The analysis of the migration of per and poly fluoroalkyl substances (PFAS) from food contact materials using ultrahigh performance liquid chromatography coupled to ion-mobility quadrupole time-of-flight mass spectrometry (UPLC- IMS-QTOF)

Paula Vera [a], Elena Canellas [a], Nicola Dreolin [b], Jeff Goshawk [b], Cristina Nerín [a,*]

[a] Analytical Chemistry Department, GUIA Group, I3A, EINA, University of Zaragoza, Mª de Luna 3, 50018, Zaragoza, Spain
[b] Waters Corporation, Wilmslow, SK9 4AX, United Kingdom

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ABSTRACT

Per-poly fluoroalkyl substances (PFASs) are a group of synthetic fluorine compounds used in food packaging materials to repel water and fats. This study assessed the chemical migration of PFAS from different food contact materials, including cardboard, recycled cardboard, biopolymer, paper and Teflon trays, from various markets. Migration assays were conducted using Tenax® as a food simulant, which was optimized by subjecting it to three consecutive extractions with 3 mL of ethanol within an hour. The resulting extractions were combined and concentrated to 0.5 mL using a nitrogen stream. The analysis was performed using ultrahigh performance liquid chromatography (UPLC) coupled with ion-mobility (IMS) quadrupole-time-of-flight (QTOF) mass spectrometry, which provided a powerful and novel tool for identifying a library of targets containing collision cross section values (CCS) and increasing confidence in subsequent identifications. Eleven PFAS compounds belonging to the family of perfluorocarboxylic acid, perfluorosulfonic acid and perfluorooctanesulfonamidoacetic acid substances (PFCAs, PFSAs and FOSAAs) were found in packaging samples obtained from China, with migrant concentrations ranging 3.2 and 22.3 μg/kg. In contrast, no detectable levels of PFAS were observed in packaging samples obtained in Spain. All trays tested were deemed to be suitable for use as food contact materials due to the fact that their migrant values were lower than 0.025 mg/kg for PFOA and its salts, and lower than a maximum concentration of 1 mg/kg for PFOA-related compounds.

1. Introduction

Per-polyfluoroalkyl substances (PFAS) refer to a group of synthetic fluorine compounds with distinctive chemical and physical properties, such as resistance to temperature and chemicals, repellency to oil and water, and surfactant characteristics. These substances have been extensively utilized in various industrial applications, including fire-fighting foams, carpeting, cleaners, cosmetics, paints, adhesives, insecticides, clothing, metal plating and food contact materials (FCMs). PFAS are widely produced and used, and their chemical and thermal stability causes them to persist in the environment. As a result, PFAS have been found to contaminate soil and water, and the bioaccumulation of these compounds in animals and humans has been detected [1–3]. Other persistent compounds in nature that have

presented challenges for environmental chemists include ultrafine silico-manganese fumes (SMF), a waste produced during steel production that has been encapsulated in alginate and lyophilized to form cryogenic SMF beads [4]; heavy metals adsorbed by synthesized fungi biosorbents [5], or Pb (II) metal adsorbed by sesame oil cake (SOC), a waste product from the oil industry [6]; and cationic dyes such as methylene blue (MB) and celestine blue (CB) adsorbed by a nano-composite of montmorillonite [7] or a nanocomposite of carbon nanotubes [8] for removal from aqueous environments.

PFAS-contaminated food is a primary source of human exposure, which occurs through direct or indirect contact with PFAS-coated surfaces. In Europe, concentrations of PFAS in individuals have been found to exceed EFSA's proposed safety threshold [9].

PFAS are present in a variety of FCMs that we use in our everyday

lives. These FCMs include surfactants found in Polytetrafluoroethylene (PTFE) materials used to manufacture kitchen utensils and to create non-stick coatings, which make it easier to clean the surfaces of pots and pans. Furthermore, PFAS can be added to packaging materials for processed foods, such as pizza boxes, potato packets and wrapping paper, to act as water repellents and oleophobic coatings that prevent fats and water from the food from transferring to the paper or cardboard packaging [10].

