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Determination of nonylphenols as pentafluorobenzyl derivatives by capillary gas chromatography with electron-capture and mass spectrometric detection in environmental matrices

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Abstract

Procedures for the trace level determination of nonylphenols, the toxic and final refractory metabolites of polyethoxylated nonylphenol, in sewage sludge and river and coastal sediments were developed. Soxhlet extracts of freeze-dried samples are cleaned up through a neutral alumina column, derivatized with pentafluorobenzyl bromide and determined by capillary GC with electron-capture detection and/or electron impact and negative-ion chemical ionization MS. The detection limits achieved by the two capillary GC–MS techniques in the selected-ion monitoring were, respectively, 10 and 2.7 pg (absolute) and 1.4 and 0.3 pg/g (for a 10-g sample).

1. Introduction

Nonylphenol polyethoxylates (NPEO, $n = 1$–18) constitute the major class of non-ionic surfactants used in industrial applications (i.e., emulsifiers, detergents, wetting and dispersing agents, radical inhibitors, etc.) and in household products [1,2].

Nonylphenols (NP) are the most toxic and refractory metabolites of NPEO [3,4] and can cause severe hazards to aquatic ecosystems. Their significant hydrophobic character (log $K_{ow} \approx 4.2$) [5] would implicate adsorption on to water column-suspended particles and sediments.

Extraction procedures for the determination of NPEO in treatment plant effluents [6–8] and river and enclosed bay sediments [9,10] have been reported. Their occurrence at high concentrations in these environmental matrices allows their determination by LC using fluorescence detection. On the other hand, the detection of NPEO by other more sensitive procedures, such as those involving capillary GC (cGC) with flame ionization detection (FID) or cGC–MS in the electron impact (EI) mode, are only partially successful owing to their lack of selectivity [11]. The use of softer ionization techniques, e.g. cGC–MS in the chemical ionization (CI) mode [12] or with a 20-eV EI energy [13], although allowing the characterization of the NP molecular ions, do not provide sufficient sensitivity for trace level determinations in environmental samples.

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The aim of this work was the development of a selective and sensitive procedure for the determination of the toxic and final refractory metabolites of NPEO, namely NP, in relevant environmental matrices containing low levels of these compounds. The use of NP pentafluorobenzyl derivatives (PFB) was evaluated in order to improve the sensitivity and selectivity in cGC–ECD and cGC–MS. Negative-ion CI (NCI) MS is evaluated for the first time and the results are compared with those obtained by cGC–EI-MS.

2. Experimental

2.1. Sample origin and handling

Sewage sludges were collected in the effluent of the Barcelona primary treatment plant during 1991–92 and coastal sediments offshore Barcelona, using a box corer, during 1988. Discrete horizons of 2 cm were obtained in situ and frozen at −20°C in aluminium trays until analysis. River sediments were collected in the Nile estuary using a grab sampler during 1991. A 24-h sample composite was obtained from the Joint Water Pollution Control Plant (JWPCP) at Los Angeles (USA) during 1987.

2.2. Reagents and materials

Neutral alumina (70–230 mesh) and pesticide-grade solvents (*n*-hexane, dichloromethane, methanol) were obtained from Merck (Darmstadt, Germany). Analytical-reagent grade sodium sulphate was purchased from Panreac (Barcelona, Spain) and was used after activation at 120°C overnight. Neutral alumina was Soxhlet extracted with dichloromethane–methanol (2:1) for 18 h and then activated at 120°C overnight. 4-Nonylphenol isomeric mixture and *p*-(1,1′,3,3′-tetramethylbutyl)phenol were obtained from Fluka (Buchs, Switzerland) and pentafluorobenzyl bromide (PFBBr) from Aldrich (Steinheim, Germany) (caution: PFBBr is a strong lachrymator and should be handled with appropriate precautions).

2.3. Analytical procedures

Freeze-dried samples were Soxhlet extracted with dichloromethane–methanol (2:1) for 24 h. *p*-(1,1′,3,3′-Tetramethylbutyl)phenol was used as a recovery standard and it was added into the sample prior to the extraction. However, some samples already contained that compound, hence for those particular samples it could not be used as an NP surrogate. Organic extracts were rotary evaporated to low volume, then concentrated under a gentle stream of nitrogen and finally fractionated by open-column chromatography using 8 g of neutral alumina (bottom) and 1.5 g of sodium sulphate (top), as described previously [14]. The NP-containing fraction (IV) was derivatized with PFBBr to yield the pentafluorobenzyl (PFB) derivatives according to previously described procedures [15]. Briefly, 100 μl of an acetone solution of 5% PFBBr reagent, 100 μl of a 10% aqueous potassium carbonate and 1.5 ml of acetone were added to fraction IV and were kept at 60°C for 1 h. Then, the derivatized nonylphenols were recovered with *n*-hexane after removing the excess of derivatization reagent with a gentle stream of nitrogen.

