HPLC-FLD determination of 4-nonylphenol and 4-tert-octylphenol in surface water samples

Ioana Cruceru · Vasile Iancu · Jana Petre · Irinel Adriana Badea · Luminita Vladescu

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Abstract A simple, sensitive and reliable HPLC-FLD method for the routine determination of 4-nonylphenol, 4-NP and 4-tert-octylphenol, 4-t-OP content in water samples was developed. The method consists in a liquid–liquid extraction of the target analytes with dichloromethane at pH 3.0–3.5 followed by the HPLC-FLD analysis of the organic extract using a Zorbax Eclipse XDB C8 column, isocratic elution with a mixed solvent acetonitrile/water 65:35, at a flow rate of 1.0 mL/min and applying a column temperature of 40°C. The method was validated and then applied with good results for the determination of 4-NP and 4-t-OP in Ialomița River water samples collected each month during 2006. The concentration levels of 4-NP and 4-t-OP vary between 0.08–0.17 μg/L with higher values of 0.24–0.37 μg/L in the summer months for 4-NP, and frequently <0.05 μg/L but also between 0.06–0.09 μg/L with higher values of 0.12–0.16 μg/L in July and August for 4-t-OP and were strongly influenced by sesonial and anthropic factors. The method was also applied on samples collected over 2 years 2007 and 2008 from urban wastewaters discharged into sewage or directly into the rivers by economic agents located in 30 Romanian towns. Good results were obtained when the method was used for analysis of effluents discharged into surface waters by 16 municipal wastewater treatment plants, during the year 2008.

Keywords 4-Nonylphenol · 4-tert-octylphenol · LLE · HPLC-FLD · Surface water

Introduction

Alkylphenol polyethoxylates (APEs) are widely used as nonionic surfactants in a large variety of industrial and commercial applications (Ying et al. 2002). These surfactants are manufactured by sequential ethylene oxide addition to a hydrophobic alkylphenol; the most common alkylphenols used for this application are 4-nonylphenol, 4-NP and 4-tert-octylphenol, 4-t-OP. Nonylphenol ethoxylates (NPEs) account for about 80–90% in the APEs big annual production (Ying 2006).

Different studies have demonstrated that APEs are not stable in the environment: they are rapidly degradated to alkylphenols—more hydrophobic and more toxic (Ying 2006)—especially nonylphenol and octylphenol, by biodegradation and photo
degradation mechanism (Zgola-Grzes’kowiak et al. 2009).

Nonylphenols, octylphenols and other alkylphenolic compounds are endocrine disruptors with high estrogenic effects in a large number of organisms, including humans (Kwack et al. 2002; Luo et al. 2005). Nonylphenol can lead to hormonal imbalance starting from a concentration of 1 \( \mu \text{g L}^{-1} \) (Schwaiger et al. 2002). They also persist in aquatic sediments and have a high tendency of bioaccumulation.

There are however many reports on alkylphenolic compounds contamination in rivers and estuaries of European and North American rivers (Jonkers et al. 2003; Vitali et al. 2004; Patrolecco et al. 2006; Cantero et al. 2006; Loss et al. 2007; Mayer et al. 2007; Cespedes et al. 2008; Zgola-Grzes’kowiak et al. 2009; Ribeiro et al. 2009; Brix et al. 2010) as well as in Asian rivers (Furuichi et al. 2004; Li et al. 2004a; Li et al. 2007; Basheer and Lee 2004; Jian et al. 2006; Ying 2006; Cheng et al. 2006; Mingzhu et al. 2007; Fu et al. 2007).

Many countries, including European Union members, have passed regulations to restrict the use of APEs in domestic applications. Due to their toxicity and harmful effects over different ecosystems, 4-NP and 4-\( t \)-OP have been identified as priority hazardous compounds and then were included in the list of 33 priority substances or groups (EC 2000). As it was reported in the literature in surface waters concentrations of nonylphenol and its short-chained ethoxylates usually range between tens of nanograms per liter and tens of micrograms per litre (Cheng et al. 2006; Loss et al. 2007).

To achieve the very low concentrations imposed by the European Directives (EC 2003) concerning environmental pollution, a number of techniques have been used for both the extraction and HPLC or GC analysis of 4-NP, 4-\( t \)-OP and other metabolites of APEs, in various environmental matrices: surface water, mineral water, marine water, wastewater influent and effluent from sewage treatment plants, river sediments, soil, biological samples. For the water analysis, the most frequently technique of isolation of nonylphenol ethoxylates, and it metabolites is the solid phase extraction (SPE), as it allows high enrichment and cleaning of the analysis (Zgola-Grzes’kowiak et al. 2009). The analytes pass through a cartridge usually containing octadecylsilica (Loyo-Rosales et al. 2003; Cespedes et al. 2008; Baugros et al. 2008), graphitized carbon black (Cheng et al. 2006), a polymeric sorbent (Loyo-Rosales et al. 2003; Basheer et al. 2005; Hoai et al. 2006; Loss et al. 2007; Li et al. 2007; Hao et al. 2008; Cespedes et al. 2008; Gadzała-Kopciuch et al. 2008; Pan and Tsa 2008) or an ion exchange resin (Cruceru et al. 2007). However, the SPE cartridges can usually be used once, but the ion exchange resins can be regenerate. The liquid–liquid phase extraction is also used in the phase of sample preparation for HPLC analysis of 4-NP, 4-\( t \)-OP and other metabolites of APEs in water samples (Li et al. 2003, 2004a, b; Zafra et al. 2003; Vitali et al. 2004; Takagai et al. 2004; Basheer and Lee 2004; Liu et al. 2004; Fu et al. 2007; Zgola-Grzes’kowiak et al. 2009).

The aim of this study was to develop a sensitive and rather simple HPLC–fluorescence detection method for routine analysis of 4-NP and 4-\( t \)-OP in different categories of water (industrial/urban wastewater and surface water).

The method was validated and then applied for the determination of 4-NP and 4-\( t \)-OP in Ialomita River water samples collected each month during 2006 year. The method was also applied on samples collected over 2 years 2007 and 2008 on samples of urban wastewaters discharged into sewage or directly into the rivers by different economic agents located in 30 Romanian towns. Good results were obtained when the method was used on effluents discharged into surface waters by 16 municipal wastewater treatment plants, during the year 2008.

**Experimental**

**Chemicals and reagents**

_Standards:_ 4-NP Pestanal, Reference Material, purity grade 99.9% from Riedel-de-Haen (Seelze, Germany); 4-\( t \)-OP Reference Material, purity grade 99.9% from Supelco (USA); nonylphenol polyethoxylates with different lengths of ethoxy chain: NP4 polyethoxylate (97%) and NP5 polyethoxylate (97%) all from Aldrich (Milwaukee, USA).