QUANTITATION OF NONYLPHENOLS IN AN INDUSTRIAL TEXTILE EFFLUENT USING GC-MS AND LC-NMR

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Introduction

Nonylphenols ethoxylates (NPEs) are a major class of nonionic surfactants used across the word. While their use in household detergents has diminished in recent year, the textile and pulp and paper industries are presently the major user of these surfactants [1]. Under anaerobic conditions, NPEs biodegradate in nonylphenols (NPs), which are persistent, lipophilic and more toxic than the ethoxylates to fish and other aquatic organisms. The presence of NPs in the environment has presently become of increasing concern since they have been shown to be strongly estrogenic compounds and to cause feminization of male fish downstream of sewage treatment plants, resulting in a lack of reproductive success [2]. In the past, several extraction, derivatization and chromatographic methods were developed, in order to characterize the principal inputs of these chemicals in the environment and to monitor their level in the industrial effluents. Generally, quantification of NPs was carried out by normal phase HPLC analysis using UV detection. In last few years, gas chromatography coupled to mass spectrometry (GC-MS) and liquid chromatography (LC) have been applied for the quantification of these chemicals in the environment [3]. Recently, liquid chromatography coupled to Nuclear Magnetic Resonance (NMR) revealed a powerful tool for environmental analysis, too.
In this work, quantification of NPs in an industrial textile effluent, directly and without any derivatization step, had been carried out with GC-MS and LC-NMR, providing a consistent quantification of the pollutants content and a detailed characterization of the industrial effluent necessary for an environmental protection policy.

Materials and methods

The sample was taken before the treatment plant from an effluent from a textile industry; its pH was 7 and its TOC (total organic carbon) was 330 mg/l.

GC-MS

Materials. Solid phase extraction (SPE) of the samples was performed using LiChrolutEN 200 mg cartridges (Merck, Darmstadt, Germany). Standard of NPs (mixture of chain isomers) was purchased from Aldrich (Milwaukee, Wisconsin, USA).

Sample preparation. Aqueous sample (50 ml) was extracted with SPE cartridges using ethyl acetate for the elution. The extract has been concentrated to 100 μl and the mixture analysed by GC-MS.

Instrumental analysis. GC-MS analysis was done with an HP 5890 SERIE II/HP 5971 SERIES The column was a Meridian MDN-5S column, 30 m length, 0.25 mm ID, 0.25 μm film thickness (Supelco, Bellefonte, PA, USA). The injector was at 280°C, in the splitless mode, helium head pressure was 40 kPA and the oven programmed for a temperature gradient from 50 to 280°C at 6

°C/min. The quadrupole was programmed for acquisition of masses from 40 to 500 (SCAN mode) after a solvent delay of 4 minutes. This procedure is part of a larger protocol for characterization of more complex mixtures (industrial effluents).

LC-NMR

Sample preparation. 1 liter of the aqueous sample was extracted with 4 amounts of 20 ml dichloromethane. The organic extracted was dried (sodium sulphate), filtered then evaporated to dryness in nitrogen stream. The residue was prepared for LC-NMR investigation by adding an acetonitrile/water mixture (50/50 V/V%).

Instrumental analysis. The sample was injected firstly in an analitycal HPLC column (LiChrosphere 100 RP 18, 250 x 4 mm ID, 5 μm film thickness).

For LC-NMR analysis a Bruker LC22 pump-Bruker DRX 600 Spectrometer was used recording 1H-NMR spectra.

Results and discussion

GC-MS

In this sample the most abundant components were NPs and nonylphenol monoethoxylates (NPE), which are the lightest isomers of the nonylphenol polyethoxylates series;

NPs appear in the GC chromatogram as a multiplet of peaks; in Figure 1 the traces of the main ions are shown.

NPs were identified by their mass spectra using the NBS75K and WILEY5 libraries and confirmed by comparison with the authentic standard, considering both the mass spectra and the retention times. Unfortunately the libraries were not able to recognize the single isomers, when resolved; generally they present quite different spectra with different relative abundances for the same ion according to the branching degree of the side chain (see Figure 2). The individual compounds are not commercially available.

Calibration curves, recovery tests and quantification of these analytes were based on monitoring the most abundant ions in the mass spectra of these substances, at m/z 107, 121, 135, 149 and 220. The totality of NPs measured with this method gave a concentration of 7470 μg/l in the aqueous effluent.

LC-NMR

Liquid chromatography has been able to detect the isomers of NPs as a single chromatographic signal and the groups of polyethoxylated derivatives (again as groups of chain isomers).

The chromatographic peak of NP shows at the NMR a multiplet of resonance protons between 7.1 and 7.2 ppm and a complex group of signals between 0 to 1.5 ppm (alkylic protons). The multiplets are depicted in Figure 3.

Quantitation of the sum of the isomers resulted in 5900 μg/l for the aqueous sample.

All the ethoxylated derivatives can be distinguished from the NPs by the signals of the ethoxylate chain and by the integral ratio of protons of the terminal ethoxylate group and protons of the polyethoxylate chain.

