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On-line LC-GC Coupling - A New Method for the Determination of Alkylphenols in Environmental Samples

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Online LC-GC Coupling, PTV, Large Volume Injection, Alkylphenolethoxylates, Nonylphenol, Estrogenic Effect

Abstract
This paper describes an online LC-GC coupling system that allows fractions from an LC eluant stream to be transferred to a standard GC system. A large volume sampler equipped with a flow-cell takes a fraction of the eluant and introduces it into a PTV using the solvent venting/stop-flow technique. Sample volumes between 10 and 1000 µl can be injected.

It will be demonstrated that this system permits the determination of alkylphenolethoxylates (APEOs) and their degradation products, at ultra-trace levels in water, sludge and biological matrices.

INTRODUCTION

Due to their surface active properties, alkylphenolethoxylates (eg. nonylphenolethoxylates, APEOs) act as efficient surface cleaners, and represent an important class of non-ionic surfactants [1]. They also have many industrial applications like flotation processes, paper production and in the production of pesticide formulations. In addition, APEOs have been extensively used in nearly all types of industrial and household detergents.

After introduction to the environment and subsequent treatment in sewage plants, the degradation products of APEO (eg. alkylphenols, APs) are present in the aquatic environment (Figure 1).

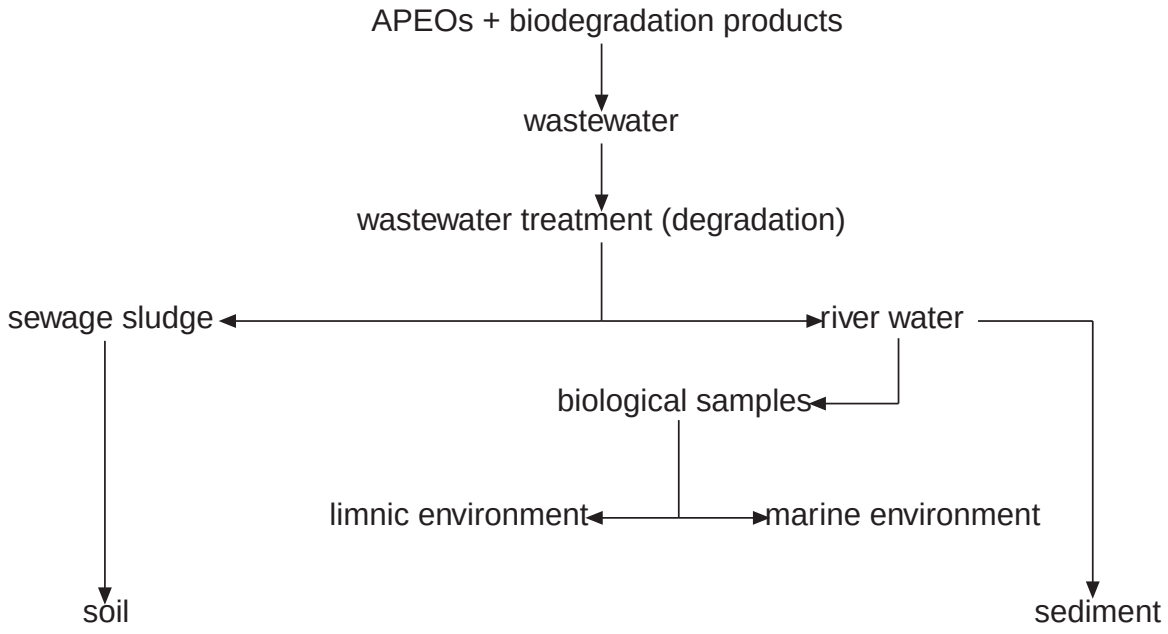

Figure 1. Environmental pathways of APEOs and their degradation products.

The degradation process is described in Figure 2:

