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Determination of chlorophenols in drinking water with high resolution gas chromatography–tandem mass spectrometry

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Abstract

A new method for the determination of sub-ppb levels of chlorophenols in drinking water by use of GC–MS–MS is proposed. Monitoring of these analytes for assurance of compliance with legally allowed limits can readily be accomplished by extraction as acetylated chlorophenols from low sample volumes (10 ml). Much lower detection limits can be achieved by preconcentrating 1 l of sample using graphitized carbon cartridges for solid extraction. Appropriate selection of parent ions and fragmentation conditions ensures not only a high sensitivity, but also clean product ion spectra that allow positive identification of every species considered (polychlorophenol isomers included).

Keywords: Water analysis; Tandem mass spectrometry; Chlorophenols

1. Introduction

There is currently great environmental interest in chlorinated phenol derivatives on account of their high toxicity and wide industrial use [1]. In response, the Environmental Protection Agency (EPA) [2] has compiled a list of eleven phenols that are considered to be priority pollutants. In 1982, the EEC issued its own pollutant list [3], which includes a large number of polychlorophenols, and established a maximum allowable overall concentration of 0.5 μg/l for these compounds in drinking water.

Few currently available analytical techniques allow the direct determination of chlorophenols at such low concentration levels. This has promoted the development of various procedures for their extraction from their matrices using liquid–liquid extraction (LLE) with organic solvents [4,5], solid phase extraction (SPE) with different sorbents such as synthetic resins [6], and C_{18} [7] or graphitized carbon cartridges [8,9]. In every case, large volumes of sample have to be processed and then the final extracts must be concentrated. This solvent evaporation step has been shown to result in major losses of several chlorophenols [10].

Chlorophenols are usually determined by use of chromatographic techniques such as HPLC [11] or GC [12]. However, because of their high polarity, they give broad, tailed peaks if separated directly (without prior derivatization) by GC. The effect worsens as the chromatographic column used ages [13]. It is therefore advisable to convert chlorophenols into less polar forms in order to improve peak shape, resolution and sensitivity [14]. Acetylation is the most frequently used reaction for this purpose [15,16]. Alternative derivatizing agents,

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such as chloroacetic acid [17] and pentafluorobenzyl [18], have also been used in this context. Even in this case, if the detector used is not selective enough, the chromatograms obtained are difficult to interpret. It is therefore preferable to use a highly selective detection technique, such as atomic emission (GC–AED) [10] or mass spectrometry (GC–MS) [19]. Tandem mass spectrometry (GC–MS–MS) allows further selectivity, since two mass separation steps takes place. In fact, this technique is particularly useful for the analysis of very complex mixtures, as it allows the separation and identification of components with different structures that are eluted at similar retention times and with widely different concentration levels. Also, increased signal-to-noise ratios afford the sensitivity needed for low trace level analysis without having to process large volumes of sample.

Tandem MS detection can be accomplished by means of multi-quadrupole [20–25] as well as by ion trap spectrometers [26–29]. In multi-quadrupole spectrometers, sequential fragment separations involve various spectrometer regions (space tandem); in ion trap spectrometers, however, these operations take place over a given period (time tandem). As a result, ion trap detectors have the advantage over multi-quadrupole ones in that no ion losses occur in transmissions between sectors. However, an ion trap can only store a limited number of ions. Removing all ions other than the parent ions from the detector reduces chemical noise and allows the ionization time to be extended in order to store as many parent ions as possible, thus decreasing detection limits.

The aim of this work was to develop a method for the routine determination of chlorophenols at the parts-per-trillion and lower levels in drinking water by use of GC–ion trap tandem MS.