At the Stockholm Convention in 2020, it was agreed that the use of PFAS should be restricted as much as possible to protect human health and the environment. The recent EU Regulation (EU) 2020/784 [11] restricted the use of PFOA, its salts and PFOA related compounds [12]. This regulation sets a maximum concentration of 0.025 mg/kg for PFOA and its salts, and a maximum concentration of 1 mg/kg for PFOA-related compounds or a combination of those compounds. In addition, Commission Recommendation (EU) 2019/794 [13] recommends the investigation of the presence of PFAS in FCM, specifically its presence in paper and board-based materials.

A range of PFAS compounds have been studied in different matrices including water, foods, air and FCMs. These studies were carried out using either non-specific methods to determine the total amount of fluorine in samples [14], or a specific method such as liquid chromatography (LC or UHPLC) coupled to a triple quadrupole mass spectrometer (TQ-MS), being a powerful analytical tool for quantitative analysis from the point of view of accuracy and precision, or a quadrupole time-of-flight mass spectrometer (QTOF-MS) [15–18]. QTOF-MS offers high mass resolution analysis, which allows for greater accuracy in differentiating ions with similar mass-to-charge (m/z) ratios. It also provides highly accurate mass measurements, allowing better identification of unknown compounds through database searches. Additionally QTOF-MS generates information-rich data in a single analysis, simultaneously generating both precursor and product ion spectra. This capability enables the detection and identification of a diverse range of compounds in a single run of complex samples. Moreover, QTOF-MS boasts a wider dynamic range than triple quadrupole, which enables it to detect and quantify a broader range of analytes at different concentrations. In contrast, TQ-MS usually provides unit mass fragments instead of high resolution MS, but the sensitivity, working with collision cell, is higher than that of QTOF-MS.

Ultrahigh performance liquid chromatography (UPLC) coupled to an ion-mobility quadrupole time-of-flight mass spectrometer (IM-QTOF-MS) is a relatively new technique and probably one of the most powerful analytical technologies for the determination and characterization of non-volatile compounds. The incorporation of travelling wave ion mobility (TWIMS) provides an additional dimension of separation. Ions introduced to the TWIMS device are separated in the ion-mobility drift region via a combination of their size, shape and charge. Precursor and fragment ions can subsequently be aligned using both retention time and drift time which results in cleaner, less complex spectra, with reduced noise and provides the potential of achieving lower limits of detection. IMS also enables the determination of collision cross section (CCS) values, which are strongly related to the size, charge and shape of the ions. As such, this technique yields a higher confidence in the identification of compounds by combining CCS with accurate mass, retention time, fragmentation pattern and isotopic distribution. The primary advantage of incorporating IMS into MS is its ability to separate isomers with similar mass-to-charge ratios but differing shapes or sizes. This is achieved through the measurement of the ion's collision cross-section (CCS), which is indicative of its size and shape. By using IMS, the accuracy of isomer identification can be improved and false positive rates can be reduced. This additional dimension of separation enhances specificity in omics studies, making it a critical technique in this field. It has been employed in recent studies to detect compounds that have migrated from various FCMs [19–27]. However, no such study has been conducted to determine the extent of PFAS migration from FCMs, with only few articles found on the analysis of PFAS in environmental water

and human serum samples [28–32]. This study aimed to identify the migration levels of various PFAS families from Food Contact Materials (FCMs) made from water repellent and oleophobic coated materials, including cardboard, paper, biodegradable materials and Teflon.

2. Materials and methods

2.1. Reagents

Perfluorocarboxylic acid substances (PFCAs): Perfluorobutanoic Acid, Perfluorohexanoic Acid, Perfluorooctanoic Acid, Perfluorodecanoic Acid, Perfluorododecanoic Acid, perfluorotetradecanoic acid.

Perfluorosulfonic acid substances (PFSAs): Perfluorobutanesulfonic acid, Perfluorohexanesulfonic Acid, Perfluorooctanesulfonic Acid.