Instrumental analyses were performed by with a Model 5890 capillary gas chromatograph equipped with an electron-capture detector and a Model 7673A autosampler (Hewlett-Packard, Palo Alto, CA USA). Helium was used as the carrier gas at 30 cm/s and a 30 m × 0.25 mm I.D. fused-silica capillary column coated with 0.25 μm of DB-5 (J&W, Folsom, CA, USA) was used. Samples were dissolved in 1 ml of isooctane and injected at 270°C in the splitless mode using a purge time of 40 s. The detector temperature was held at 310°C. The column temperature was programmed from 70 to 130°C at 20°C/min, then to 280°C at 6°C/min and to 310°C at 15°C/min, holding the final temperature for 10 min.

cGC–MS in the EI mode was performed with a Fisons (Milan, Italy) MD 800 instrument. The ion source and transfer line temperatures were held at 200 and 300°C, respectively. cGC–MS in the NCI mode was performed with a Finnigan (San Jose, CA, USA) XL system using 22.5 bar of methane in the analyser. The ion source and transfer line temperatures were held at 130 and 300°C, respectively. A 30 m × 0.25 mm I.D. fused-silica capillary column coated with 0.25 μm of DB-5MS (J&W) was used. The oven temperature was programmed from 70 to 130°C at 20°C/min, then to 250°C at 6°C/min and finally to 300°C at 10°C/min. Other chromatographic conditions were similar to those described above. Selected-ion monitoring (SIM) in the EI [m/z 246 (internal standard, I.S.), 301, 302, 315, 316, 329, 330, 343 and 400] and NCI (m/z 205 and 219) acquisition programmes were used with a dwell time of 0.08 and 0.4 s per single ion, respectively. 1-Phenyldodecane was used as the I.S. for quantification by cGC–EI-MS. Blanks for every batch were processed as real samples. The recovery of NP from spiked sediments (ca. 100 ng/g, dry mass) was 70 ± 10% ($n = 4$).

3. Results and discussion

3.1. *cGC–ECD of PFB derivatives*

Technical NP constitutes a complex mixture of isomers due to the substitution pattern in the alkyl chain. The complete resolution of all isomers has not yet been achieved, but the use of trimethylsilyl (TMS) derivatives leads to an improvement in their resolution when non-polar stationary phases are used [8,11]. However, the determination of NP as TMS derivatives by cGC–FID is prone to the presence of interferences due to the lack of selectivity in FID.

In order to overcome this problem, the use of PFB derivatives and ECD was evaluated in this study. The cGC–ECD profile of a PFB-derivatized NP standard mixture is shown in Fig. 1A. The isomeric distribution pattern is very similar to that found in the original mixture, showing the quantitative derivatization of all the isomers. Conversely, the NPEO cannot be derivatized owing to the lower activity of the ethoxy group.

Derivatization with PFBBr and cGC–ECD determination have been reported previously for chlorophenolic compounds in water, with a limit of detection (LOD) of 0.1 ng/l [15,16]. However, this is the first time that the PFB derivatization procedure has been applied to the trace level determination of NP. The absolute LOD of PFB NP derivatives is in the picogram range. However, the limit of quantification (LOQ) is several orders of magnitude higher owing to the presence of many interferences in the cGC–ECD trace (Fig. 1B and Table 1).

3.2. *cGC–MS of PFB derivatives*

In order to circumvent the interferences in the cGC–ECD trace, cGC–MS in the EI mode was developed. Fig. 2A shows the mass spectra of a selected isomer in the EI mode. The fragmentation pattern shows a base peak at m/z 181, which corresponds to the cleavage of the PFB group, and it is common for all the isomers. Other fragments corresponding to the alkyl chain cleavage are isomer specific because the cleavage occurs in the substitution position (Table 2) [17]. Despite the high abundance of the m/z 181 ion, it is non-specific for NP because is common to all PFB derivatives. Instead, the ions corresponding to the alkyl cleavage were used (m/z $301 + n \times 14$, $n = 1$–4). The shift of these fragments to higher masses in comparison with underivatized NP (m/z $107 + n \times 14$, $n = 1$–6) leads to an improved selectivity. The absolute LOD [signal-to-noise ratio (S/N) = 3) of the SIM method in the EI mode for total NP was 1.4 pg.