2. Experimental

2.1. Reagents

HPLC grade methanol and *n*-hexane were supplied by Merck (Darmstadt, Germany). Potassium carbonate, acetic anhydride and anhydrous sodium sulphate were also obtained from Merck. Tetramethylammonium hydroxide (TMAOH) was purchased from Aldrich (Milwaukee, WI, USA). Supelclean Envi-Carb SPE graphitized carbon black cartridges, of 0.25 g load, were provided by Supelco (Bellefonte, PA, USA). 2-Chlorophenol, 3-chlorophenol, 4-chlorophenol, 2,6-dichlorophenol, 2,4-dichlorophenol, 2,5-dichlorophenol, 3,5-dichlorophenol, 2,3-dichlorophenol, 3,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,6-trichlorophenol, 2,3,5-trichlorophenol, 2,4,5-trichlorophenol, 2,3,4-trichlorophenol, 2,3,5,6-tetrachlorophenol, 2,3,4,6-tetrachlorophenol, pentachlorophenol and 4-chloro-3-cresol standards of high purity were obtained from either Aldrich or Merck and used to prepare stock solutions containing 4 mg/ml of each compound in methanol. The stock solutions were stored at 4°C in the dark. Working solutions were made by appropriate dilution of the stocks.

2.2. Preparation of standards

The lack of commercially available standards for chlorophenol acetates compelled us to synthesize them from available chlorophenol standards. For this purpose, 1 ml of the methanol solutions containing each chlorophenol were mixed with 1 ml of 5% potassium carbonate, 2 ml of *n*-hexane and 0.2 ml of acetic anhydride. After mixing for 1 min, the organic phase was removed and the aqueous phase was extracted with 1 ml of *n*-hexane. The two organic phases were combined (3 ml) and dried over anhydrous sodium sulphate. This process for the preparation of standards yields 90±1% acetylated chlorophenols, as has been shown elsewhere [30].

2.3. Preparation of samples

Prior to solid-phase extraction, chlorophenols were derivatized according to Soniassy et al. [31]. We used 10- or 1000-ml samples of MilliQ or tap water that were spiked with variable amounts of chlorophenols. The sample pH was adjusted to 11–11.5 with anhydrous potassium carbonate. Then, acetic anhydride was added and the mixture was stirred mechanically for 15 min. Finally, 2% methanol was added and the sample was thus made ready for passage through a graphitized carbon cartridge that had been preconditioned as follows: cartridge was washed with 5 ml of methanol and activated with 5

ml of MilliQ water adjusted to pH 2–3 with HCl. The sample was slowly passed through the cartridge, which was then dried with a N_2 stream for 10 min. Retained compounds were eluted upstream with 3 ml of *n*-hexane containing 1% TMAOH. In this way, a concentration factor of 3.33 and 333 was obtained for water samples of 10 ml and 1 l, respectively. In the latter case, the procedure continued with concentration of the extract to 0.5 ml by use of a nitrogen stream in a Zymark Turbovap (Hopkinton, MA, USA) at 14 p.s.i. and 30°C. This raised the concentration factor to 2000.

2.4. Gas chromatography

A Varian 3400 (Walnut Creek, CA, USA) gas chromatograph fitted with an on-column Septum programmed temperature injector (SPI) was used for GC separations. Injections (1 μl) were carried out using the following programme: 60°C for 0.1 min; ramp to 260°C at 300°C/min; and 260°C for 10 min. The capillary column used was a 30 m×0.25 mm I.D. DB-5MS from JW Scientific (Folsom, CA, USA), of 0.25 μm film thickness, and the temperature program was as follows: 60°C for 1 min; ramp one to 115°C at 15°C/min; 115°C for 5 min; ramp two to 175°C at 3°C/min; ramp three to 250°C at 30°C/min and finally 250°C for 5 min. Helium (99.999% pure; Carburos Metálicos, Madrid, Spain) was used as the carrier and collision gas. The column head pressure was 8 p.s.i. and provided a flow-rate of 1 ml/min.