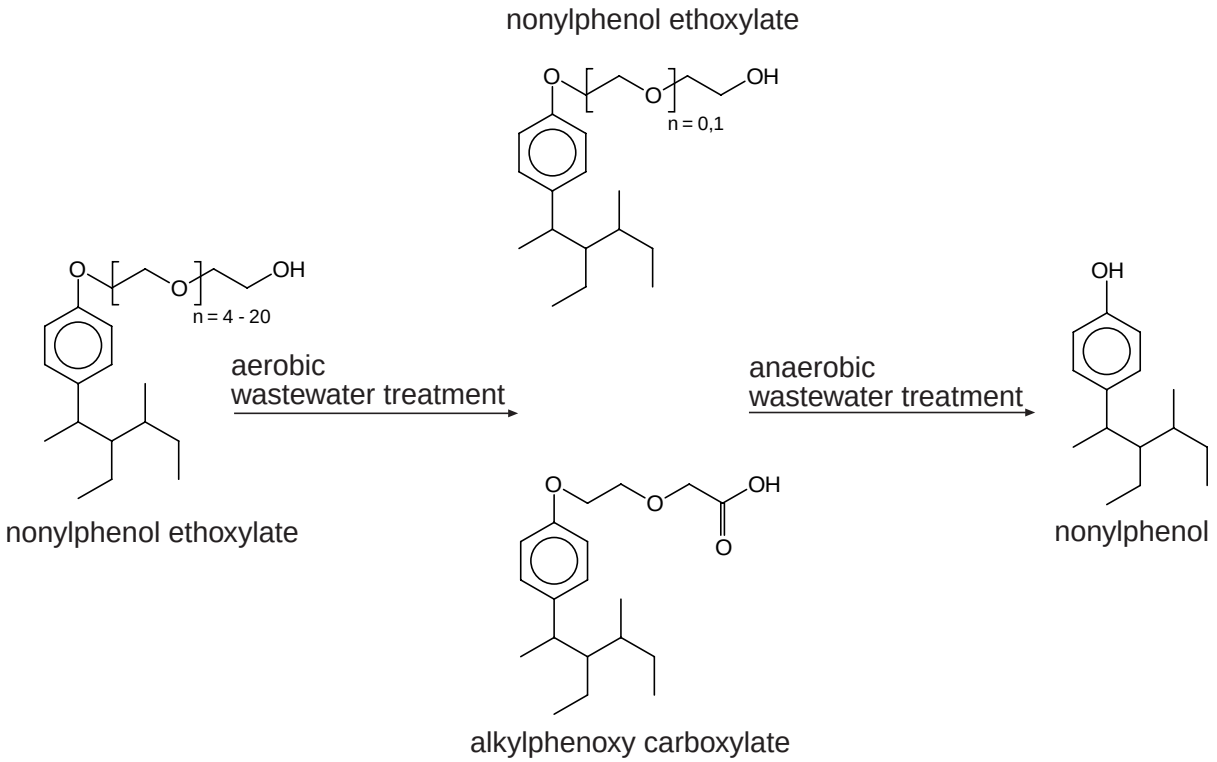

Figure 2. Degradation of APEOs in sewage plants.

The degradation products of APEOs are toxic, persistent, and due to a structural relationship to estradiol-17ß [2,3,4], estrogenically active. In particular, the para-position of the phenolic OH-group and the branched alkyl chain are supposed to be decisive parameters for the pseudo-estrogenic effect (Figure 3).

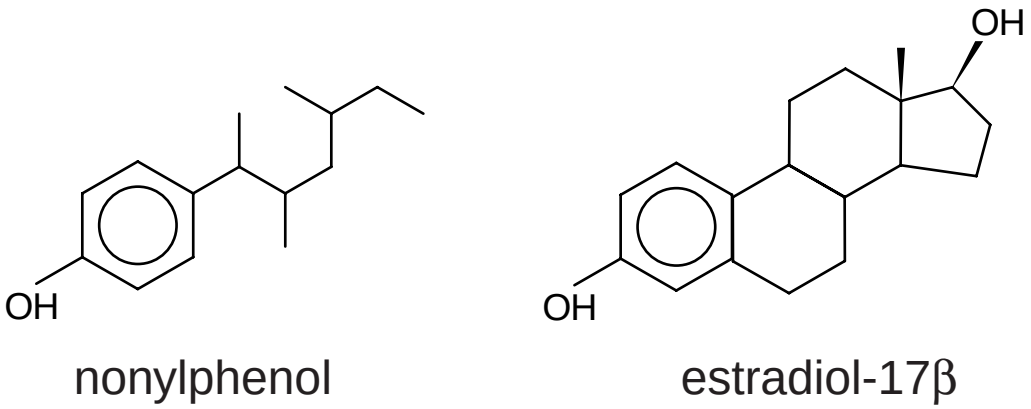

Figure 3. Structural relationship between nonylphenol and estradiol-17ß.

The effect is caused by the OH-group of the APs which is bonded to the hormone receptor replacing estradiol-17ß. Since not all AP-isomers show this pseudo-estrogenic effect, the analytical separation and differentiation of these isomers is of extreme importance.