The NCI mass spectrum shown in Fig. 2B is common to all the isomeric NP. The molecular ion was not detected under the analysis conditions used. Instead, a base peak at m/z 219 was the base peak which corresponds to a dissociative electronic capture fragmentation. It is worth mentioning that the ion at m/z 219 corresponds to the alkylphenolate anion, which is the complementary fragment at m/z 181 found in the EI mode. The NCI mass spectrum of underivatized NP (Fig. 2C) shows a complex fragmentation pattern with the [M + 1] anion attributable to radical–molecule reactions [18]. Further, the sensitivity was significantly reduced in comparison with the PFB derivatives. Consequently, NP can only be determined by GC–MS

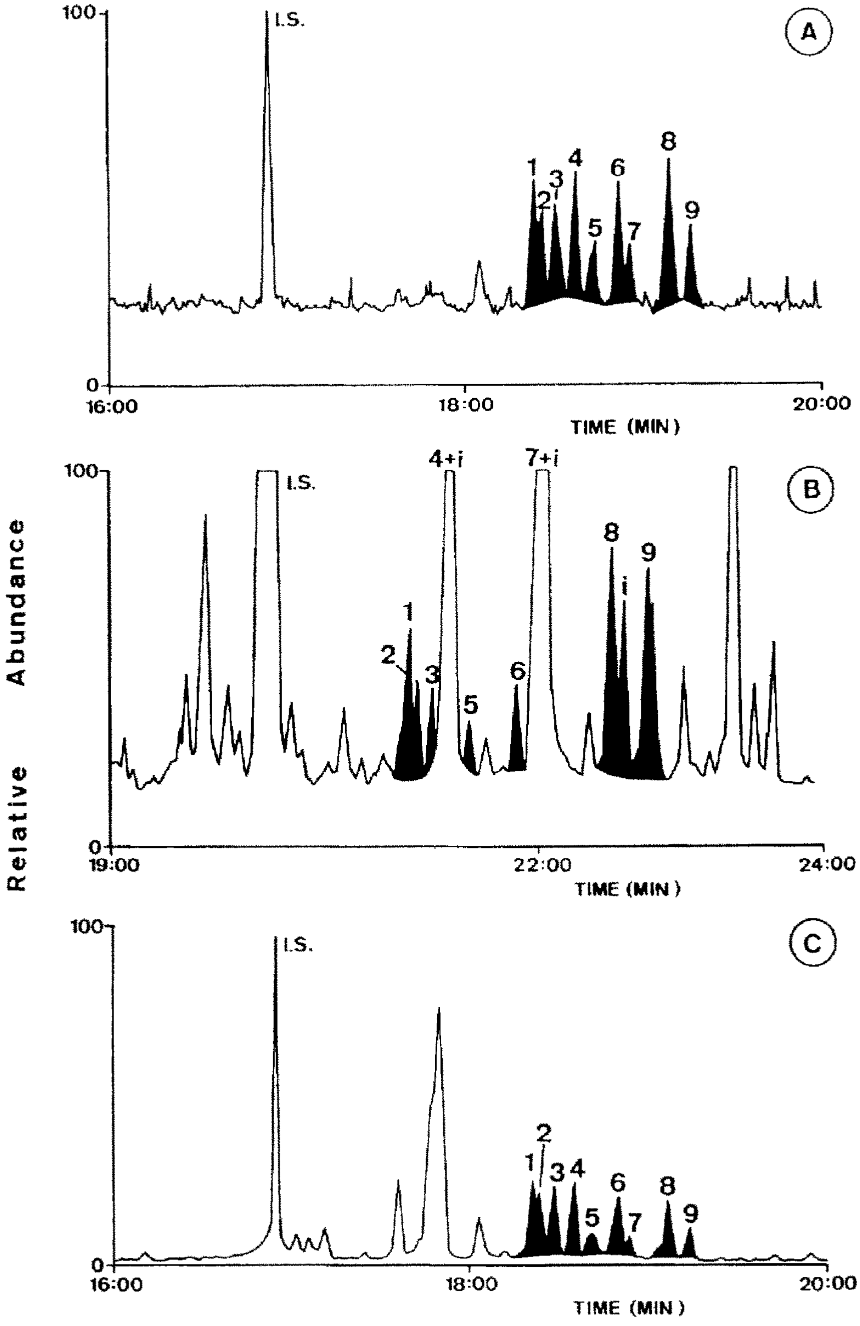

Fig. 1. (A) cGC–ECD of standard mixture of octyl-PFB (I.S., 0.5 ng) and NP-PFB derivatives (2 ng). (B) cGC–ECD of a marine sediment (50 ng/g). (C) cGC–NCI-MS with SIM of NP-PFB from the same sample. NP components are shaded and numbered on the peak apex. Interferences to NP are indicated as i.

Table 1
Intercomparison between detection systems used for the PFB derivatives of NP with cGC

Detection	Linearity	LOD		R.S.D.[b] (%) ($n=3$)
		Absolute (pg)	Relative[a] (pg/g)	
ECD[c]	10^3	20	2.9	2.2
EI-MS	10^3	10	1.4	2.1
NCI-MS	10^2	2	0.3	2.7

[a] For a 10-g (dry mass) sample.

[b] Relative standard deviation of the determination; the R.S.D. of whole analytical procedure is 10%.

[c] The LOQ is several orders of magnitude higher owing to ECD interferences.

in the NCI mode when the PFB derivatives are prepared.

Accordingly, a SIM acquisition procedure was developed using the diagnostic ions of both octyl- and nonylphenols (m/z 205 and 219). The relative LOD for total NP was in the range 0.3 pg/g ($S/N=3$) and is one order of magnitude lower than in the SIM method in the EI mode. The higher sensitivity can be accounted for by the absence of fragmentation found under the NCI conditions, allowing the use of a smaller number of ions for the NP determination. Further, the precision of the cGC–NCI-MS profiles with SIM (R.S.D. = 2.7%, $n=3$) compares favourably with those of other cCG–MS methods (Table 1). Fig. 1C illustrates the application of this procedure to the trace level determination of NP in marine sediments free of interferences, in clear contrast with the ECD trace obtained from the same sample.