Perfluorooctanesulfonamidoacetic acid substances (FOSAAs): N-methyl perfluorooctane sulfonamidoacetic acid, N-ethyl perfluorooctane sulfonamidoacetic acid.

Perfluorotelomer sulfonates (FTSs): Sodium 1H,1H,2H,2H perfluoro-1,1-hexanesulfonate, sodium 1H,1H,2H,2H perfluoro-1,1-decanesulfonate and sodium perfluoro-1-pentanesulfonate [penta-sulfate] were purchased from Sigma-Aldrich, Química SA (Spain).

High purity ethanol, water, methanol and acetonitrile for HPLC were purchased from Scharlau Chemie S.A (Spain). Tenax® and Ammonium Acetate were supplied by Supelco (Bellefonte, PA).

Individual standard solutions of 1000 µg/g were prepared in ethanol by weighing 0.01 g of each compound in 20 mL vial of capacity. Approximately 18 g of ethanol was added to dissolve them. The resulting solutions were then diluted further to a concentration of 10 µg/g. Subsequently, a stock solution containing a mixture of 14 certified standards was prepared at 1 µg/g and serial dilutions were prepared using ethanol.

2.2. Samples collection

A range of food contact materials, with an emphasis on those for baked products, were studied. In general, the basic criterion for the collection of real samples was designed to ensure that the samples were from different supermarkets, of different materials and also that they were representative and differentiated from two regions such as Spain and China. All of the samples were water repellent and oleophobic coated and were made from cardboard, paper, recycled cardboard, biodegradable sugar cane and starch and Teflon.

All but one of the samples were trays principally used as substrates for either hot pastries, such as croissants, slices pizza, bakery products and hot dogs, or for sushi. One sample was a Teflon coated fabric used to wrap or heat sandwiches directly in the pan. Additional information on

Table 1
Samples of paper, cardboard and Teflon studied.

Code	Description	Material	Origin
Tray 1	Tray for croissants or slices pizza	Cardboard	Spain
Tray 2	Tray for croissants or slices pizza	Recycled cardboard	Spain
Tray 3	Tray for bakery	Compact paper	Spain
Tray 4	Tray for hot dogs	Recycled cardboard	Spain
Tray 5	Tray for bakery	Biodegradable material made of sugar cane	Spain
Tray 6	Tray for sushi	Cardboard	Spain
Tray 7	Tray for bakery	Cardboard	China
Tray 8	Tray for slices pizza	Cardboard	China
Tray 9	Tray for bakery	Recycled cardboard	China
Tray 10	Tray for bakery	Biodegradable starch material	China
Tray 11	Tray for sushi	Cardboard	China
Tray 12	Tray for sushi	Recycled cardboard	China
Coating	Coating of Teflon used to wrap or heat sandwiches directly in the pan	Cardboard	Spain

the samples is provided in Table 1.

It was anticipated that all materials could contain PFAS compounds added to their formulation to avoid the transfer of fats and water from the food to the packaging material.

2.3. UPLC-IMS- QTOF analysis

An ACQUITY UPLC® I-Class system coupled to a Vion IMS QTOF mass spectrometer with electrospray ionization (Waters, Wilmslow, UK) was used to analyze the samples. A UPLC BEH C18 column (1.7 μm particle size, 2.1 mm × 100 mm) was used with a flow rate of 0.3 mL/min at 35 °C [33]. ACQUITY UPLC® I-Class system is equipped with a binary solvent manager pump that delivers precise and accurate gradients for optimal chromatographic separations.

The mobile phase and the gradient were optimized as follows: solvent A: water/acetonitrile 90:10 (v/v) with 20 mM ammonium acetate, solvent B: methanol/acetonitrile 60:40 (v/v). The gradient was A: 85%/B: 15% (0min), A: 65%/B: 35% (2min), A: 45%/B: 55% (4min), A: 25%/B: 75% (6min), A: 5%/B: 95% (8min), A: 85%/B: 15% (10min). The injection volume was 10 μL.

