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Universal screening method for the determination of US Environmental Protection Agency phenols at the lower ng l^{-1} level in water samples by on-line solid-phase extraction–high-performance liquid chromatography–atmospheric pressure chemical ionization mass spectrometry within a single run

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Abstract

The applicability of a previously optimized method for the analysis of the US Environmental Protection Agency (EPA) regulations phenols, based on on-line solid-phase extraction coupled to liquid chromatography with mass spectrometric (MS) detection in different matrix loaded water samples is demonstrated. The comprehensive optimization of the mobile phase conditions and their influence on the ionization process in atmospheric pressure ionization is described in detail. In particular, MS detection of the weakly acidic phenols such as phenol, monochlorinated phenols and methylated phenols requires the absence of acidic mobile phase modifiers and buffers. Thus lower retention times and slight peak broadening of the more acidic dinitrophenols are obtained if the entire range of EPA phenols is analyzed within a single chromatographic run. The figures of merit for the method were determined and the applicability to real water samples was investigated. Limits of detection for phenols ranging from 40 to 280 ng l^{-1} and relative standard deviations below 8% in SCAN mode are obtained for all phenols if only 10-ml river water samples with low dissolved organic carbon (DOC 5 mg C l^{-1}) concentrations are preconcentrated. The method was used to detect 2-nitrophenol and 4-nitrophenol in river water samples in the lower ng l^{-1} range. The analysis of highly matrix-loaded samples (DOC 210 mg C l^{-1}) requires a reduced enrichment volume resulting in decreased sensitivity. Still the method is capable of reaching excellent detection limits which demonstrates its excellent suitability for screening analysis.

Keywords: Water analysis; Environmental analysis; Mass spectrometry; Phenols

1. Introduction

Among the various methods developed for the analysis of phenols in surface and wastewater samples, liquid chromatographic methods with MS detection [1–6] are particularly favorable due to the fact that analysis of the polar compounds is possible without prior derivatization. Further benefits are the inherent selectivity of mass spectrometric detection and the possibility of integrating sample preparation and enrichment on-line [7–10]. Although the use of MS detection for liquid chromatography offers advantages in terms of selectivity, it also imposes additional limitations to the liquid chromatographic

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separation of phenols and their on-line solid-phase enrichment [2,5,11,12,28].

Liquid chromatography of phenols is generally carried out with the addition of acids or buffers to the mobile phase [1–5,13–26]. Their function is to suppress the ionization of both the analytes and the residual silanols of the stationary phase base material, which otherwise would either decrease retention on the analytical column or lead to uncontrolled interactions of the analytes and the stationary phase, resulting in lower separation efficiencies. Nevertheless, liquid chromatography without mobile phase modifier for phenols has been suggested by several authors [11,28,29,32].

The group of US Environmental Protection Agency (EPA) phenols is rather inhomogeneous with respect to their pK_a values, which range from 4 to 11 [25]. Therefore most of the on-line solid-phase extraction (SPE)–HPLC methods reported so far to offer superior sensitivity for the analysis of the entire US EPA phenol range without derivatization make either use of a dual detector set-up or they require two separate runs. The first approach uses electrochemical detection for weakly acidic phenols and diode array detection (DAD) for more acidic phenols, respectively [16,19–24]. The second approach requires two separate chromatographic runs with atmospheric pressure ionization (API)-MS detection. Atmospheric-pressure chemical ionization (APCI)- and electrospray ionization (ESI)-MS detection (which may even require rather unusual conditions for the chromatographic separation [2]) had to be performed independently for more acidic phenols and hardly acidic phenols, respectively. The increasing sensitivity of highly halogen substituted phenols in APCI-MS detection as a result of their higher acidity was also described by Eiceman et al. [36], whereas the determination of hardly acidic phenols still remains difficult.

Apart from this approach, the determination of the entire range of phenols with on-line SPE–HPLC with DAD is possible [15,24,30], but the achieved detection limits are significantly lower.

