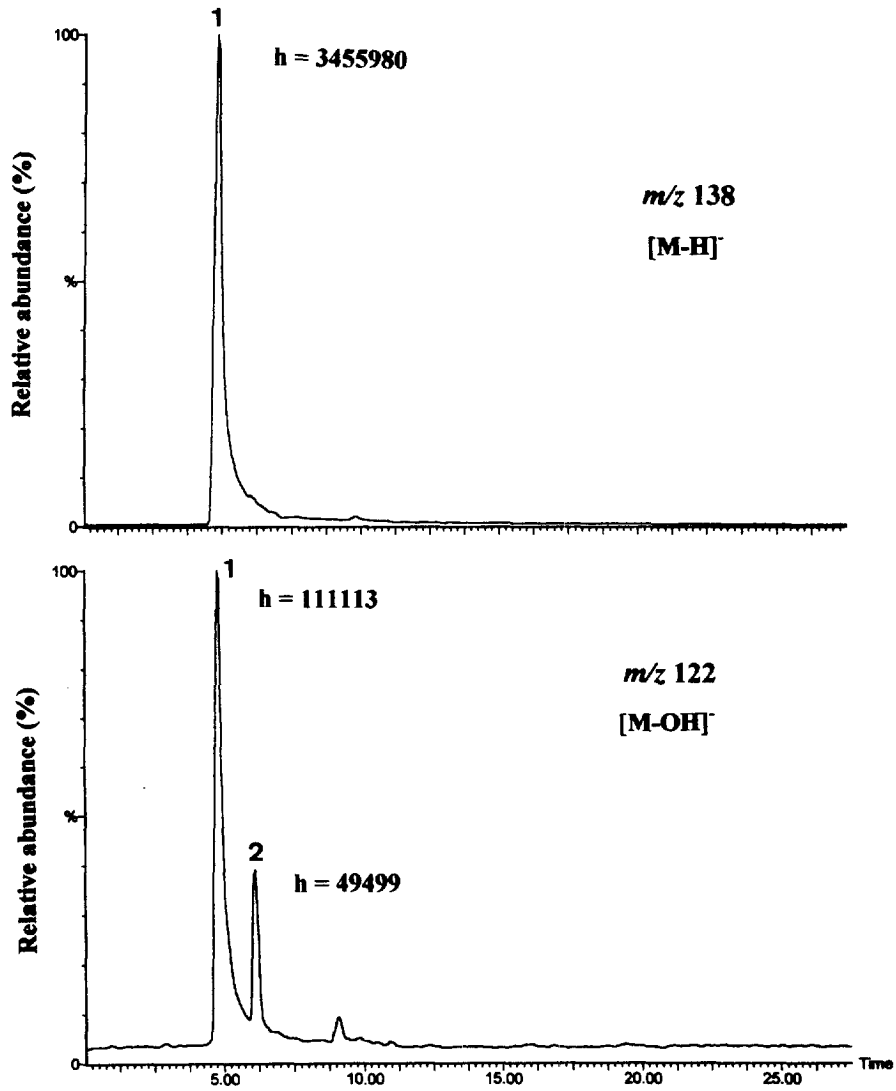

Fig. 3. LC–APCI-MS reconstructed ion chromatograms for 4-nitrophenol (1) and 2-nitrophenol (2) for the injection (50 μl) of a standard solution of phenols (1 mg l^{-1}). Conditions as described in Section 2.2. *h*: Peak height.

achieved. In seawater, LODs were higher than for tap water using both LC–API-MS techniques, ranging from 0.1 to 3 μg l^{-1} for ES and from 0.004 to 5 μg l^{-1} for APCI (Table 3). Comparing the LODs (based on ng injected) for both tap water and sea water, it can be deduced that matrix effects were not relevant when API techniques were used. For most of the compounds the LODs obtained in this study are lower than 0.1 μg l^{-1} and better than those reported by using on-line solid-phase extraction (SPE)–LC–TSP-MS [38]. On-line SPE could improve these LODs as Puig and Barceló have recently reported [15].