The Vion IMS QTOF was operated in ESI- ion (sensitivity mode), with a capillary voltage of 1 kV and a cone voltage of 30 V. The source and desolvation temperatures were set to 120 °C and 500 °C, respectively, while nitrogen was used as desolvation gas with a flow rate of 800 L/h. The LockSpray, containing Leucine-Enkephalin ([M − H]- adduct, m/z 554.2620) at a concentration of 100 ng/mL, was infused at a rate of 15 μL/min to enable real time mass correction. Argon was used as the collision gas and nitrogen was used as the ion-mobility gas. IMS gas flow rate was 25 mL/min, wave velocity 250 m/s, IMS pulse height 45 V. Mass and CCS calibration was performed using Major Mix kit (Waters Corp.)

The data were acquired in high definition MS^E ($HDMS^E$) mode and both data acquisition and processing were performed using the UNIFI v1.9 Scientific Information System (Waters, Wilmslow, UK).

2.4. Migration assays

The migration tests were carried out using Tenax® as a food simulant for two main reasons. Firstly, most of the packaging samples were cardboard or paper trays and Tenax is used as solid simulant, mimicking the characteristics of dried foods, and therefore representative of the foods exposed to this type of material. Secondly, the intended use of the samples is for the preservation or preparation of cereal products, pastries, cakes and other baking products and Tenax is appropriate for the simulate these food classes as stated in REGULATION (EU) Nº 10/2011 [34].

Some of the food products that may be exposed to the packaging samples could be represented by a food simulant for high fats content, food simulant D (95% ethanol), for example. However, it was found that this simulant partially dissolved the samples so it was not possible to prepare a complementary assay due to the incompatibility between the samples and the simulant.

2.4.1. Sample preparation and extraction procedure

Prior to migration analysis, the optimal number of extractions needed to achieve the highest compound recoveries from Tenax simulant was determined. 0.32 g of Tenax samples were spiked with 100 μL of a standard solution containing the 12 PFAS at a concentration of 1 μg/g. Two experiments were subsequently developed. In the first experiment, two consecutive extractions were carried out in an ultrasonic bath, each lasting an hour, using 3 mL of ethanol. The extracts were combined and subsequently concentrated to 0.5 mL under a nitrogen stream. In the second experiment, three consecutive extractions were performed, each lasting an hour, using 3 mL of ethanol. Again, the extracts were combined and concentrated to 0.5 mL [35]. Three repetitions of each experiment were carried out to ensure accuracy. The percentage of

recovery was calculated for each compound in both experiments by analyzing the samples using UPLC-IMS-QTOF analysis, as previously described. The areas obtained from each compound spiked after two and three extractions were divided by the areas obtained after injection of the same compound at a concentration of 0.2 μg/g (taking into account 100 μL of a standard solution spiked at a concentration of 1 μg/g and a final volume of 0.5 mL after concentration).

2.4.2. Migration assays and risk assessment

To avoid false positive results and contaminated blanks, the Tenax used as a simulant was cleaned with ethanol in a Soxhlet for 8 h and dried.

Each food packaging sample was cut into 2 × 4 cm pieces, and 0.32 g of Tenax was spread evenly on the inner surface of each sample, following the UNE-EN 14338 standard of 4 g Tenax/dm^2 [36]. The samples were then placed on Petri plates and kept in an oven set at 40 °C for 3 days to simulate challenging usage conditions (20 °C < T ≤ 40 °C, 1 day < t ≤ 3 days) [34]. The Teflon-coated samples, which are used to heat sandwiches directly in a pan, were subjected to additional conditions of 175 °C for 5 min, which is the most challenging condition of their use (t ≤ 5 min and 150 °C < T < 175 °C). Three replicates of each sample and a blank were prepared.

After the migration assays were completed, the samples were extracted and analyzed by UPLC-IMS-QTOF, with calibration curves prepared using standard solutions in ethanol for quantitation. Migration values were calculated by determining the absolute mass migrating in mg and dividing it by 0.08 dm^2 to account for the sample size. The factor of 6 dm^2 of simulant per kg was also taken into account according to EU regulation [34]. The migration levels of each compound were compared to the maximum concentrations set by EU regulation (EU 2020/784) [11], which is 0.025 mg/kg for PFOA and its salts, and 1 mg/kg for PFOA-related compounds or a combination of those compounds.