2.5. Mass spectrometry

Electron ionization (EI) mass spectra were recorded on a Saturn 4 GC–MS (ion trap, ITD) system from Varian, equipped with a Wave-Board which controls MS–MS operation. The transfer line was kept at 260°C and the ion trap manifold at 170°C. The scan rate was 1 scan/s. The Wave-Board produced time-programmed waveforms at the user's request that were applied to the ion trap electrodes. Saturn 5.0 software, controlling the whole system, also allowed the isolation and storage of selected ions for each compound from EI full-scan spectra and their subsequent fragmentation by collision-induced dissociation (CID). A scheme showing the isolation and fragmentation processes in ITD–MS–MS has been published by Schachterle et al. [28]. Broadband isolation waveforms were applied to the upper and lower end-cap electrodes of the ion trap during and after ionization, to eject all ions with an m/z value different from that for the parent ion. After the parent ion was isolated, a non-resonant voltage at an amplitude and excitation time that had been previously optimized by the user, to ensure correct fragmentation of the parent ion, was applied to the end-cap electrodes. Non-resonant excitation shifted the equilibrium position for stored ions (potential energy). The restoration force of the trap field converted this potential energy increment into a translational kinetic energy increment for the ions. Part of this kinetic energy was converted into internal vibrational energy on collision with the neutral reactive gas (helium) generating fragmentation of the parent ions. The main advantage of using non-resonant rather than resonant energy for excitation [28] is that the former does not require the adjustment of the dipole frequency applied to the end-cap electrodes to the vibrational frequency of the ion. Therefore, such variables as stray electrons, space–charge effects or the analyte concentration are uninfluential and spectra for daughter ions are more reproducible. CID always competes with ejection of product ions. Therefore, increasing the excitation amplitude entails optimizing the radio frequency (RF) storage level.

3. Results and discussion

3.1. GC–EI full-scan analysis

Fig. 1 shows the reconstructed total ion chromatogram (GC–MS–RTIC) for the chlorophenols studied at a concentration of 100 μg/l, acquired over the m/z range 50–300. The peaks numbered 6 and 7 in this figure (2,4-dichlorophenol and 2,5-dichlorophenol) were completely overlapped and could not be resolved by altering the temperature programme. The EI spectra of chlorophenols obtained under the described analytical conditions corresponded to previously referenced fragmentation [32]. The base peaks in the spectra were selected as parent ions. With chlorophenols, the electron ionization tech-