Problems related to the determination of alkylphenols in environmental samples are; by-product and matrix interferences, low analyte concentration and losses during sample preparation. Neither LC or GC analysis alone can solve these problems. Table I shows a comparison of the advantages and disadvantages of each technique for the determination of APs.

Table I. Comparison of advantages (+) and disadvantages (-) of HPLC and GC.

	HPLC		GC
+	injection of large sample volumes	-	only small sample volumes are transferred to the capillary column
		-	normal concentration close to the detection limit
		-	problematic signal-to-noise ratio
-	separation of single isomers impossible	+	separation of the individual NP isomers
+	fractionation: separation of NP/NPEO (short chain ethoxylates)		
+	separation of free phenols		
-	internal standard and analyte coelute	+	separation of analyte/internal standard
+	selective detection of interesting compounds in the matrices by fluorescence detection	+	selective detection using PID or M

For the reasons listed above, a significant improvement in the determination of APs can be achieved through online coupling of these two different chromatographic techniques.

EXPERIMENTAL

Sample preparation and clean-up.

1. Steam distillation / liquid-liquid extraction using the VEITH-KIWUS apparatus.
2. Evaporation of the organic phase nearly to dryness.
3. Addition of 1 ml n-hexane
4. Analysis with online LC-GC.

Instrumentation. The LC eluant passes through a flow-cell, where the large volume sampler draws an eluant fraction at a pre-determined time. This fraction is then injected into the PTV, which is kept at a low temperature with the split vent open, to allow solvent venting and concentration of analytes in the PTV liner.

When the solvent is evaporated the split vent is closed and the PTV is ramped to transfer the analytes to the analytical GC-column.

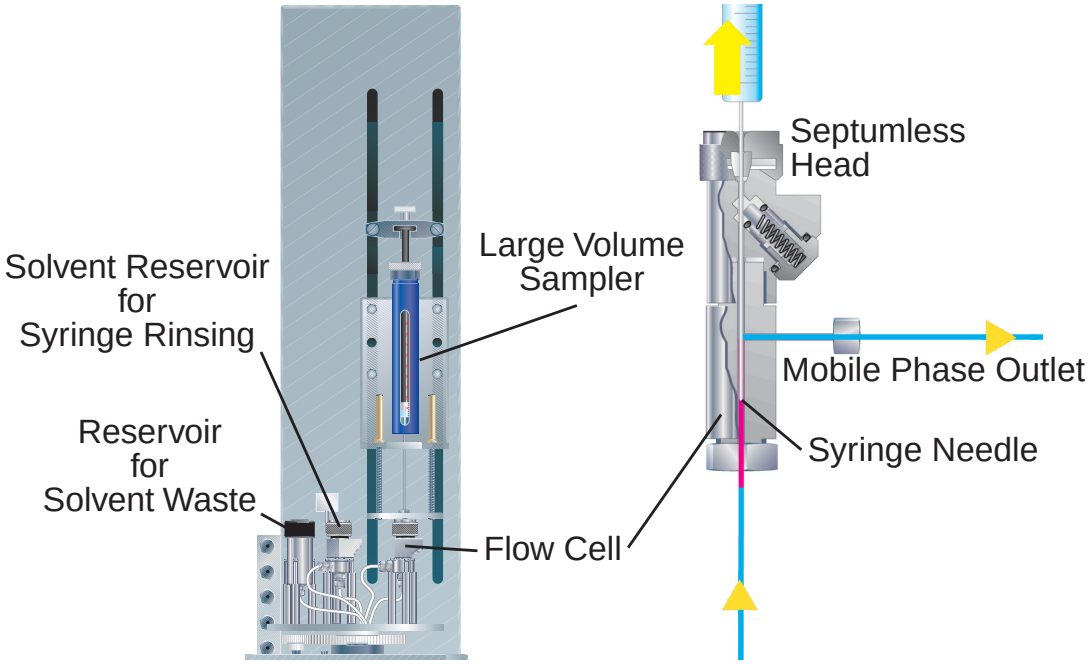

Figure 4. Schematic drawing of the LC-GC interface (left: general view, right: detail of the flow cell).

Analysis Conditions HPLC.

Injection:	20 µl, sample loop
Column:	150 mm Zorbax NH_2 x 5 µm, d_i= 4.6 mm
Solvents:	A: hexane B: hexane/2-propanol (80/20)
	flow rate 1 mL/min
Detector:	Fluorescence

Analysis Conditions GC.