Due to the recent introduction of the new polymeric phases such as Spark Hysphere GP and Hysphere SH, Merck LiChrolut EN or Waters Oasis which are particularly suited for on-line SPE even of the weakly retained phenol, the preconcentration of phenols from spiked water samples can be performed without significant losses, as reported earlier by our group [11]. Similar results have also been reported by Patsias et al. [24] with HPLC–DAD where on-line SPE was performed under optimized conditions for liquid chromatography with phosphate buffer at pH 3 or by Lacorte et al. [31] with off-line SPE–HPLC–DAD. The use of on-line SPE coupled to LC–MS for phenols in highly matrix-loaded samples has not been reported to date.

The determination of the weakly acidic phenols like phenol itself or 2,4-dimethylphenol by HPLC–ESI-MS requires atypical conditions with pure methanol as eluent and ammonium acetate buffer as additive which were used on a pyrolytic graphitic carbon (PGC) stationary phase [2]. Other studies by Jáuregui and co-workers [3,5] were restricted to the analysis of halogenated and nitrated phenols with APCI- and ESI mode with an isocratic acetonitrile–water mixture acidified with acetic acid.

In contrast to these methods, the on-line SPE–HPLC–APCI-MS based method using a methanol–water gradient without mobile phase modifier recently presented by our group [11] significantly extends the range of phenols that can be detected within a single chromatographic run. The present paper reports on the applicability of this method to the analysis of real samples for the detection of all US EPA phenols with similar sensitivity. Both the influence of the matrix as well as the influence of various mobile phase additives (such as acids and buffers) will be described in detail.

2. Experimental

2.1. Chemicals

The phenol standards used in this study had a purity of at least 99% and were obtained from following sources: 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol, 2-nitrophenol and pentachlorophenol from Fluka (Vienna, Austria), phenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 4-chloro-3-methylphenol, 4-nitrophenol, 4-methyl-2-nitrophenol, 5-methyl-2-nitrophenol and 3-methyl-4-nitrophenol from Aldrich (Vienna, Austria) and 2,4,6-

trichlorophenol and 2,4-dimethylphenol from Riedel-de Haen (Vienna, Austria).

All standards were dissolved in methanol, stored in the dark at 4 °C and a working solution in the ng l^{-1} range was prepared daily by diluting the mixed stock solution (mg l^{-1} concentration range per phenol) with water. Solvents for reversed-phase liquid chromatography (methanol G Chromasolv and acetonitrile Chromasolv) were purchased from Riedel-de Haen. The high-purity water was taken from a Milli-Q water system (Millipore, Eschborn, Germany). Mobile phase modifiers like formic acid, acetic acid, trifluoroacetic acid and ammonium acetate were obtained from Merck (Vienna, Austria) and were at least analytical reagent grade.

2.2. HPLC–API-MS analysis

Liquid chromatographic separation and mass spectrometric detection were performed with a 1100 series HPLC–MSD system from Hewlett-Packard (now Agilent, Waldbronn, Germany and Palo Alto, CA, USA). Both the APCI interface (G1947A) and the ESI interface (G1948A), respectively, were used here. Parameters for the mass selective detector and the interface, like fragmentor voltage or capillary voltage and the influence of solvent composition or the addition of mobile phase modifiers on the response were optimized during flow injection analysis (FIA) sequences. Concentrations of single phenols for FIA measurements ranged from 5 to 15 mg l^{-1} (100 to 300 ng absolute in 20-μl injection volume) to obtain a sufficiently good signal-to-noise ratio for the comparison of different ionization conditions.