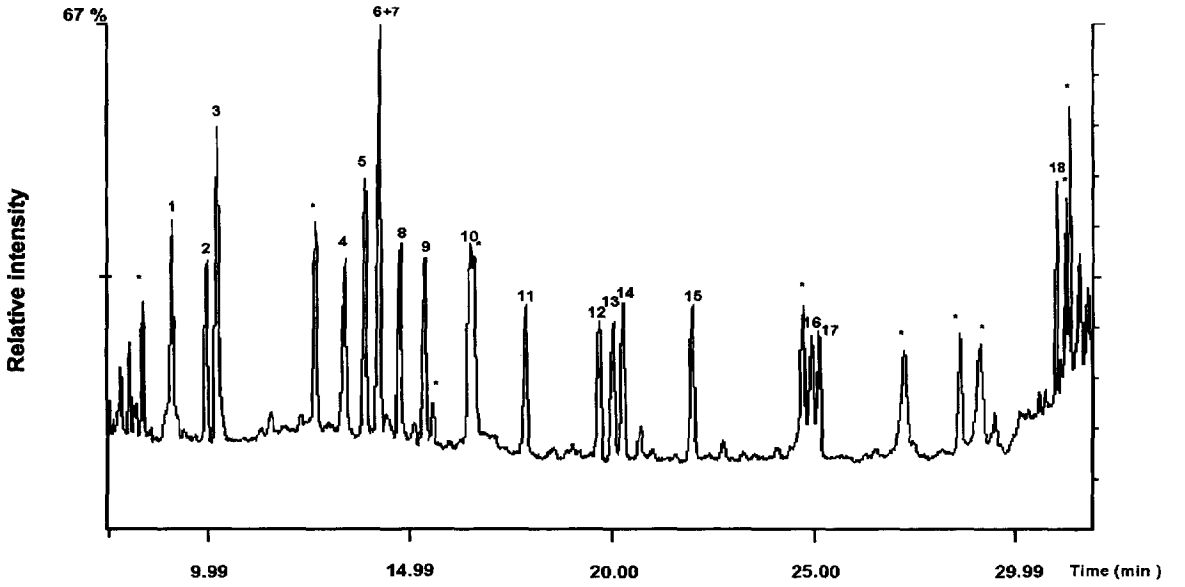

Fig. 1. RTIC for chlorophenol standards (100 μg/l) obtained by GC–MS in the full-scan mode (mass acquisition range 50–300 m/z). Peaks labeled with asterisks correspond to solvent and derivatization reagent impurities. At the bottom, the time segments and mass fragment selected are schematically depicted.

nique provides spectra containing low abundant fragments' ions and hence high ion parent intensities that dispense with the need for chemical ionization recommended by many authors [21,22,26,28,33]. Although a comparison of experimental GC–MS spectra with those in the NIST90 library stored in the instrument data station allowed tentative identification of the compound families, the EI spectra for the different isomers within each group were very similar, which precluded positive individual identification in highly dilute samples.

3.2. GC–tandem MS

3.2.1. Optimization of the isolation and fragmentation of parent ions

To program the isolation of parent ions for every compound along the chromatographic run, the overall run time was split into seven segments (see Fig. 1) for the separation of as many compound groups as possible. Each segment was assigned to a m/z fragment viz. the base ion obtained from the EI mass spectrum for each isomeric group. The parent ions chosen accordingly were as follows: monochlorophenols, m/z 128 (M_r 128); dichlorophenols, m/z= 162 (M_r 162); trichlorophenols, m/z 198 (M_r 196); tetrachlorophenols, m/z 232 (M_r 230); pentachlorophenol, m/z 266 (M_r 264), and 4-chloro-3-cresol, m/z 142 (M_r 142) (Fig. 2). The time segment where 4-chloro-cresol was eluted appears between the two segments for dichlorophenols (see Fig. 1).

Inside each time segment, parent ions were isolated in two steps. In the first one, a gross selection was carried out by ejecting from the trap those ions whose m/z lay outside a ± 1 unit window around the chosen parent m/z value. This was accomplished by increasing the amplitude of the RF field using axial modulation on the end-cap electrodes (to eject ions having masses smaller than the lower limit) and by means of a broadband multifrequency waveform (to eject ions having masses greater than the upper limit). This process ensures that no losses of the parent ion could take place, thus granting maximum sensitivity. In the second step, a much more selective window was defined via the low-DAC and high-DAC, RF potential offsets [28].

Once the parent ions from each isomeric group were isolated, fragmentation conditions were optimized to achieve a compromise between sensitivity and selectivity. To do this, parent ions were CID-