PTV	0.3 min solvent vent (300 mL/min), splitless (3 min) 30°C, 10°C/s, 300°C (3 min)
Column:	30 m DB-5 (J&W), d_i= 0.32 mm, d_f= 0.25 µm
Pneumatics:	He, P_i= 40 kPa,
Oven:	40°C (2 min), 30°C/min, 130°C (2 min), 10°C/min 180°C (2 min), 8°C/min 280°C (3 min)
Detector:	FID

Results and Discussion

Each of the three examples show one LC and one GC chromatogram. The LC separation has the 4-nonylphenol isomers (4-NP) and the internal standard 4n-nonylphenol (4n-NP) elute as one peak. This peak is transferred to the GC, where the isomers and the internal standard are fully separated.

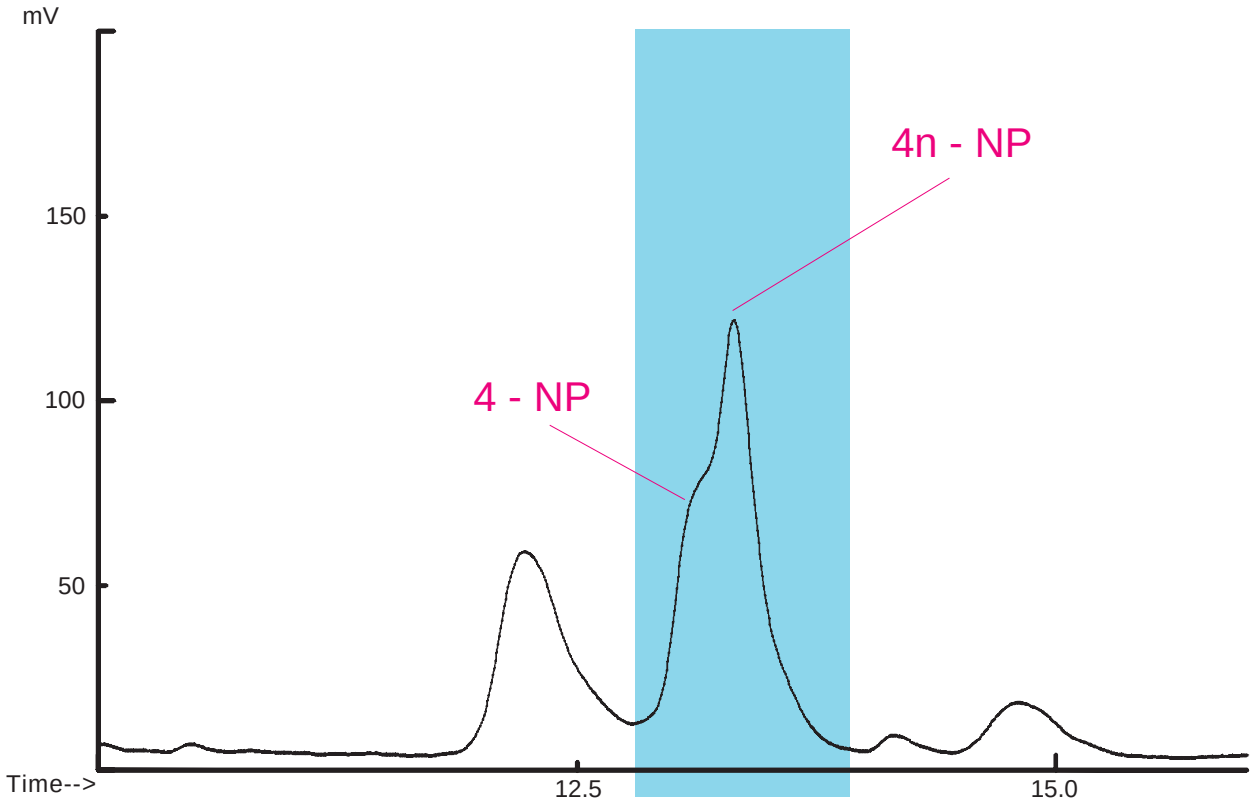

Figure 5. LC-chromatogram of a water sample from the river rhine, marked fraction transferred to GC.