The measurements were performed in negative and positive ion mode at 400 °C vaporizer temperature (only APCI), 350 °C drying gas temperature, 5 l min^{-1} for APCI (13 l min^{-1} for ESI) drying gas flow, 50 p.s.i. vaporizer gas pressure, (1 p.s.i.= 6894.76 Pa), and 1500 V capillary voltage. The drying and nebulizer gas (nitrogen, purity >99.5%) was produced by a Whatman nitrogen generator connected to a compressor. The corona current for APCI was set to 4 μA in the positive ion mode and to 10 μA in the negative ion mode. Full scan data acquisition (SCAN) was performed scanning from m/z 80 to 280 using a cycle time of 1 s and a peak width of 0.1 s and the fragmentor voltage was set to 90 V. Selected ion monitoring (SIM) mode measurements were performed in the time scheduled mode by measuring from 0 to 9.50 min at m/z 183 and 197; 9.51–12.75 min at m/z 93; 12.76–18.30 min at m/z 121, 127 and 138; 18.31–21.00 min at m/z 121, 141, 161 and 265; and 21.01–28.00 min at m/z 195 and 265.

Chromatography was performed at 25 °C with a methanol–water gradient without acid addition to the mobile phase. The LC gradient was: 40% MeOH (6 min isocratic), increased to 100% MeOH (linearly between 6 and 20 min) and held for 8 min at a flow-rate of 0.8 ml min^{-1}. The Kromasil C_{18} analytical column (250 mm×4 mm I.D., 5 μm spherical) was obtained through the Austrian Research Center (Seibersdorf, Austria).

Postcolumn addition was accomplished by merging the chromatographic effluent directly after the diode array detector via a polyether ether ketone (PEEK) T-piece (Upchurch Scientific) with a stream of the respective base in methanol at 0.3 ml min^{-1}, supplied by a Jasco 880-PU HPLC pump in combination with a LO-Pulse pulse damper from Supelco (Vienna, Austria). All postcolumn addition solvents were degassed on-line with the HP1100 vacuum degasser resulting in a more stable baseline and in a lower baseline noise in the mass selective detector.

An ion suppressor module CMMS-II from Dionex (Vienna, Austria) was installed directly in front of the mass-selective detector interface, to minimize the back pressure in the membrane module, for the investigation of its applicability to remove the organic acid from the chromatographic liquid phase.

2.3. Sampling and sample pretreatment

River water samples were taken from the river Danube in Vienna, Austria, and from the river Mur in Bruck a. d. Mur, Styria, Austria. Wastewater treatment plant (WWTP) influents and effluents (which were drained into the river) samples were taken from a paper-producing factory in Bruck a. d. Mur, equipped with a WWTP and from a paper-producing factory in Gutenstein, Lower Austria, whose WWTP treats both the communal wastewater from the village and the industrial wastewater from the fac-

tory. Water samples were collected in dark Pyrex borosilicate glass bottles and immediately acidified with sulphuric acid to pH 2.5. Within 2 h of sampling they were filtered through a cellulose nitrate filter (0.45-μm pore size, Wagner and Munz, Vienna, Austria) in the laboratory.

Dissolved organic carbon (DOC) concentrations were determined with a GO-TOC 100L instrument (Gröger and Obst, Berg am Starnbergsee, Germany). Because of the required sample filtration step and the fact that a measure for the concentration of the dissolved matrix was required to characterize the sample matrix being preconcentrated and eluted into the LC–MS system, the DOC concentration was determined. For the DOC measurement the samples were 1:1000 diluted with distilled water, 2 ml were acidified with 10 μl HNO_3 (to remove dissolved CO_2 and carbonates) and 300 μl per sample were injected at 5 ml min^{-1} into an oven (800 °C) where immediately the quantitative oxidation of organic substance was effected. The CO_2 was cryo-trapped and the concentration was determined by IR absorption.

2.4. Solid-phase extraction

The configuration of the SPE system and the optimized conditions have been reported elsewhere [11]. Only polymer based SPE adsorbents, namely Hysphere GP from Spark (polydivinylbenzene, 5–15 μm particle size, spherical shape) or Oasis HLB material (macroporous polydivinylbenzene-*N*-vinylpyrrolidone copolymer) from Waters (Vienna, Austria) in specially designed cartridges of 10 mm×2 mm I.D. were used for on-line SPE.

An ultra-low volume precolumn filter with a 0.45-μm frit from Bartelt (Graz, Austria) was positioned in the transfer capillary in front of the analytical column to avoid clogging of the system.