3.3. Application to environmental samples

In Table 3 are listed the concentration ranges found in potential sources of coastal pollution such as rivers (Nile) and sewage effluents (JWPCP and Barcelona) and sediment samples collected offshore Barcelona. It is remarkable that the same procedure permits the determination of NP in a variety of environmental samples at different levels and the estimated relative LODs (for a 10-g sample they are 0.3 and 1.4 pg/g for the NCI and EI modes, respectively) are below the environmental levels found in coastal sediments (Table 3), which could allow their determination at remote sites.

The occurrence of NP is coastal sediments is reported here for the first time. Although their concentration in this particular matrix is at the low ng/g level, their high toxicity [19] makes their determination necessary for a better assessment of their fate in the marine environment and the possible effects on ecosystems.

4. Conclusions

The intercomparison between different detection systems (ECD, EI-MS and NCI-MS) for the detection of NP in different environmental matrices has shown that the use of PFB derivatives confers sensitivity and selectivity for the trace level determination of these compounds in a variety of environmental samples.

The main limitation of the procedure concerns the restricted applicability of the derivatization reaction to non-ethoxylated compounds. Further, the use of aqueous bases as catalysts in the derivatization reaction makes the solvent evaporation step time consuming, which can lead to some losses by volatilization. In this respect, volatile organic bases could be more suitable for the PFB derivatization reaction.

Finally, the use of cGC–NCI-MS for the determination of PFB derivatives of NP enhances the sensitivity of the cGC–ECD and cGC–EI-MS determination procedures. The highest selectivity of NCI yielded the lowest