3. Results and discussion

3.1. Determination of PFAS using UPLC-IMS-QTOF

This technique resulted in cleaner and less complex spectra by aligning precursors and fragment ions based on both retention time and drift time. Furthermore, in addition to providing accurate m/z values of precursor and fragmentation ions, ion-mobility mass spectrometry allowed for the determination of a Collision Cross Section (CCS) value, which indicated the size and shape of each molecule. The chromatogram of the investigated compounds analyzed by UPLC-IMS-QTOF was shown in Fig. 1.

The PFAS studied can be grouped into families as shown in Table 2 in which retention times, precursor and fragment ions and CCS values are also reported. CCS values were calculated as the average of all CCS values obtained for each compound at all seven calibration points analyzed in triplicate. All compounds were detected in ESI-, appearing either as deprotonated adducts, or [M − Na]- adducts in the case of FTSs and PFPeS. For PFCAs, the most abundant ions observed in the low energy spectrum were the [M − H]- and the [2M − H]- adducts. In the high energy spectrum, the most abundant fragment observed was the loss of 43.9897 (CO_2) and several other common fragments, such as m/z values 118.9925, 168.9805, 218.9861, corresponding to C_2F_5, C_3F_7 and C_4F_9 respectively, were detected. Fig. 2a provides an example of the mass spectra for perfluorooctanoic acid compounds. The CCS values for this class of compounds generally increased with the length of the perfluorocarboxylic chain, except for perfluorododecanoic acid and perfluorotetradecanoic acid, for which the CCS values were lower than those of compounds with shorter chain lengths.

One major difference noted between PFCAs and PFSAs was the low intensity or absence of the [2M − H]- ion in the low-energy spectrum for latter compound class PFSAs. Moreover, the intensities of the product ions for PFSAs were lower in the high-energy spectra compared to those
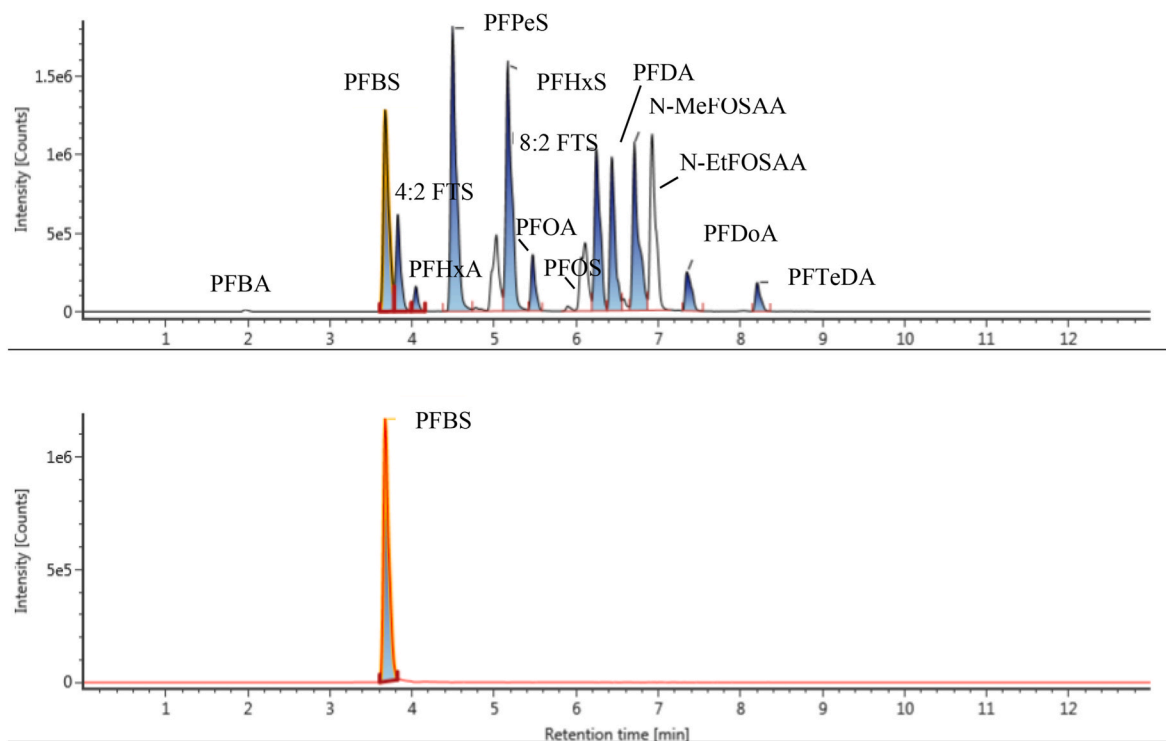
Fig. 1. Chromatogram of the investigated compounds analyzed by UPLC-IMS-QTOF at the top and the extracted ion chromatogram of the PFBS compound at the bottom.

