MATRIX SOLID-PHASE DISPERSION COMBINED TO LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY FOR THE DETERMINATION OF PARABENS AND TRICLOSAN IN MOLLUSKS

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The aim of this work was the development of a method for the extraction and determination of triclosan and seven parabens (including methyl- (MeP), ethyl- (EtP), propyl- (*i,n*-PrP), butyl- (*i,n*-BuP), benzylparaben (BzP) and two chlorinated derivatives) in mollusks samples. Matrix solid-phase dispersion (MSPD) was employed as sample preparation technique and liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) as separation and determination systems. Parabens and triclosan are widely used as preservative and antimicrobial in cosmetics, pharmaceutical and processed food and regulated in European Union countries under several directives which establish for cosmetics: for MeP and EtP 0.4 % for a single ester an 0.8 % for the mixture of esters and for *n*-PrP and *n*-BuP between 0.14 and 0.8 % [1], and between 0.2 and 0.3 % for triclosan [2]. Thus, they can reach the aqueous environment, including the sea, and be bioaccumulated by mollusks.

Extraction was performed by MSPD ought to its simplicity, low volume of solvent and quantity of sample required, low global price and integration of extraction and clean-up into a single step. Different solid supports, clean-up sorbents and solvents were tested by means of a Box-Behnken experimental design to optimize their respective amounts. Under optimal conditions in the final method, 0.5 g of freeze-dried mollusk was dispersed with 1.2 g of precleaned silica and transferred to a polypropylene syringe containing 3 g of C18 as clean-up sorbent, followed by the elution of analytes from the matrix with 10 mL of acetonitrile. Validation of the method was evaluated by the study of linearity, precision in terms of relative standard deviation (RSD), accuracy in terms of recoveries and limits of detection and quantification (LODs and LOQs, respectively). Satisfactory linearity (R^2>0.999 %), RSD values (bellow 27 %), recoveries between 71 and 117 % (except for dichlorinated derivative ~ 44 %), and LODs and LOQs levels lower than 0.43 and 1.43 ng g^{-1} dry weight, respectively, were achieved. Finally, the method was applied to different mollusk samples (mussels, clams and cockles). The most toxicological parabens, chlorinated derivatives and BzP, and triclosan were not detected in any of the samples. However, in agreement with the production rates and literature, the most applied parabens (MeP, EtP, *n*-PrP and *n*-BuP) were detected in all samples. MeP presents the highest concentrations, up to 7 ng g^{-1} dry weight, followed by EtP with levels between 0.09 and 0.3 ng g^{-1} dry weight.

ACKNOWLEDGEMENTS: Spanish Ministry of Economy and Competitiveness (Ministerio de Economía y Competitividad) and FEDER funds: project no. CTQ2009-08377 and CTM2014-56628-C3-2-R, and FPI grant (E. Villaverde de Sáa). Finally, we are indebted to INTECMAR for kindly providing of mollusks samples.

[1] Commission Regulation EU No 1004/2014 of 18 September 2014 amending Annex V to Regulation (EC) No 1223/2009 of the European Parliament and of the Council on cosmetic products, Official Journal of the European Union L282, 26/09/2014, p. 5-8.

[2] Commission Regulation EU No 358/2014 of 9 April 2014 amending Annexes II and V to Regulation (EC) No 1223/2009 of the European Parliament and of the Council on cosmetic products, Official Journal of the European Union L107, 10/04/2014, p. 5-9.