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Development of an innovative and "green" stir bar sorptive extraction-thermal desorption-gas chromatography-tandem mass spectrometry method for polycyclic aromatic hydrocarbons quantification in marine biota samples

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Abstract:

There is a growing awareness of the need to reduce the negative impact of chemical analyses on the environment and to develop new eco-friendly and sustainable analytical methods without compromising performance. In this study, we developed a "green" analytical method enabling the accurate and simultaneous routine analysis of 21 polycyclic aromatic hydrocarbons (PAHs) in reduced quantities (100 mg and 1g wet weight (WW)) of marine biota samples (fish muscle, mussel and oyster tissues) using alkaline digestion combined with stir bar sorptive extraction-thermal desorption-gas chromatography-tandem mass spectrometry (SBSE-GC-MS/MS). The innovative method provides good selectivity and specificity for most compounds. In 1g WW samples, limits of quantification (LOQs) ranged from 1 to 10 µg/kg WW in fish muscle and from 0.5 to 10 µg/kg WW in mussel tissue. The method enables most analytes to be quantified below the restrictive limits established by the European Commission (2 and 10 µg/kg WW in fish muscle and bivalve mollusc, respectively). Higher LOQs were obtained in 100 mg WW samples ranging from 1 to 50 µg/kg WW . Recovery and linearity were assessed for all analytes. The results were satisfactory for most compounds with recoveries ranging from 94 to 117% in 1g WW mussel samples at spike concentration of 10 ng/g WW with standard deviation not exceeding 12%. However, results confirmed that the SBSE efficiency is affected by the complexity of biological matrices, especially for high molecular weight compounds in lipid-rich mussel tissue. Because of the matrix effects, matrix-matched calibrations were carried out. Validation was performed using the standard reference material 1974c with recovery ranging from 71 to 119% except for naphthalene, anthracene and benzo(e)pyrene that were therefore not validated. Overall, the developed method meets analytical validation criteria for most compounds. Thanks to the combination of alkaline digestion and SBSE, which greatly simplifies sample treatment and limits solvent use to ethanol, the developed method followed most green analytical chemistry principles.

Keywords: PAHs, SBSE-GC-MS/MS, marine biota, pollution monitoring, green analytical chemistry

1. Introduction:

Polycyclic aromatic hydrocarbons (PAHs) are highly toxic pollutants commonly found in the marine environment. They derive mostly from oil and partial combustion of organic substances and are discharged in huge amounts into the marine environment via transfer from the atmosphere, surface runoff, industrial and urban effluents or due to accidental pollution. Due to their hydrophobic nature, when discharged in water, they tend to adsorb on lipid-rich particles and bio-accumulate in aquatic organisms such as fish and molluscs after filtration and/or ingestion of contaminated particles [1], and then represent a serious environmental issue. Sixteen PAHs are included in the priority pollutants list of the US Environmental Protection Agency (US EPA), fifteen are classed as potentially genotoxic and carcinogenic to humans by the Scientific Committee on Food of the European Union [2] and thanks to a recent amendment of the European Water Framework Directive [3], environmental quality standards (EQS) have been defined for eight compounds in water, which have been extended to biota for five compounds [4]. In this context, chemical data are required in case of chronic or accidental pollution to assess either the ecotoxicological impact of PAH