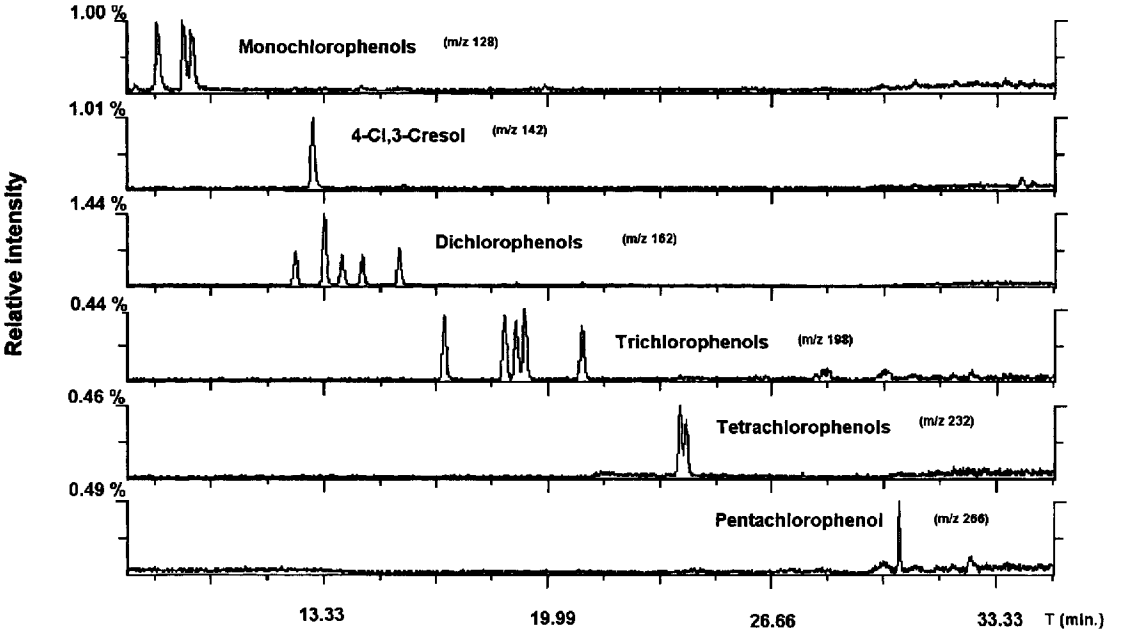

Fig. 2. Mass chromatograms for chlorophenol standards (15 μg/l) obtained by GC–MS–MS.

fragmented with the aim of obtaining one to three specific daughter ions (see Table 1) of high relative intensity that afforded accurate quantification, while preserving a certain proportion of the parent ions. At the same time, the CID conditions had to give different intensity ratios between the daughter ions in the MS–MS spectrum of each isomer, to ensure unequivocal identification of each compound. Both

Table 1
Figures of merit of the MS–MS spectra obtained for the chlorophenols studied

Compound (key numbers in Fig. 1)	Excitation amplitude (V)	RF storage level (m/z)	MS–MS spectrum Mass abundance (%)	Daughter ions selected for quantification
2CP (1)	68	60	128(100),100(36),92(29),65(6),126(3)	65+100
3CP (2)	68	60	100(100),128(69),65(19),92(7),127(3)	65+100
4CP (3)	68	60	128(100,100(95),65(16),92(4),73(3)	65+100
26DCP (4)	81	75	162(100),126(42),99(23),134(4),98(2)	99+126
25DCP (6)	81	75	162(100,99(59),126(13),134(10)	99+126
24DCP (7)	81	75	162(100),126(24),99(19),134(4),98(4)	99+126
35DCP (8)	81	75	99(100),162(73),134(20),126(7)	99+126
23DCP (9)	81	75	126(100),162(94)98(22),99(5),91(3)	99+126
34DCP (10)	81	75	162(100),99(70),134(18),126(3)	99+126
246TCP (11)	74	70	97(100),162(48),99(44),198(35),160(24)	97+135
236TCP (12)	74	70	97(100),99(47),162(17),198(11),98(10)	97+135
235TCP (13)	74	70	97(100),99(48),135(10),98(10),198(9)	97+135
245TCP (14)	74	70	135(100),198(83),97(68),133(55),99(32)	97+135
234TCP (15)	74	72	97(100),99(45),198(21),162(12),98(10)	97+135
2356TCP (16)	82	80	133(100),131(99),232(42),168(17),196(13)	131+133
2346TCP (17)	82	80	131(100),134(95),232(97),196(25),168(21)	131+133
PCP (18)	92	90	167(100),165(60),266(51),230(17),202(13)	167
4-Cl-3-cresol (5)	60	55	107(100),77(30),142(9),141(4)	77

aims can be achieved by appropriate selection of the non-resonant excitation amplitude and RF storage level [28].

Table 1 summarizes the results of this optimization process. The excitation time was kept constant at 20 ms. In this table, it can be seen that the CID optimum conditions for each isomeric group are a function of the number of chlorine atoms in the molecules. Groups having up to three chlorine atoms require lower amplitudes and RF storage levels compared to tetrachlorophenols and pentachlorophenol. In the fourth column of Table 1, a MS–MS spectrum is given for each compound. As can be seen, under identical CID conditions, isomer spectra differed significantly in the relative intensities of their ions.