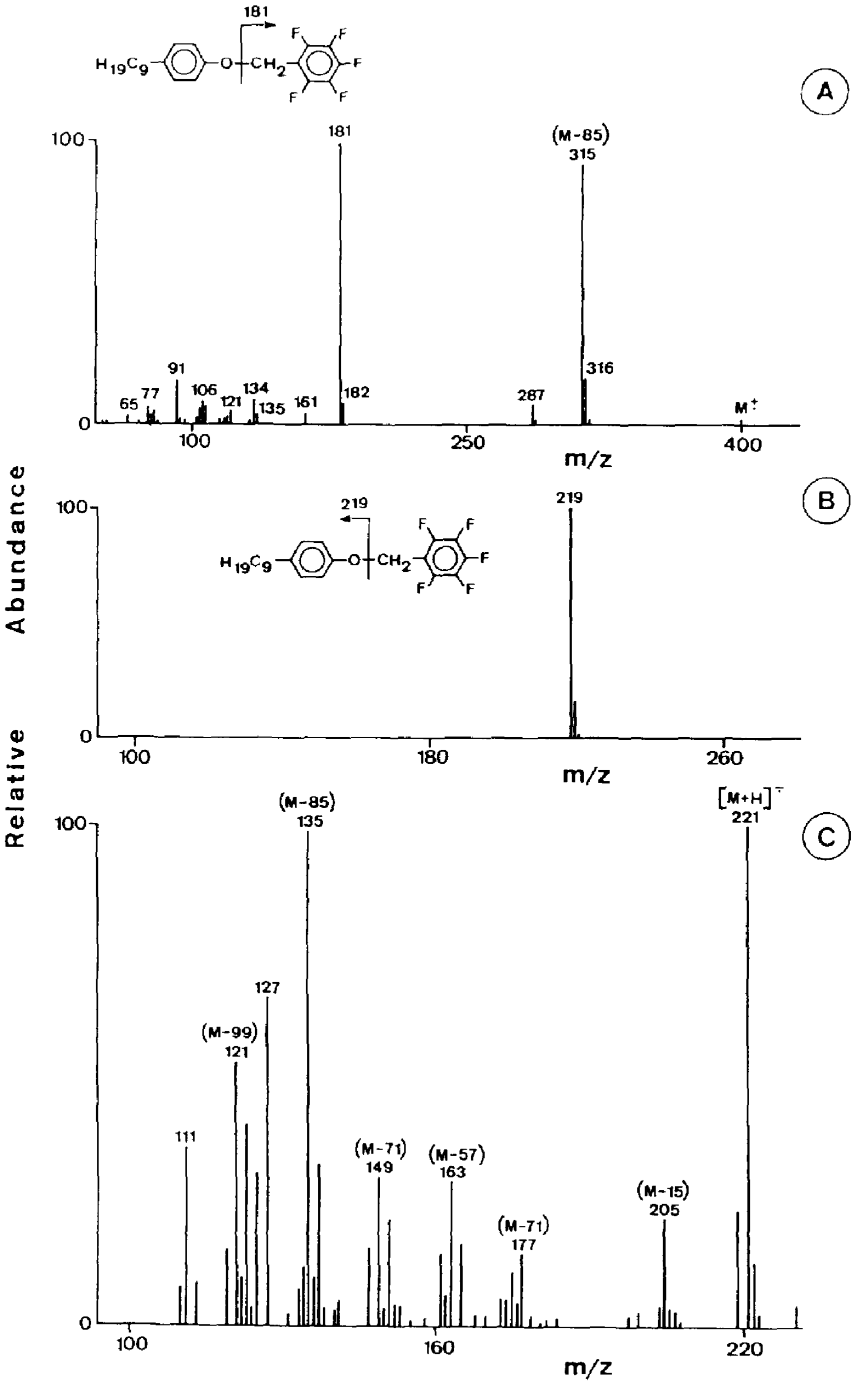

Fig. 2. Mass spectra of isomeric NP obtained: (A) cGC–EI-MS and, (B) cGC–NCI-MS of PFB derivatives and (C) cGC–NCI-MS of underivatized NP.

Table 2
Assignment of some of the diagnostic ions (m/z) of the PFB derivatives of NP used in the cGC–MS SIM acquisition programmes

Mode	M^+	$M-C_7H_2F_5$	$M-C_4H_9$	$M-C_5H_{11}$	$M-C_6H_{13}$	$M-C_7H_{15}$
EI	400	–[a]	343	329	315	301
NCI	–	219	–	–	–	–

[a] Not detected.

Table 3
Concentrations of NP in selected environmental matrices

Matrix	Sampling site	No. of samples	Concentration range
Sewage sludge[a]	Barcelona (Spain)	4	20–350 μg/g
Sewage sludge[b]	Los Angeles (USA)	1	370 μg/g
River sediment	Nile estuary (Egypt)	2	19–44 ng/g
Coastal sediment	Offshore Barcelona (Spain)	4	6–69 ng/g

[a] Primary treatment plant effluent.
[b] Primary–partially secondary effluent.

LOQ, exhibiting a similar precision between the detection systems evaluated.

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