To study the reproducibility, a standard solution (0.5 mg l^{-1} of each phenol) was analyzed. For this purpose calibration curves were recorded for each phenol on three different days and the standard solution of 0.5 mg l^{-1} was quantified. Run-to-run and day-to-day precisions were calculated in terms of concentration and are given in Table 4. Good

Table 3
Detection limits for phenols under the HPLC–API-MS conditions described in Section 2.2

Compound	ES					APCI				
	Detection limit[a]					Detection limit[a]				
	Standard solution[b] (ng)	Tap water[c] (ng)	Tap water[c] ($\mu g\ l^{-1}$)	Sea water[d] (ng)	Sea water[d] ($\mu g\ l^{-1}$)	Standard solution[b] (ng)	Tap water[c] (ng)	Tap water[c] ($\mu g\ l^{-1}$)	Sea water[d] (ng)	Sea water[d] ($\mu g\ l^{-1}$)
2CP	13	25	>0.5	75	3	15	25	0.5	125	>5
4NP	4	7	0.15	5	0.2	0.02	0.3	0.01	0.2	0.01
2NP	9	25	0.5	22	1	3	5	0.1	8	0.3
4C3MP	10	12	0.25	38	2	20	12	0.5	50	2.0
24DCP	9	12	0.25	32	1	0.1	2	0.1	3	0.1
24DNP	3	3	0.03	5	0.2	0.05	0.1	0.003	0.1	0.004
246TCP	5	5	0.05	12	0.5	0.1	0.2	0.01	0.5	0.02
2M46DNP	2	2	0.02	3	0.1	0.05	0.1	0.002	0.2	0.01
PCP	4	5	0.05	8	0.3	0.5	1	0.02	1	0.03

For abbreviations see Section 2.1.
[a] 100 μl injected.
[b] In 0.05% acetic acid–acetonitrile (50:50, v/v).
[c] 500 ml of tap water preconcentrated.
[d] 250 ml of sea water preconcentrated.

reproducibility was obtained for run-to-run precision (between 2 and 11%) and for day-to-day precision (between 6 and 14%) for both ion sources being better than those reported by on-line SPE–LC–AP-CI-MS exceeding 25% [15].

3.3. Application

The developed LC–API-MS methods were applied to the analysis of spiked tap water (500 ml) and sea water (250 ml) at 0.5 and 5 $\mu g\ l^{-1}$, respectively. Extraction of samples was performed by SPE using two PS–DVB membrane extraction disks as described. The organic extracts were analyzed by LC–ES-MS, with post-column addition of dimethylamine, and with LC–APCI-MS. For identification and quantification purposes, extraction voltages of −30 V in ES and −20 V in APCI were used.

Table 4
Reproducibilities for phenols under the HPLC–API-MS conditions described in Section 2.2

Compound	ES		APCI	
	Reproducibility (%)		Reproducibility (%)	
	Run-to-run ($n=5$)	Day-to-day ($n=15$)	Run-to-run ($n=5$)	Day-to-day ($n=15$)
2CP	5	12	6	13
4NP	2	12	6	12
2NP	5	13	5	14
4C3MP	11	13	6	12
24DCP	5	6	7	14
24DNP	5	12	7	11
246TCP	5	7	4	11
2M46DNP	9	12	6	13
PCP	3	6	6	7

For abbreviations see Section 2.1.

For confirmation, a higher extraction voltage (−50 V) was applied recording the characteristic ions (Table 1) of the previously identified compounds. The high fragmentation in APCI allowed a more reliable confirmation at −50 V although in ES, −80 V had to be applied with a decrease in the sensitivity. As an example, Fig. 4 shows the reconstructed ion current (RIC) and the ion chromatogram for the non-spiked and spiked tap water samples (0.5 μg l^{-1}) using both ES (−30 V) and APCI (−20 V).