Quantification of compounds was carried out by monitoring one or two characteristic masses in the MS–MS spectra showing the maximum signal-to-noise ratio. The last column in Table 1 shows the selected ions in each case. The parent ion was not used, even when it was the base peak.

A custom library was created by injecting the acetylated standards at a concentration level of 15 μg/l. This library was then used to identify the compounds in the samples. Even when analysing very dilute samples (0.25 pg injected) the degree of fitting and purity obtained was quite satisfactory (70–90% purity in the worst case).

3.3. Linearity

Calibration curves were obtained from six concentration levels (0.25, 0.5, 1, 2.5, 5 and 10 μg/l) of the mixture of acetylated standards. Chromatographic peak areas were measured for each compound by monitoring the daughter ion(s) specified in Table 1. For all compounds, calibration curves appeared linear with correlation coefficients that were better than 0.999. The repeatability, calculated from ten replicate injections of the standard mixture, at a concentration of 0.25 μg/l, was 3.1–15.7% as the relative standard deviation (Table 2).

3.4. Limits of quantitation

LOQs were calculated at a S/N ratio of 6. As can be seen in Table 2, they ranged from 0.08 to 0.19 μg/l. This should allow the direct detection and quantitation of the analytes at the legally established limits for some (0.5 μg/l) in drinking water. Based on the concentration factors for the samples (3.33 for 10 ml and 2000 for 1-l samples), this technique affords detection levels between 24–60 ng/l in 10-ml samples and between 40–95 pg/l in 1-l samples. As can be seen in Table 3, the LODs are two to three orders of magnitude lower than those obtained with GC–AED [34] or gas chromatography–Fourier transform infrared spectrometry (GC–FTIR) [30]. In fact, reported LODs obtained with GC–ion trap–EI-MS [35] are 1–10 μg/l by processing 5 l of water, whereas those for the proposed GC–tandem MS method should be 0.16–38 pg/l when extracting the same volume of sample.

Table 2
Limits of quantification (LOQ) and repeatability obtained with the proposed GC–MS–MS method

Compound	LOQ ($S/N=6$) (μg/l)	Repeatability R.S.D. (%) ($n=10$)
2CP	0.14	8.0
3CP	0.12	5.5
4CP	0.08	14.7
26DCP	0.08	9.1
24+25DCP	0.09	8.4
35DCP	0.08	3.1
23DCP	0.08	15.7
34DCP	0.08	9.3
246TCP	0.11	6.5
236TCP	0.08	11.9
235TCP	0.08	7.7
245TCP	0.08	15.7
234TCP	0.16	13.8
2356TCP	0.19	13.9
2346TCP	0.13	13.0
PCP	0.1	15.6
4-Cl-3-cresol	0.11	7.6

3.5. Application to samples of drinking water

The low LODs obtained prompted us to check the feasibility of determining the chlorophenols in a direct fashion using small sample volumes. For this purpose, a volume of 10 ml of tap water, spiked with each phenol compound at a concentration of 0.33 μg/l, was extracted with 3 ml of n-hexane. Coeluted

Table 3
Comparison of the LODs for chlorophenols obtained with the proposed GC–MS–MS method and alternative techniques. Values refer to a water sample volume of 1 l in all cases

Compound	LOD (ng/l) $S/N=3$			
	GC–MS–MS[a]	GC–MS(ITD)[b]	GC–DD–FTIR[c]	GC–AED[d]
2CP	0.07	50	34	79
3CP	0.06	50	37	–
4CP	0.04	50	39	–
26DCP	0.04	10	35	–
25+24DCP	0.05	10	34	67
35DCP	0.04	10	35	–
23DCP	0.04	10	37	–
34DCP	0.04	10	45	–
246TCP	0.06	5	35	33
236TCP	0.04	5	39	27
235TCP	0.04	5	39	–
245TCP	0.04	5	44	45
234TCP	0.08	5	44	–
2356TCP	0.09	–	42	39
2346TCP	0.07	–	48	–
PCP	0.05	–	39	52
4-Cl-3-cresol	0.06	50	–	106

