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OCCURRENCE OF BISPHENOL A AND ITS MAJOR METABOLITE 4-HYDROXYACETOPHENONE IN SOME MUNICIPAL WASTEWATER TREATMENT PLANTS IN ROMANIA

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Introduction

Contamination of wastewater from wastewater treatment plants (WWTP) and their discharge into the emissaries is one of the main environmental problems nowadays, due to micro pollutants that are present in concentrations in the order of ng/L or µg/L. A significant part of these contaminants end up in the environment either not transformed or as metabolites contributing to environmental pollution, with a negative impact on human health and wildlife. Among this type of micro pollutants, Bisphenol A (BPA) is an endocrine disruptor with high estrogenic activity and with increased presence in the environment. Similar to other emerging contaminants, Bisphenol A, well known for its endocrine disruptor properties, may undergo different transformations depending on the environment or the technological treatment processes sometimes producing transformation products or metabolites that can have a different ecotoxicological behaviour and profile. The most common metabolite of BPA is 4-hydroxy-acetophenone. In this study a new LC-MS/MS method was developed and optimized for detection of BPA and BPA metabolite, 4-hydroxyacephenone in wastewater samples which, after treatment, are discharged in emissaries.

Materials and methods

Standards of Bisphenol A (BPA), 4-hydroxyacetophenone and isotopically labelled BPA ($^{13}C_{12}$-BPA) which was used as internal standard were purchased from Sigma-Aldrich. Methanol and acetonitrile of HPLC-grade purity were acquired from Merck and Acetic Acid (AA) from Sigma-Aldrich. Analyses were performed using an Agilent 1260 series LC system (Waldbronn, Germany) coupled with an Agilent 6410B triple-quadrupole mass spectrometer with electrospray ionization source (ESI).

Results and conclusions

In order to obtain a good separation and lowest possible quantitation limit (LOQ), all liquid chromatographic and mass spectrometric parameters were optimized (Table 1). The values that generated the highest analytical signal were chosen.

Table 1. Liquid chromatographic and mass spectrometric parameters

LC Parameters	MS Parameters
Chromatographic column: Luna C18 Column temperature: 35ºC Injection colum: 5µL Mobile phase: Aq. 0.01% AA/ MeOH 35 / 65 (v/v) Flow rate: 0.15 mL/min Sample solvent: Aq 0.01% AA/ MeOH 50 / 50 (v/v) Elution type: isocratic Run-time: 7 min	ESI ionization source: negative Gas temperature: 300ºC Gas Flow: 6L/min Nebulizer pressure: 40 psi

To account for its performance, the developed SPE-LC-MS/MS method was validated. Analyte recovery values were 94% for BPA and 73% for 4-Hy-ACF due to surrogate internal standard correction. Overall method LOQs were 4.8 ng/L for BPA and 2.2 ng/L for 4-Hy-ACF.

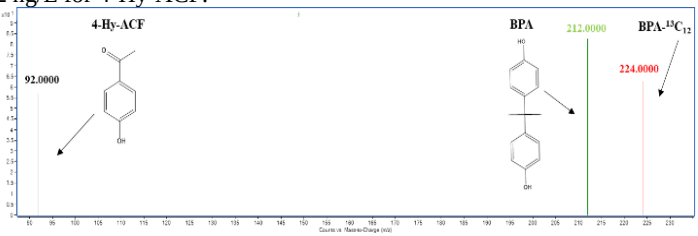

Figure 1. MS spectra of a 50 µg/L standard solution spiked into an effluent matrix free of analytes.

The developed method was used to determine the contamination levels of effluents from wastewater treatment plants with BPA and the metabolite 4-Hy-ACF. The waste water samples consisted of effluents of the WWTP from Braila (E1-E4), Focsani (E5-E8) and Targu Jiu (E9-E12) collected on different days.

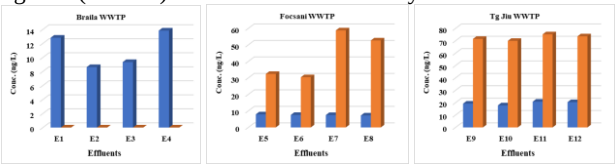

Figure 2. Determined concentrations of BPA and 4-Hy-ACF in the WWTP analysed effluents

From all three WWTP, only the effluents collected from Braila WWTP doesn't contained both of the investigated analytes, being detected only the 4-Hy-ACF in concentration between 8.62 si 13.82 ng/L. For samples collected from Focsani and Targu Jiu WWTP, the concentration values determinated for BPA were situated between 30.4 - 58.8 ng/L and 70 - 75 ng/L respectively, while the 4-Hy-ACF concentration values were around 7 ng/L and 20 ng/L respectively.

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