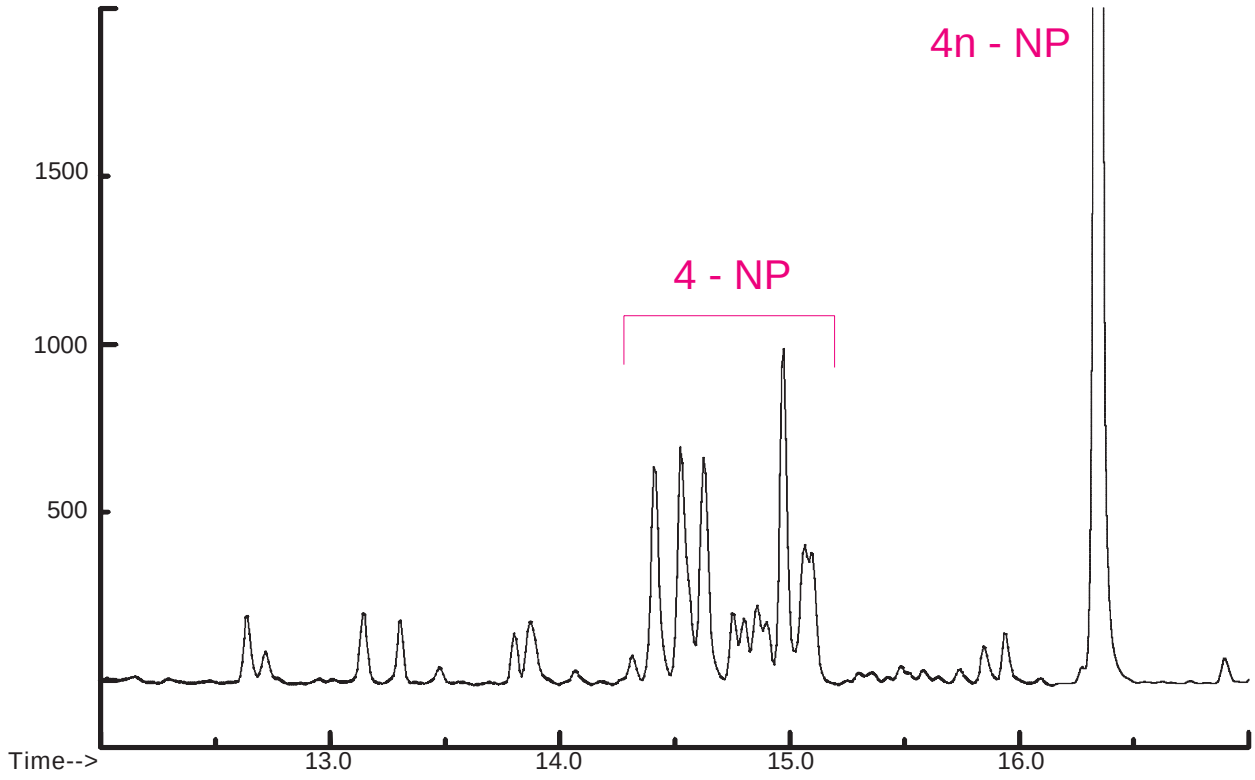

Figure 6. GC-chromatogram of the transferred LC-fraction (water sample from the river rhine), 4-NP contents= 490 ng/l.