[a]Values calculated from experimental data obtained in this work.
[b]From Ref. [35] (Gas chromatography–ion trap–electron ionization–mass spectrometry).
[c]From Ref. [34] (Gas chromatography–direct deposition–Fourier transform infrared spectrometry).
[d]From Ref. [30] (Gas chromatography–atomic emission detection).

compounds that may interfere with the detection of the chlorophenols at such low concentration levels when using GC–MS should be of little concern when GC–MS–MS is applied. For example, Fig. 3 shows a partial view of the GC–MS chromatogram (TIC) obtained for a sample whose extract had a final chlorophenol concentration of 1 μg/l, alongside the fragmentograms obtained for monochlorophenols by using GC–MS–MS. The mass spectrum of the first noticeable peak revealed the presence of a strong interference from some component, the spectrum of which did not include the isotopic peak of chlorine, in the water that overlapped completely with 2-chlorophenol. A comparison of the mass spectrum with the NIST90 library showed that the interferent was naphthalene. The identification of naphthalene (of M_r 128) was confirmed by GC–FTIR. It exhibits a base ion at m/z 128 and can therefore be fragmented within the time segment where the parent ion at m/z 128 for monochlorophenols was selected. However, by monitoring daughter ions of m/z values 65 and 100 (selected as being characteristic for monochlorophenols) the spectrum for 2-chlorophenol could be readily resolved from that of the interferent. The specificity of the CID fragments for 2-chlorophenol allow for its quantitation at concentrations as low as 0.25 μg/l in the presence of a naphthalene concentration of at least 100 times higher. The repeatability of the analytical procedure was estimated from three replicates of water samples from the same source; the R.S.D. ranged from 1.7 to 33%, depending on the particular compound (Table 4). Also, recoveries varied between 78% and 106%. Parts-per-trillion levels of the analytes in water were determined by spiking 1 l of MilliQ water with the chlorophenol mixture at a 6 ng/l concentration. The expected final concentration in the extract was 12 μg/l, so the S/N ratio was very high (over 50 for most of the analytes). The proposed method therefore allows one to quantify very low concentrations of chlorophenols in drinking water. The repeatability and recoveries obtained in the analysis of four water samples containing 6 ng/l of chlorophenols in 1 l are given in Table 5.

