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# OPTIMIZATION OF A RAPID AND GREEN ANALYTICAL METHOD FOR THE DETERMINATION OF PERFLUOROALKYL ACIDS IN FRUITS IRRIGATED WITH RECLAIMED WASTEWATER

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Agriculture is typically characterized by a high-water demand, since about 70% of worldwide freshwater (FW) withdrawals is used for agricultural irrigation [1]. On the other hand, limited FW availability is a problem of increasing concern and the reuse of treated wastewater (TWW) for irrigation could be an efficient tool of reducing water shortage. However, the TWW reuse is currently far to be fully realized, due to several barriers, such as potential risks for the environment and the human health in the reuse of wastewater improperly treated, due to residual concentrations of priority and/or emerging organic micropollutants (e.g. perfluorinated compounds) [2]. In this regard, fruits characterized by different chemical composition and water percentage may represent interesting models for this kind of investigations. Accordingly, strawberry and olive have been selected.
Based on the aforementioned considerations, this work focused on the development of an analytical method for the identification and determination of selected linear perfluoroalkyl acids (PFAAs) in strawberries and olives fruits obtained by irrigation with TWWs. The method is based on the QuEChERS approach, which include the liquid/liquid partition of analytes between salty water and acetonitrile [3], combined with dispersive solid phase extraction (d-SPE) as clean-up step, followed by liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) analysis. Different d-SPE sorbent phase – i.e. octdecylsilica (C18), primary secondary amine (PSA) and graphitized carbon black (GCB) – have been tested in order to evaluate the best compromise between matrix effect (ME%) and analyte recoveries. For strawberry, the d-SPE clean-up step was found unnecessary, since even in absence of the extract purification, signal suppressions or enhancements lower than 20% were observed with the sole exception of perfluorohexanesulphonic acid (PFHxS), which showed a signal suppression of about 35%. Recoveries included in the range of 83-111% were achieved. Method quantification limits were in between 3.9 and 477 *pg* $g^{-1}$ d.w. Hence, the method herein proposed represented a general improvement in terms of simplicity and total analysis time, as well as sensitivity in comparison with previously published methods focusing on the determination of PFAAs in strawberry and other small fruits [4-8].
Conversely, for olives the use of the d-SPE clean-up step was mandatory, due to the high amount of co-extracted fatty matrix components that influence the chromatographic behavior of target analytes, as well as overall performances of the analytical method. Among

the d-SPE phases investigated, C18 and GCB provided the best results, whereas PSA gave rise to retention of target analytes due to its character of anion exchanger. The d-SPE clean-up allowed for obtaining extracts that can be analyzed with reproducible results and without problems of method robustness. However, the absolute value of matrix effect remained high, thus making necessary the matrix matched calibration approach and/or the use of spiking procedure with labelled PFAAs for the analysis of real samples. More in detail, a suppressive ME% was observed for the investigated PFAAs with the only exceptions of perfluorobutanesulphonic acid (PFBuS) and perfluoropentanoic acid (PFPeA), which were amplified. High recovery (i.e. > 75%) and sensitivity (tens-hundreds of $pg\ g^{-1}$ d.w.) have been obtained also for olives, indicating that the QuEChERS procedure is suitable for the analysis of PFAAs in fruits characterized by very different chemical composition.

**References**

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