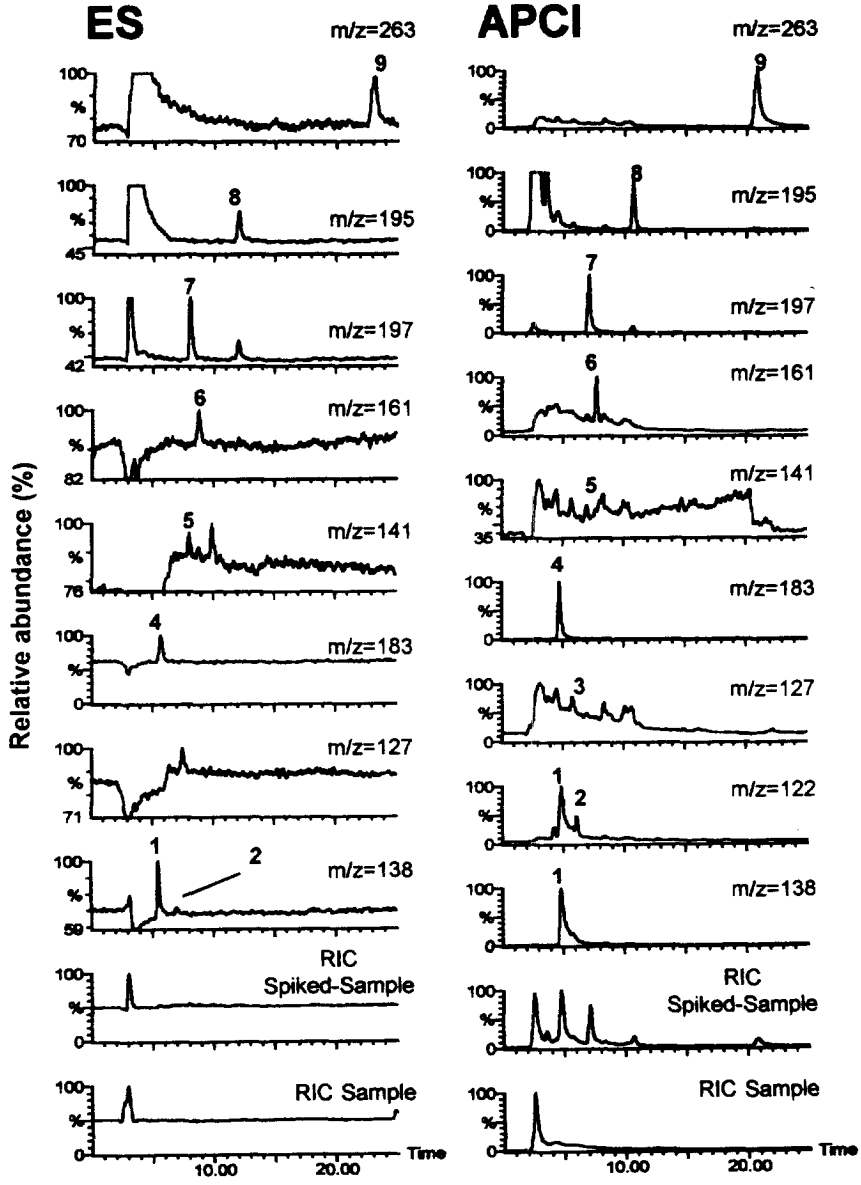

Fig. 4. Ion chromatograms with negative ion detection of phenolic compounds in tap water (500 ml) using LC–ES-MS (tap water, June 1996) with post-column addition of dimethylamine (100 m*M*, 400 μl min^{-1}) and LC–APCI-MS (tap water, September 1996). The two lower traces are the RIC obtained for the non-spiked and spiked (0.5 μg l^{-1}) samples. Peaks: (1) 4NP, (2) 2NP, (3) 2CP, (4) 24DNP, (5) 4C3MP, (6) 24DCP, (7) 2M46DNP, (8) 246TCP and (9) PCP. Conditions as described in Section 2.2.

Both techniques can be applied to the analysis of these water samples. However, APCI gives a better performance with better signal-to-noise ratios.

4. Conclusions

The application of LC–API-MS techniques in negative ion detection for the determination of phenolic compounds in tap and seawater in the low $\mu g\ l^{-1}$ level has been studied. In ES, post-column addition of dimethylamine has been used to improve the responses of some phenols. Working at low extraction voltages, the $[M-H]^-$ ion for each compound was obtained. At least one major fragment ion signal was observed when the extraction voltage was increased, thus providing structure information. APCI produced a major fragmentation than ES even at low extraction voltages. Losses of HCl units for chlorophenols and NO and NO_2 for nitrophenols were observed using both ion sources. Moreover, in APCI losses of OH was produced for o-nitro compounds. Good linearity and reproducibility were obtained for both ion sources. Low detection limits, down to 2 $ng\ l^{-1}$, were obtained for tap water being slightly higher than for sea water samples. In all the cases, APCI gave better sensitivity for the detection of phenolic compounds providing a powerful tool for the screening and quantification of these substances in natural waters at low $\mu g\ l^{-1}$ level as regards of its sensitivity and confirmatory capability.

Acknowledgements

Dr. Isidre Casals from Serveis Científico Tècnics of the University of Barcelona is gratefully acknowledged for LC–MS technical support and laboratory assistance. This work was partially financed by Comissionat per Universitats i Recerca de la Generalitat de Catalunya (Contract number 1995SGR00458).

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