Table 2
Compounds analyzed by UPLC-IMS-QTOF, with their retention times (RT), ion detected, precursor and fragment ions and collision cross section (CCS).

Name	Acronym	RT (min)	Ion detected	Precursor ion (m/z)	Fragment ion 1 (m/z)	Fragment ion 2 (m/z)	Fragment ion 3 (m/z)	CSS (Å²)
Perfluorocarboxylic acid substances (PFCAs)								
Perfluorobutanoic Acid	PFBA	1.96	[M − H]	**212.9787**	168.9890			167.3 ± 0.1
Perfluorohexanoic Acid	PFHxA	4.05	[M − H]	**312.9725**	268.9825	118.9921		198.8 ± 0.4
Perfluorooctanoic Acid	PFOA	5.49	[M − H]	**412.9666**	368.9769	168.9892	218.9861	229.7 ± 0.2
Perfluorodecanoic Acid	PFDA	6.53	[M − H]	**512.9606**	468.9708	218.9861	268.9829	259.1 ± 0.5
Perfluorododecanoic Acid	PFDoA	7.36	[M − H]	**612.9558**	568.9646	168.9892	218.9861	190.5 ± 0.7
Perfluorotetradecanoic Acid	PFTeDA	8.21	[M − H]	**712.9486**	668.9592	168.9892	218.9859	208.9 ± 0.9
Perfluorosulfonic acid substances (PFSAs)								
Perfluorobutanesulfonic acid	PFBS	3.68	[M − H]	**298.9435**	168.9896	118.9927	218.9868	129.6 ± 0.1
Perfluorohexanesulfonic acid	PFHxS	5.12	[M − H]	**398.9371**	168.9893	229.9479	279.9435	146.3 ± 0.9
Perfluorooctanesulfonic acid	PFOS	6.26	[M − H]	**498.9312**	168.9892	118.9927	279.9446	163.6 ± 0.3
Perfluorooctanesulfonamidoacetic acids substances (FOSAAs)								
N -methyl perfluorooctane sulfonamidoacetic acid	N-MeFOSAA	6.72	[M − H]	**569.9676**	418.9732	218.9858	511.9619	189.1 ± 0.6
N-ethyl perfluorooctane sulfonamidoacetic acid	N-EtFOSAA	6.93	[M − H]	**583.9827**	525.9777	265.1508	168.9889	192.7 ± 0.7
Fluorotelomer sulfonates substances (FTSs)								
Sodium 1H,1H,2H,2H perfluoro-1,1-hexanesulfonate	4:2 FTS	3.83	[M − Na]	**326.9640**	306.9672	286.9619	202.9932	146.9 ± 0.3
Sodium 1H,1H,2H,2H perfluoro-1,1-decanesulfonate	8:2 FTS	6.44	[M − Na]	**526.9619**	506.9556	486.9495	392.9767	181.9 ± 0.1
Perfluoroalkanesulfonates substances (PFASs)								
Sodium perfluoro-1-pentanesulfonate	PFPeS	4.50	[M − Na]	**348.9394**	168.9885	229.9477	341.1974	137.8 ± 0.1