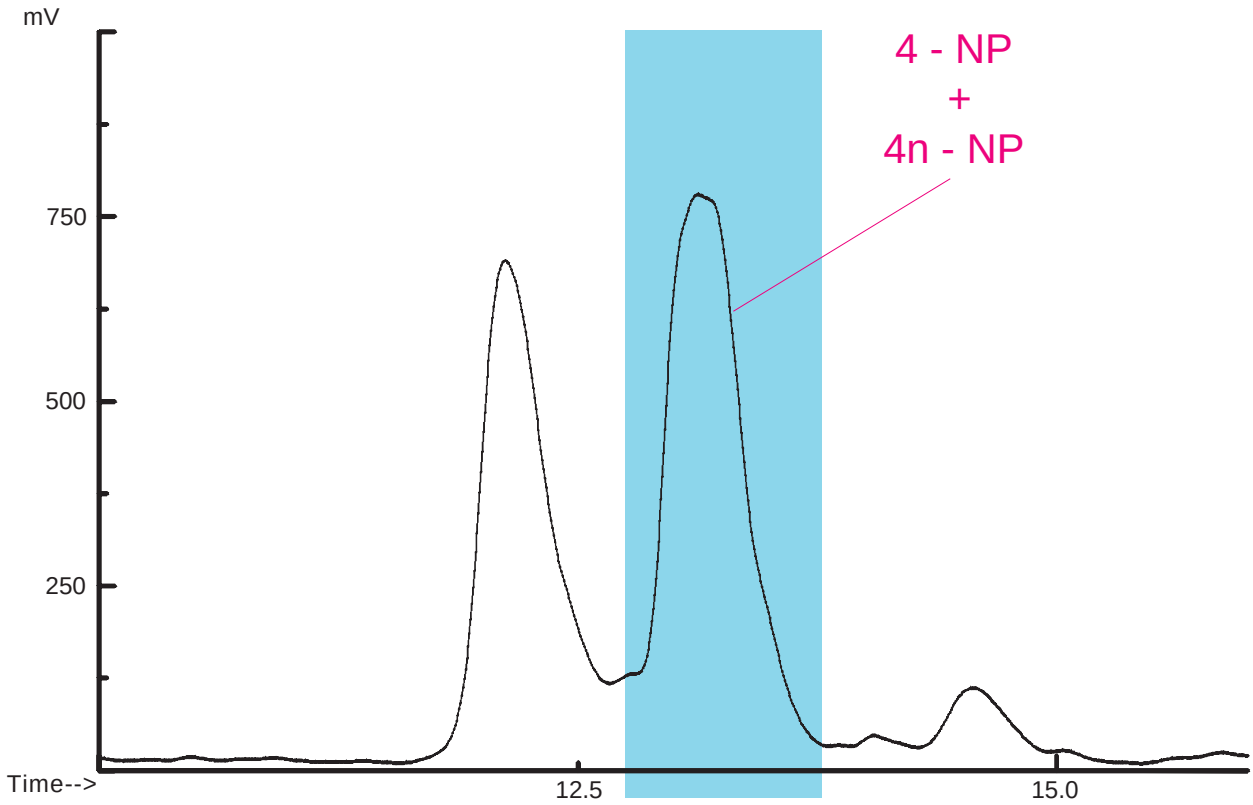

Figure 7. LC-chromatogram of sewage sludge sample, marked fraction transferred to GC.