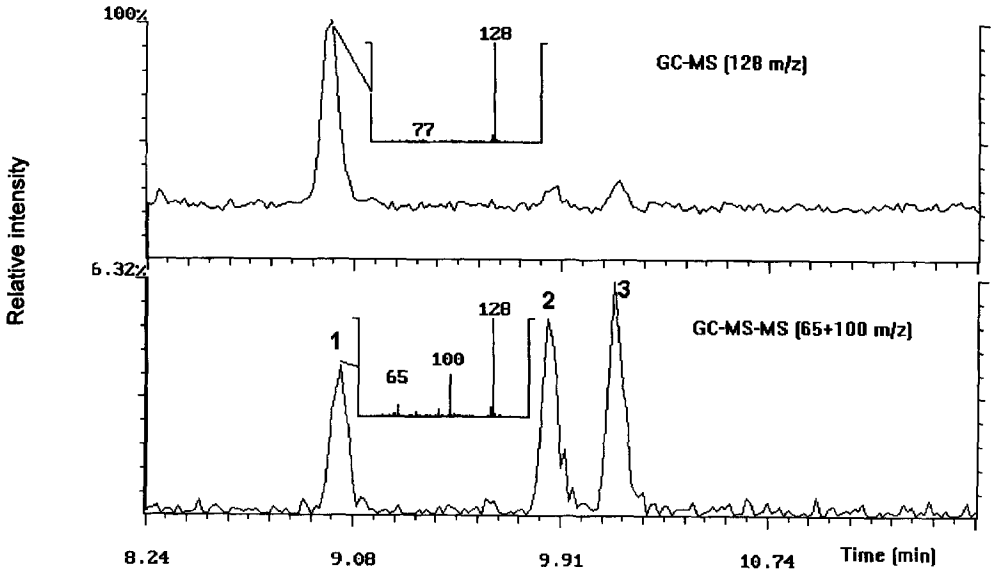

Fig. 3. GC–MS and GC–MS–MS chromatograms obtained (first time segment, corresponding to monochlorophenols) in the analysis of a 10-ml sample of drinking water containing 0.33 μg/l of chlorophenols (final concentration in the *n*-hexane extract 1 μg/l).

4. Conclusions

Based on the results obtained in this work, GC–MS–MS allows the quantitation of chlorophenols in the pg/l range in drinking water, by solid phase extraction from sample volumes of 1–5 l. In the routine quality control analysis of drinking water, very low sample volumes (10 ml) have to be processed by derivatization and subsequent straightforward extraction. In addition, the proposed method

Table 4
Repeatability (peak areas) and recoveries obtained for 10-ml water samples spiked with 0.33 μg/l of chlorophenols (concentration factor 3.33)

Compound	Repeatability			Recovery		
	Mean	S.D.	R.S.D. (%)	Mean	S.D.	R.S.D. (%)
2CP	461	294.0	6	101	28.00	28.0
3CP	509	86.0	2	89	31.00	35.0
4CP	610	410.0	7	97	23.00	23.0
26DCP	264	123.0	5	96	42.00	44.0
24+25DCP	593	991.0	17	88	63.00	71.0
35DCP	323	136.0	4	91	41.00	45.0
23DCP	70	193.0	28	99	25.00	25.0
34DCP	291	196.0	7	89	32.00	36.0
246TCP	117	90.0	8	91	14.00	16.0
236TCP	185	187.0	10	84	48.00	56.0
235TCP	164	182.0	11	84	6.00	7.0
245TCP	168	126.0	8	92	130.00	14.0
234TCP	167	189.0	11	78	119.00	15.0
2356TCP	109	365.0	33	82	4.00	5.0
2346TCP	101	183.0	18	79	16.00	2.0
PCP	87	244.0	28	106	244.00	2.5
4-Cl-3-cresol	519	458.0	9	96	280.00	2.6

Table 5
Repeatability (peak areas) and recoveries obtained for 1-l water samples spiked with 6 ng/l of chlorophenols (concentration factor 2000)

Compound	Repeatability			Recovery		
	Mean	S.D.	R.S.D. (%)	Mean	S.D.	R.S.D. (%)
2CP	1246	225	18	81	0.7	0.9
3CP	1187	203	17	100	8.4	8.5
4CP	1348	167	1.2	79	10.2	13.0
26DCP	675	95.3	14	96	3.6	3.8
24+25DCP	1084	259	24	88	3.9	4.4
35DCP	792	19	2.4	85	5.6	6.6
23DCP	155	12	8.1	98	12.4	12.7
34DCP	826	93	11	81	10.7	13.3
246TCP	442	53	12	107	1.6	1.5
236TCP	500	57	11	97	9.3	9.6
235TCP	355	69	20	90	11.2	12.5
245TCP	442	70	16	104	13.0	12.6
234TCP	438	46	10	91	9.4	10.3
2356TCP	437	65	15	102	4.9	4.8
2346TCP	380	50	13	105	6.2	5.9
PCP	289	22	8	82	6.6	8.0
4-Cl-3-cresol	1325	284	21	90	13.4	15.0

allows one to positively confirm the nature of each species and to distinguish between polychlorophenol isomers, a clear advantage over other techniques customarily used for the analysis of phenols. The low cost of benchtop instruments for implementation of the proposed method make it a serious choice for the routine determination of chlorophenols in drinking water and other types of samples of environmental interest.

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