Journal of Chromatography A 1621 (2020) 461038

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Optimization and validation of a method based on QuEChERS extraction and liquid chromatographic–tandem mass spectrometric analysis for the determination of perfluoroalkyl acids in strawberry and olive fruits, as model crops with different matrix characteristics

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ARTICLE INFO

Article history:
Received 27 January 2020
Revised 5 March 2020
Accepted 7 March 2020
Available online 14 March 2020

Keywords:
LC–MS/MS
d-SPE
Perfluorinated compounds
Fruit safety
Organic micropollutants
Irrigation by wastewater

ABSTRACT

A QuEChERS method was optimized and validated for the LC–MS/MS analysis of perfluoro-*n*-pentanoic acid (PFPeA), perfluoro-1-butanesulfonic acid (PFBuS), perfluoro-*n*-hexanoic acid (PFHxA), perfluoro-*n*-heptanoic acid (PFHpA), perfluoro-1-hexanesulfonic acid (PFHxS), perfluoro-*n*-octanoic acid (PFOA), perfluoro-*n*-nonanoic acid (PFNA), perfluoro-1-octanesulfonic acid (PFOS) and perfluoro-*n*-decanoic acid (PFDA) in freeze-dried strawberry and olive, as model fruits characterized by very different chemical compositions. The method was evaluated for apparent recovery, intra-day and inter-day precision, matrix effect and recovery. The method optimized for strawberry provided for most compounds absolute values of matrix effect ($|ME\%| \leq 11\%$, except for PFHxA, which showed a signal suppression of 22%. The extraction efficiency was tested at the spike levels 500–5000 pg/g d.w. for PFPeA, PFBuS, and PFHxA, and 100–1000 pg/g d.w. for the other target analytes, evidencing as a whole recoveries in the range of 65–89%. For olive fruits, due to their high fat content, an ultrasound-assisted extraction was necessary to obtain an efficient sample disgregation so as to increase the extraction yield and its precision. Moreover, a d-SPE clean-up with GCB allowed to achieve $|ME\%| \leq 8\%$ (except for PFBuS, which showed a signal enhancement of 19%) and recoveries calculated at the aforementioned spike levels were in the range 75–97%. The two methods provided very good linearity ($R^2 \geq 0.9984$) from 10,000 pg/g down to compound specific quantification limits, which were included in the ranges of 2.9–393 pg/g and 2.6–127 pg/g for strawberry and olive fruit, respectively. The methods were applied to the analysis of PFAAs in strawberry and olive fruits commercially available in two Italian supermarkets, as well as obtained under irrigation with various treated wastewaters (TWWs), evidencing in both cases a higher PFAAs occurrence in olives than in strawberry. However, PFAAs concentrations determined in the investigated fruit matrixes were quite low, being their sum 1.9 ng/g d.w. in the worst case (i.e. olive fruits grown under irrigation with TWWs).

1. Introduction

Food safety is a very important and topical issue, since foodstuffs can be contaminated through different ways, alongside production and distribution stages [1]. This contamination does not only concern chemical substances intentionally used within the food production chain, such as pesticides in agriculture. In fact, foodstuffs can come into contact with various environmental micropollutants before human consumption [2].

Among organic micropollutants, those most recently identified in environmental matrices and/or recognized as environmentally hazardous, are obviously of major concern in the scientific community and have been included in the so-called group of "emerging

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https://doi.org/10.1016/j.chroma.2020.461038
0021-9673/