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BOOK OF ABSTRACTS

Development of a DMSPE method using graphene oxide–silica functionalized with 1 vinyl 3 hexylimidazolium octane sulfonate for the determination of tebuconazole in orange juice

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Tebuconazole (TBZ) is a widely used fungicide with high efficacy and low toxicity [1], but it can pose health risks due to environmental accumulation and persistent residues in food. TBZ is authorized for use in Europe on certain citrus fruits, including oranges, which are highly nutritious. Orange juice is widely consumed in Spain, a leading producer both globally and within Europe [2]. Considering that TBZ is a predominantly hydrophobic compound (log K_ow = 3.7), Graphene oxide–silica functionalized with 1 vinyl 3 hexylimidazolium octane sulfonate (GO@Sil-[VHIm]+OS-) was evaluated for dispersive solid-phase microextraction (DSPME), with subsequent determination by LC-MS/MS. GO@Sil-[VHIm]+OS- showed superior sorption compared to other synthesized sorbents with different anions (PF6-, Br-) and to conventional sorbents (Strata-X and C8). Consequently, it was selected for further DSPME method optimization. The DSPME protocol, optimized by univariate and multivariate approaches, involved adding 5 mg of sorbent to 1 mL of orange juice (pH adjusted to 9 with 0.1 M NaOH), followed by ultrasonication (10 min) for extraction. After centrifugation (10 min, 14,000 rpm) and discarding the supernatant, desorption was performed with CPME:MeOH (46.43:53.57, v/v) under ultrasonication and centrifugation under the same previous conditions. The supernatant was filtered, dried, and reconstituted in 100 µL of mobile phase for LC-MS/MS analysis. The method was validated for orange juice following EU SANTE/11312/2021 guidelines. It provided satisfactory separation and detection, with linearity from 50–900 ng mL^{-1} (r^2 = 0.9972), RSDs below 15%, and recoveries of 105.7%, 117.1%, and 98% at 300, 600, and 900 ng mL^{-1}, respectively. LOD and LOQ were 0.06 and 0.19 ng mL^{-1}. The matrix effect was –15.3%, confirming method applicability. Sorbent reusability was demonstrated over five consecutive extractions at 100 ng mL^{-1}, with recoveries >60% and inter-extraction RSD of 13.1%. Eight natural orange juice samples purchased in Madrid were stored at –5 °C until analysis. TBZ was detected in two samples at 12.0 and 12.5 ng mL^{-1}, corresponding to 1.33% and 1.38% of the European MRL (900 ng mL^{-1}). These results confirm compliance with regulations and underscore the need for sensitive analytical methods to monitor low pesticide levels in beverages. Sustainability assessments using AGREEprep and BAGI yielded favorable scores (0.57 and 60.0, respectively), highlighting the environmental performance of the method. Overall, this study presents a promising and eco-friendly analytical approach for monitoring TBZ in orange juice.

REFERENCES
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