3. Results and discussion

3.1. Optimization of mass selective detection conditions

In preliminary experiments, the suitability of both APCI and ESI was investigated. APCI provided a significantly higher response for the entire set of EPA phenols compared to ESI, even if postcolumn addition of organic bases was performed, which is in contrast to an earlier reported method [2]. The higher sensitivity of both dinitrophenols and pentachlorophenol in ESI could be explained by their higher acidity, which is also reflected in their pK_a values [25], whereas partial thermal decomposition in the heated APCI interface occurred for both dinitrophenols. On the other hand the practically undissociated weakly acidic phenols like phenol, 2,4-dimethylphenol 2-chlorophenol, 4-chlorophenol and other methylated phenols (results are not given) were only detected with APCI (Table 1). This is in line with the general opinion that less polar analytes are more easily detected in the APCI mode than in the ESI mode [35].

The composition of the mobile phase was observed to most strongly affect the detectability of the weakly acidic phenols. With both types of API techniques, the sensitivity of these phenols decreased by about one order of magnitude if the methanol content in the mobile phase was successively replaced by an increasing fraction of acetonitrile or water during FIA as demonstrated in Table 2. Consequently, instead of using an acetonitrile–water eluent as reported in the literature [2,5], liquid chromatography and on-line SPE were adapted to a methanol–water gradient to enable the determination of the entire EPA phenol range with a sensitivity in the same order of magnitude as reported previously [11].

Table 1
Comparison of relative response of EPA phenols with MS detection in negative APCI and ESI modes, respectively[a]

	Ph	2,4-DMP	2-CP	2-NP	4-NP	4-C-3-MP	2,4-DCP	2,4-DNP	2,4,6-TCP	2-M-4,6-DNP	PCP
Absolute response with APCI (normalized response = 100%)	8669	26 101	24 553	56 310	97 112	79 196	65 496	61 137	51 494	125 737	31 891
Relative response with ESI (%)	0	0	0	0	59	30	8	248	21	162	187

[a] Response was determined in FIA mode, and abbreviations and acquisition parameters are given in Experimental.

Table 2
Influence of mobile phase composition on the relative APCI-MS response of weakly acidic phenols like phenol, 2,4-dimethylphenol, 2-chlorophenol and 4-chloro-3-methylphenol[a]

Mobile phase composition	Relative response (%)			
	Ph	2,4-DCP	2-CP	4-C-3-MP
Methanol–water (50:50)	100	100	100	100
Methanol–acetonitrile–water (25:25:50)	53	55	70	71
Acetonitrile–water (50:50)	0	23	46	40

[a] Response was determined in the FIA mode and abbreviations and acquisition parameters are given in Experimental.

Addition of volatile organic acids of increasing acid strength like acetic acid, formic acid or trifluoroacetic acid to the mobile phase reduces the dissociation of dinitrophenols and pentachlorophenol in the mobile phase resulting in stronger retention on the analytical column and reduced peak tailing. On the contrary, chromatography of methylated, mononitrated or mono-, di- and trichlorinated phenols was hardly influenced, whereas signal suppression in API-MS detection of weakly acidic phenols with higher pK_a values like phenol, 2,4-dimethylphenol, 2-chlorophenol or 4-chloro-3-methylphenol decreased dramatically even if lowest concentrations of these volatile acids were added to the mobile phase [32]. The sensitivity of these weakly acidic phenols decreased by about one order of magnitude by the increase of the concentration of volatile organic acid in the mobile phase. This effect was observed for APCI and ESI and could be explained by the suppression of ion formation and release of ions in the gas phase [27,28].

Independently of the applied ionization technique, signal suppression of weakly acidic phenols was not even diminished by postcolumn addition of volatile bases like ammonium hydroxide or triethylamine above 200 mg l^{-1} which is sufficient to neutralize the acid concentrations of 10–100 mg l^{-1} used in the chromatographic gradient. Although the same approach was found useful for the determination of more acidic phenols [2,5].