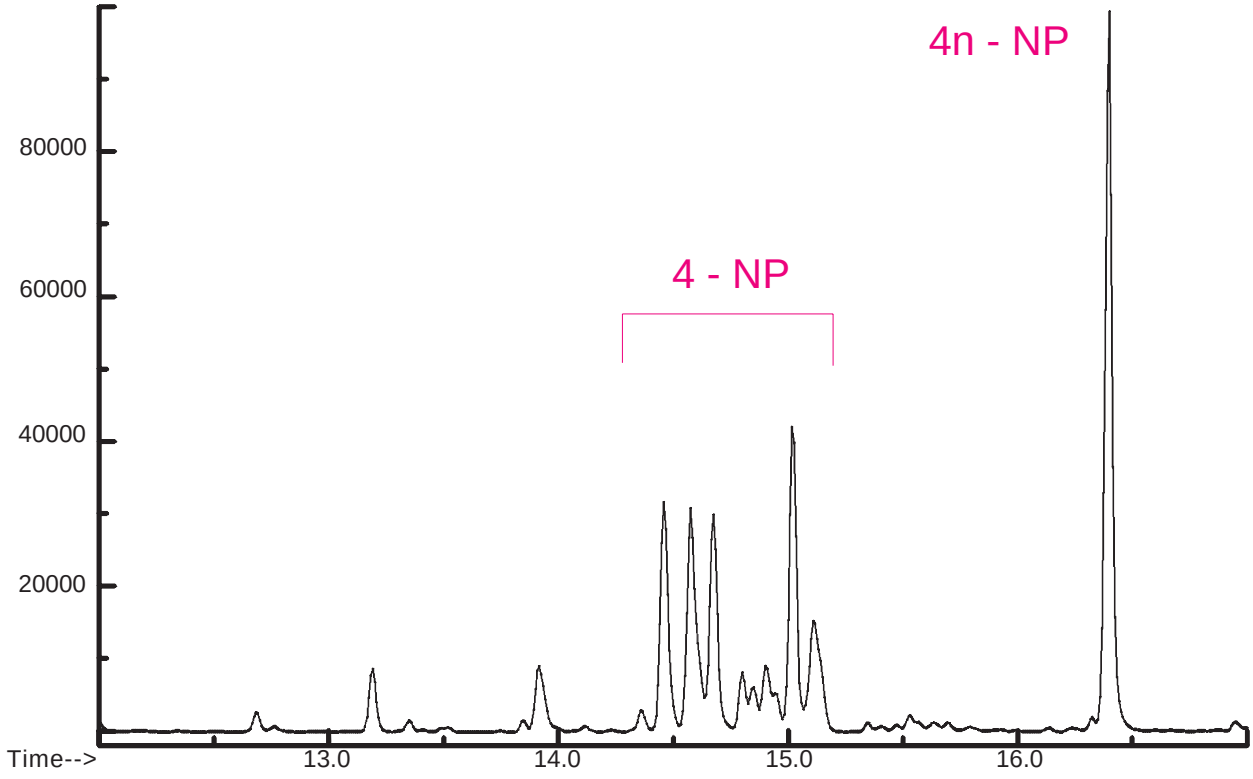

Figure 8. GC-chromatogram of the transferred LC-fraction (sewage sludge sample), 4-NP contents=4 mg/kg.

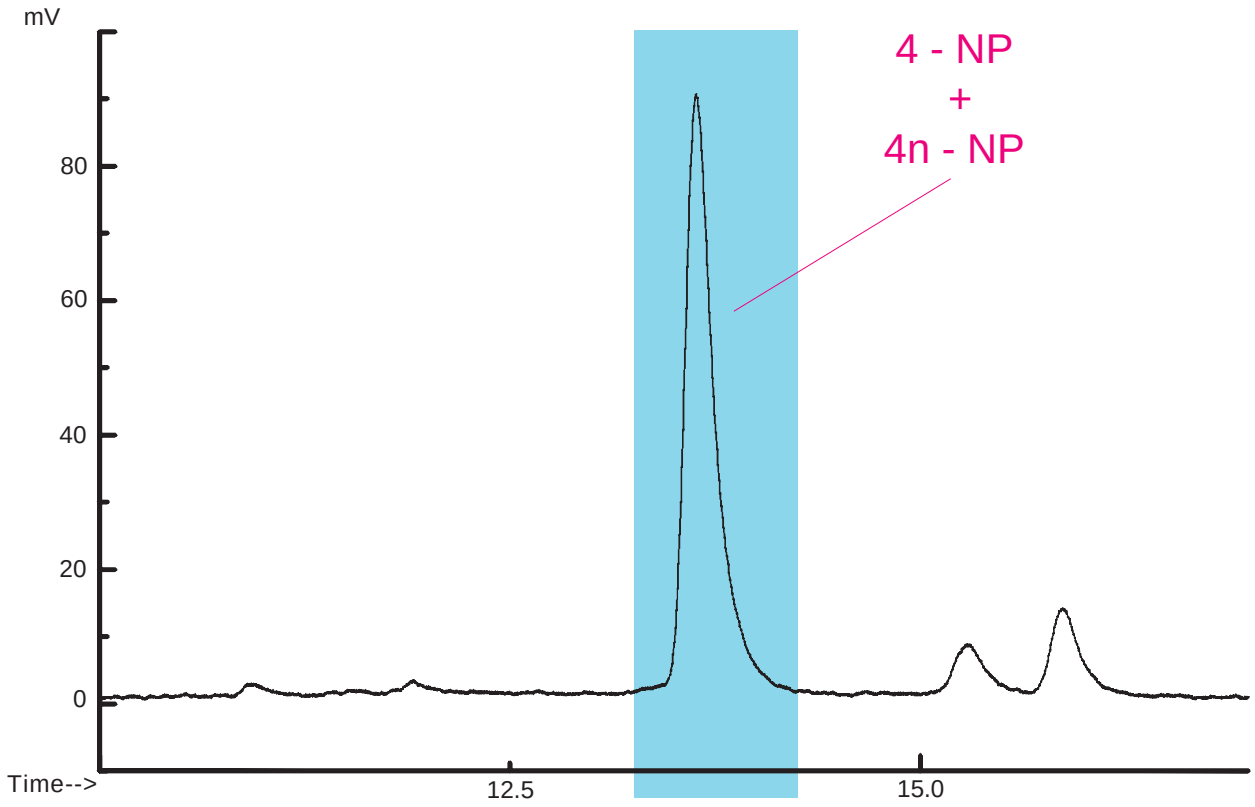

Figure 9. LC-chromatogram of a mineral water from a PET-bottle, marked fraction transferred to GC.