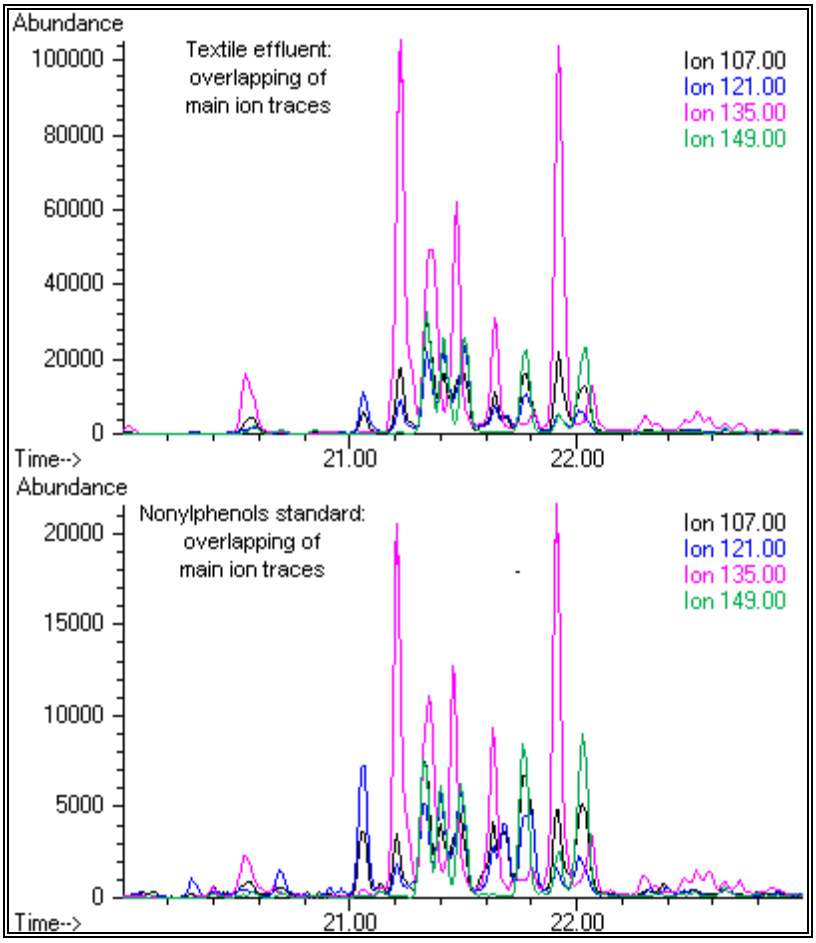

Fig 1. Chromatograms of the not derivatized isomers of nonylphenol.
Top: effluent sample Bottom: standard

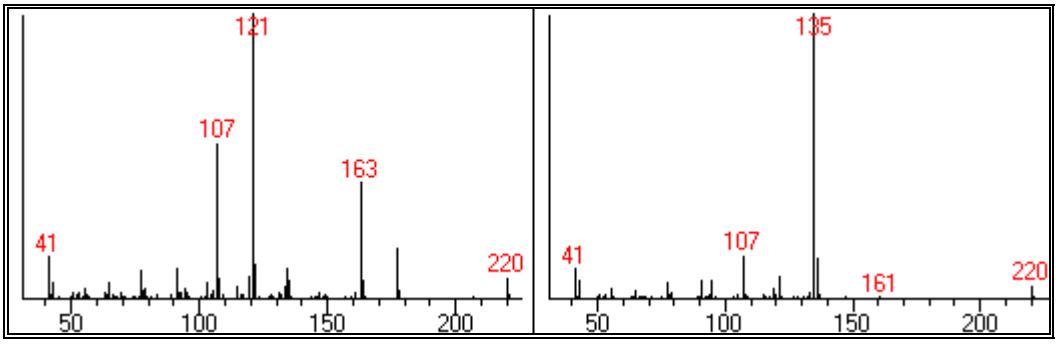

Fig. 2. Mass spectra of two isomers of nonylphenol

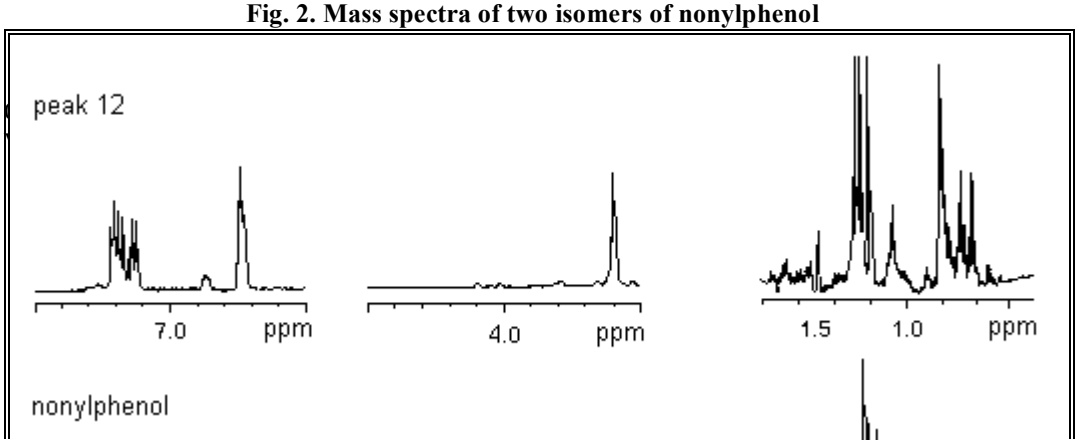

Fig 3. NMR spectra of nonylphenols. Top: real sample. Bottom:standard

The analytical procedures so far described have been developed to quantify NPs directly without derivatization. Results show good agreement. Indeed the difference is about 20 % and the methods have different extraction, chromatographic separation and detection.
The present study shows the feasability of GC-MS and LC-NMR for quantification of NPs in complex samples.
It represents one of the first applications of LC-NMR in environmental quantitative analysis. GC-MS allows to separate several isomers and a better sensitivity.
Further work is on going to check the performances of these methods and to improve separation of the single isomers.

Acknowledgement
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