Besides the fact that pH values higher than the pK_a values of the weakly acidic phenols could not be adjusted by postcolumn addition of organic bases to accomplish their complete deprotonation in the liquid phase for ESI, increased concentrations of bases during postcolumn addition resulted in significantly higher baseline noise.

A different approach, making use of an ion suppressor to remove the free organic acids from the mobile phase without the formation of salts was not successful. Irreversible adsorption of all investigated phenols on the membrane was observed in all cases, independently of the applied regenerant media—triethylamine in water or pure water.

3.2. Analytical figures of merit

The analytical figures of merit, derived from the data from calibration with external standards after on-line SPE of spiked distilled water and spiked river water, were used for the characterization of the developed method. Linearity of the calibration curve was given over two orders of magnitude in both distilled water samples and in river water samples. Excellent reproducibility (for $n=4$ parallel determinations) in both the SCAN and SIM modes (relative standard deviation (RSD) $<8\%$) was obtained for concentrations about one order of magnitude above the limits of detection (LODs). The instrument was stable for at least 2 days of continuous operation, resulting in the low RSD values mentioned above.

The LOD values were determined by extending the calibration graph to lower concentrations near the detection limit. The LODs were calculated with the EXCEL macro VALIDATA of Wegscheider et al. [33] after measurement of seven equidistant levels in the concentration range of the LODs in the SCAN and SIM modes, respectively. The EXCEL macro VALIDATA is based on the calibration method as specified in the German standard DIN 32 645 [34]. This procedure is using the 95% confidence interval of the regression line at concentration zero for calculation of the LOD.

Although only 10 ml of sample was preconcentrated, the achieved LODs in the upper ng l^{-1} range

Table 3
Detection limits in the SCAN mode and the time scheduled SIM mode of target phenols in distilled water and in river water using on-line SPE with APCI-MS detection (10 ml preconcentrated)

Substance	Detection limits (ng l^{-1})			
	SCAN		SIM	
	Dist. water	River water	Dist. water	River water
Phenol (Ph)	197	195	14	70
2,4-Dimethylphenol (2,4-DMP)	207	56	36	3
2-Chlorophenol (2-CP)	126	48	8	4
4-Chlorophenol (4-CP)	57	25	3	1
4-Nitrophenol (4-NP)	65	52	11	6
2-Nitrophenol (2-NP)	55	49	11	4
4-Chloro-3-methylphenol (4-C-3-MP)	63	29	3	4
2,4-Dichlorophenol (2,4-DCP)	42	30	2	4
2,4-Dinitrophenol (2,4-DNP)	95	71	6	6
2,4,6-Trichlorophenol (2,4,6-TCP)	132	80	5	3
2-Methyl-4,6-dinitrophenol (2-M-4,6-DNP)	178	104	41	13
Pentachlorophenol (PCP)	288	251	8	5

in the SCAN mode (values are given in Table 3) were at least one order of magnitude lower than by the method reported earlier by Puig et al. [2] who preconcentrated 100 ml of sample. For the more acidic compounds, pentachlorophenol and both dinitrophenols, the improvement of LODs by a factor of five compared to the method of Puig et al. was somewhat smaller. This fact could be explained by broader peak shapes of the two early eluting dinitrophenols and the last eluting pentachlorophenol as a consequence of performing the chromatographic separation without mobile phase modifiers.

When using the SIM mode (Table 3) an improvement in sensitivity of at least one order of magnitude was obtained and permits phenols to be determined at the low ng l^{-1} range by preconcentration of only 10 ml of water sample.

The major improvement of the suggested method is that it allows the whole EPA phenol range to be detected within a single chromatographic run with only one interface, thus providing an excellent screening method that at the same time provides remarkable sensitivity.