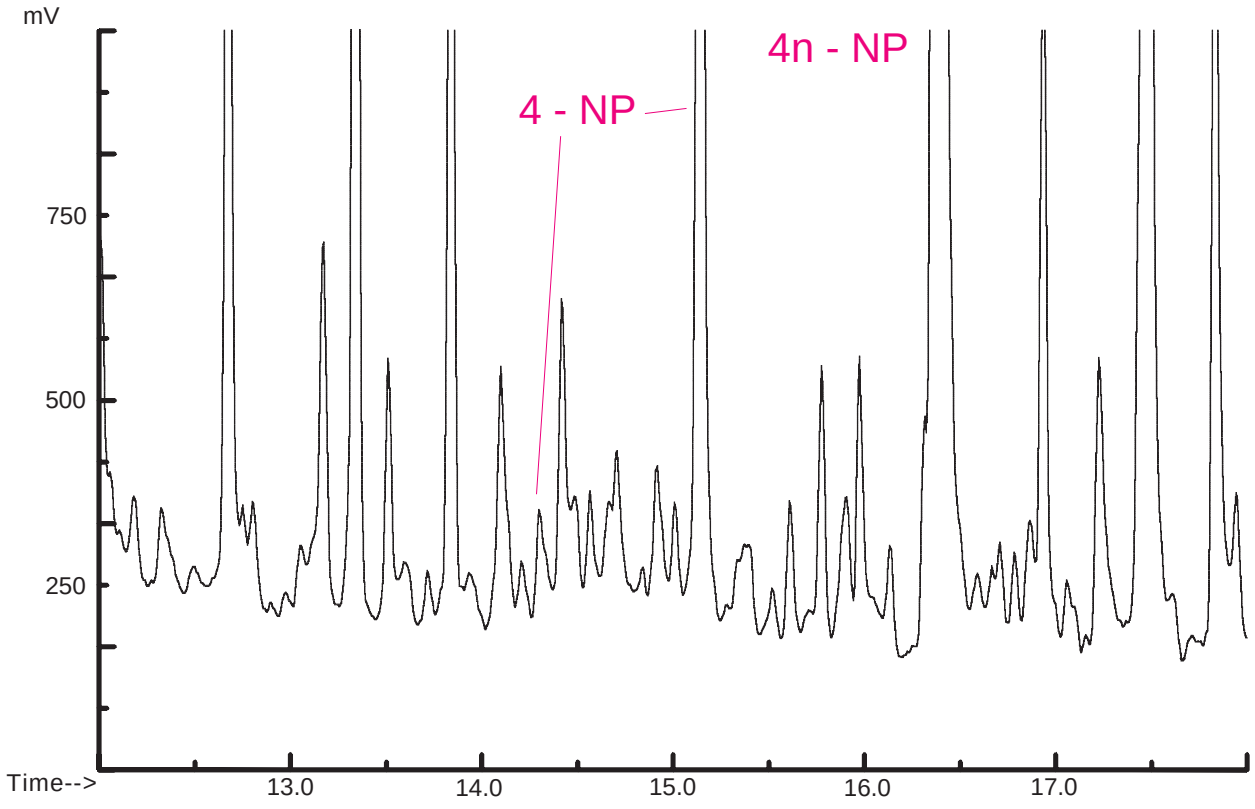

Figure 10. GC-chromatogram of the transferred LC-fraction (mineral water), 4-NP contents=125 ng/l.

Conclusion

The determination of alkylphenols in environmental samples using the described system is possible in a simple and efficient way. Online LC-GC coupling using large volume injection and PTV technology provide detection limits far below those obtained using 1 µl injection volumes, and give improved signal-to-noise ratios. Structural analysis of NP-isomers, even with PID or MS detection is now possible without loss of separation efficiency. The presented method will soon be applied to other matrices eg. common mussels, hens‘ eggs, and herring gull-eggs.

References

[1] H.J. Poremski, "Use Pattern of nonylphenolethoxylates and their application properties", in: Swedish environmental protection agency report 3907, Seminar on nonylphenolethoxylates and Nonylphenol. February 6-8, 1991

[2] W. Giger, E. Stephanou and C. Schaffner, Chemosphere 10 (1981), 1253-1263

[3] D. McLeese, V. Zitko, C. Metcalfe and D. Sergeant, Chemosphere 9 (1980), 79-82

[4] A. Soto, H. Justicia, J. Wray and C. Sonnenschein, Environmental Health Perspectives 92 (1991), 167-173

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