The precursor ions (m/z) highlighted were used to determine the CCS value.
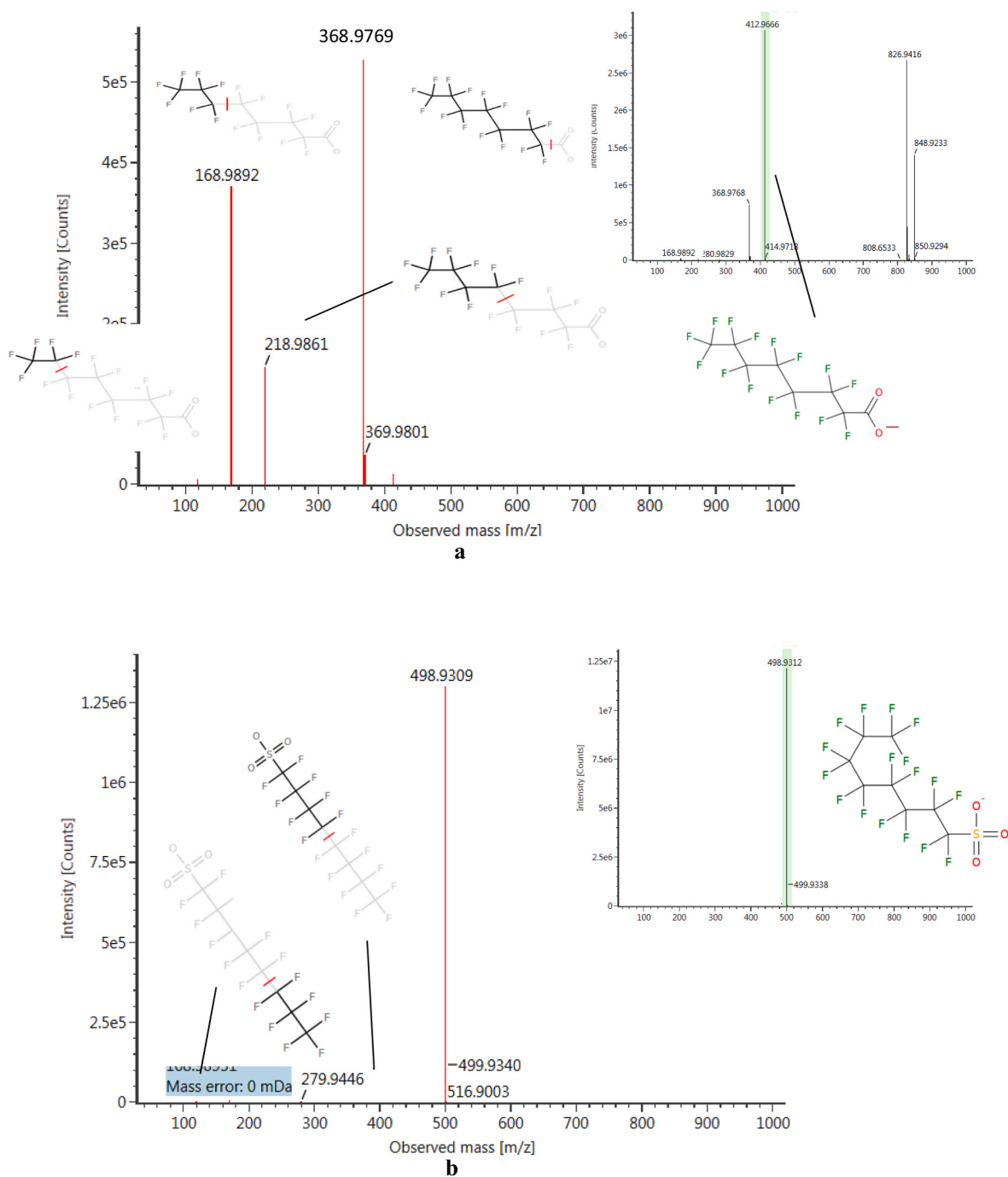
Fig. 2. a. The high-energy spectrum of perfluorooctanoic acid with the corresponding low-energy spectrum inset to the right.
b. The high-energy spectrum of perfluorooctanesulfonic acid with the corresponding low-energy spectrum inset to the right.
c. The high-energy spectrum of N -methyl perfluorooctane sulfonamidoacetic acid with the corresponding low-energy spectrum inset to the right.
d. The high-energy spectrum of sodium 1H,1H,2H,2H perfluoro-1,1-hexanesulfonate with the corresponding low-energy spectrum inset to the right.