3.3. Applications

The recoveries of phenols from spiked distilled water samples with on-line SPE HPLC–APCI-MS have been described previously [11]. Quantitative recoveries for phenols from spiked river water samples with low DOC (5 mg l^{-1}) obtained with the polymeric Waters Oasis cartridges are given in Table 4. Neither significant losses for the extraction of the investigated phenols from spiked river water samples were found, nor signal suppression by the matrix during the ionization in the interface. No significant differences in the response were observed up to a DOC content in the aqueous sample of about 5 mg l^{-1}. Consequently no significant differences of LODs compared to spiked distilled water samples were observed (Table 3).

Table 4
Recoveries and (relative standard deviations) of EPA phenols from spiked river water samples with Waters Oasis SPE (2×10 mm) cartridges

Substance	Recovery % (RSD, %)
Phenol	98 (2)
2,4-Dimethylphenol	99 (9)
2-Chlorophenol	97 (1)
4-Chlorophenol	90 (8)
2-Nitrophenol	98 (4)
4-Nitrophenol	101 (2)
4-Chloro-3-methylphenol	101 (7)
2,4-Dichlorophenol	103 (4)
2,4-Dinitrophenol	98 (4)
2,4,6-Trichlorophenol	104 (2)
2-Methyl-4,6-dinitrophenol	102 (7)
Pentachlorophenol	105 (1)

Retention times for all methylated, mononitrated and chlorinated phenols were unaffected by the river water matrix and RSD values of retention times below 0.5% were obtained. This holds true except for both dinitrophenols that showed a significantly higher retention time and the RSD of their retention times was above 1% if matrix loaded water samples were analyzed.

The target analytes could be clearly separated from the huge humic substance peak appearing at the beginning of the chromatogram. Only 2,4-dinitrophenol and 2-methyl-4,6-dinitrophenol could not be separated efficiently from the matrix band. Nevertheless, detection and quantitative analysis of these two analytes is possible in the APCI negative detection mode even after acid addition (which shifts their retention time to significantly higher values and thus away from the humic acid peak) due to their excellent sensitivity (Fig. 2b).

The method was applied to the analysis of a river Danube water sample. It allowed us to detect 4-nitrophenol and 2-nitrophenol at levels of 40 ng l^{-1} and 30 ng l^{-1}, respectively, in the river Danube water sample in the SIM mode after preconcentration of a 10-ml sample (chromatogram presented in Fig. 1). The identification of the analytes was achieved by detection of the quasi-molecular ion at the expected retention time, and quantitative analysis by standard-addition. In the SCAN mode, detection was not possible at these low concentrations.

In the analysis of more strongly contaminated samples (DOC of 23 mg l^{-1} and up to 217 mg l^{-1}), the high content of dissolved organic matter became the limiting factor. Since neither the clean-up of the preconcentrated sample could be further improved due to the early breakthrough of phenol, nor the selectivity during preconcentration by the use of more selective adsorbents, the preconcentration volume had to be decreased for the analysis of highly matrix loaded samples. Consequently a preconcentrated volume of 1 ml spiked WWTP effluent was analyzed in order to avoid overload of the chromatographic column and signal suppression in the mass spectrometer due to the matrix. A typical total ion chromatogram of a matrix loaded water sample after on-line SPE–LC–APCI-MS detection with a methanol–water gradient is given in Fig. 2A.

While the use of organic acids as mobile phase modifiers resulted in signal suppression of the weakly acidic phenols, the presence of matrix did not quench the signal. Assuming a constant absolute sensitivity for the analytes, relative sensitivity decreased by a factor of about 10 compared to the values given in the Table 3 for the SCAN and for

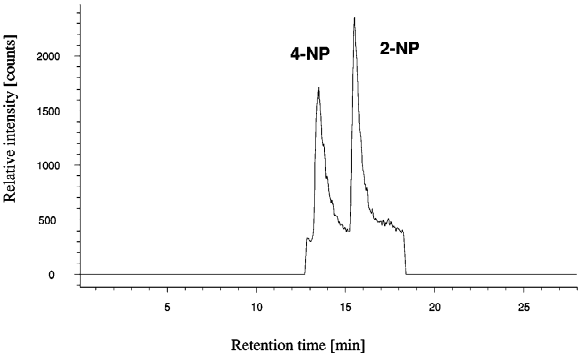

Fig. 1. Selected ion chromatogram of 10 ml preconcentrated Danube river water sample using on-line SPE–HPLC–APCI-MS negative mode detection in the time scheduled SIM mode for the determination of 4-nitrophenol ($c \approx 30$ ng l^{-1}) and 2-nitrophenol ($c \approx 40$ ng l^{-1}) with a methanol–water gradient.

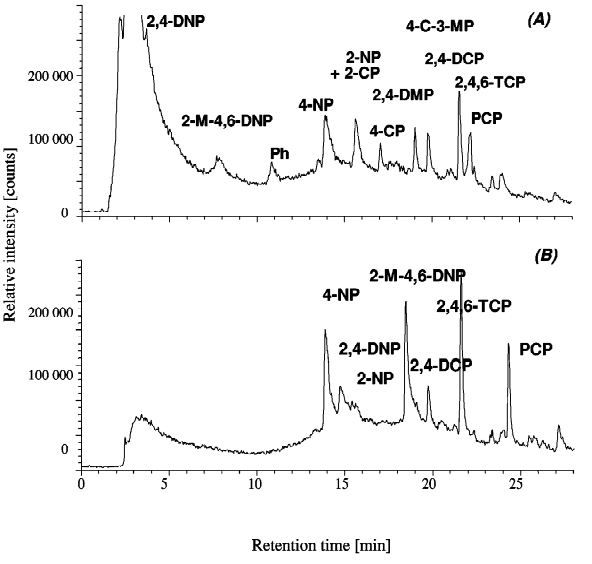

Fig. 2. Comparison of the total ion chromatograms of waste water treatment plant effluent spiked with EPA phenols at 10–70 μg l^{-1} absolute per compound in the SCAN mode (m/z 80–280) using on-line SPE (1 ml preconcentrated) with HPLC–APCI-MS detection with a methanol–water gradient (A) and with a methanol–water gradient with 0.1 ‰ formic acid (B).

SIM modes, due to the reduced enrichment volume necessary for the analysis of highly-contaminated samples.

If the determination of the weakly acidic phenols is of minor importance, higher sensitivities and higher precision can be achieved in the determination of dinitrophenols or pentachlorophenol by the use of an acidified mobile phase. As demonstrated in a typical total ion chromatogram in Fig. 2B, significantly higher retention times and improved peak shapes for these more acidic phenols were achieved in addition to a certain reduction of the ionization of the humic substance peak. However, an acidified mobile phase would certainly also lead to a signal suppression of weakly acidic phenols like phenol, 2,4-dimethylphenol, 2-chlorophenol, 4-chlorophenol and 4-chloro-3-methylphenol after on-line SPE–LC–APCI-MS detection of a matrix loaded water sample.

4. Conclusion

The proposed method, based on on-line SPE–HPLC–MS with APCI allows to determine the whole range of EPA phenols in water samples with low to medium organic carbon content within a single chromatographic run. This demonstrates its great potential as a screening method for phenols. Only minimal sample volumes (=10 ml) are required to attain LODs at ng l^{-1} levels in the SCAN and SIM modes which also significantly cuts the time required for sample preparation. MS signal suppression due to commonly used mobile phases remains a severe problem for the sensitive detection of weakly acidic phenols like phenol and methylated phenols. Of the different ways that were investigated to circumvent this difficulty, only the avoidance of acid addition to the mobile phase proves to be feasible. The resulting chromatographic method is sufficiently robust for the analysis of low matrix containing water samples as demonstrated by the analysis of river water samples. For the analysis of highly matrix loaded samples, like wastewater treatment plant effluents, it is not the lack of robustness that impairs the applicability of the presented method, but rather the lack of selectivity despite MS detection. Although MS detection generally offers high selectivity and sensitivity, the dissolved matrix remains the limiting factor and either demands a reduction of the sample volume to e.g. 1 ml in the enrichment step, or a more selective detector such as a triple–quadrupole MS.

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