of PFCAs. Some common product ions observed for PFCAs at lower intensities were 129.9598, 229.9479 and 279.9446 m/z (CF_2O_3S, $C_3F_6O_3S$ and $C_4F_8O_3S$, respectively) which were associated with the fragmentation of the sulfur-containing chain. An illustration of the low and high energy mass spectra for perfluorooctanesulfonic acid is given in Fig. 2b.

The family of compounds known as perfluorooctanesulfonamidoacetic acids could be identified by the presence of strong fragments, with the loss of 58.0057 ($C2H2O2$) being the most prevalent. Additionally, common fragments with m/z values of 118.9925, 168.9805 and 218.9861 were also detected. An example of the mass spectra for the

compound N-methyl perfluorooctane sulfonamidoacetic acid can be seen in Fig. 2c.

Finally, the FTSs and PFPeS families had distinct characteristics compared to other compound classes, as they exhibited the loss of Na. The fluorotelomer sulfonate substances family shared a common fragment ion resulting from the loss of 20.0065 (HF). However, for sodium perfluoro-1-pentanesulfonate, only minimal fragments were detected. An example of the mass spectra for Sodium 1H,1H,2H,2H perfluoro-1,1-hexanesulfonate is shown in Fig. 2d.
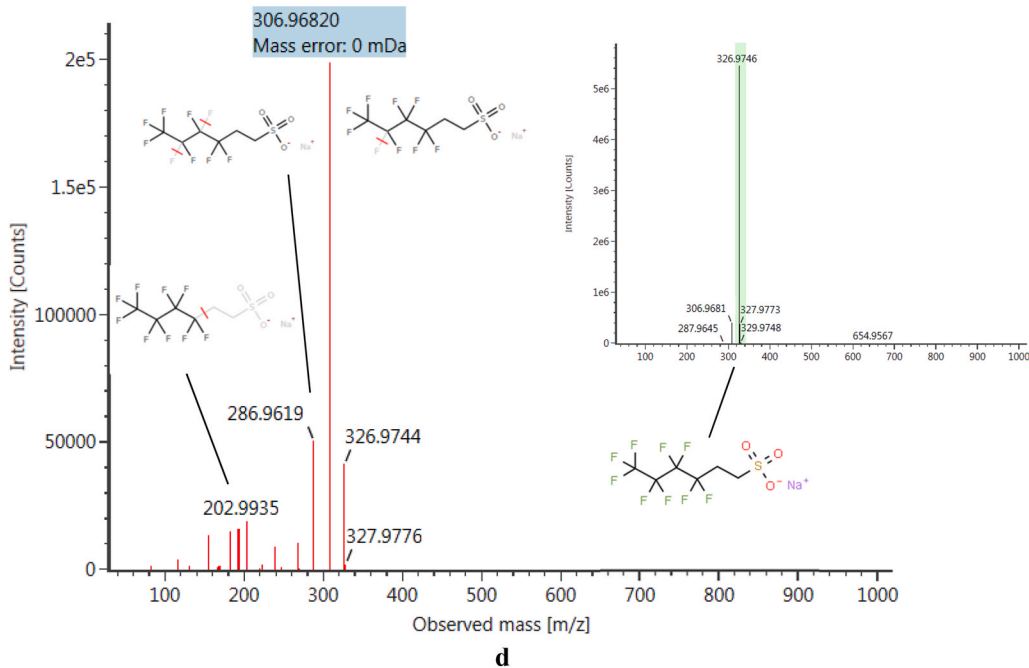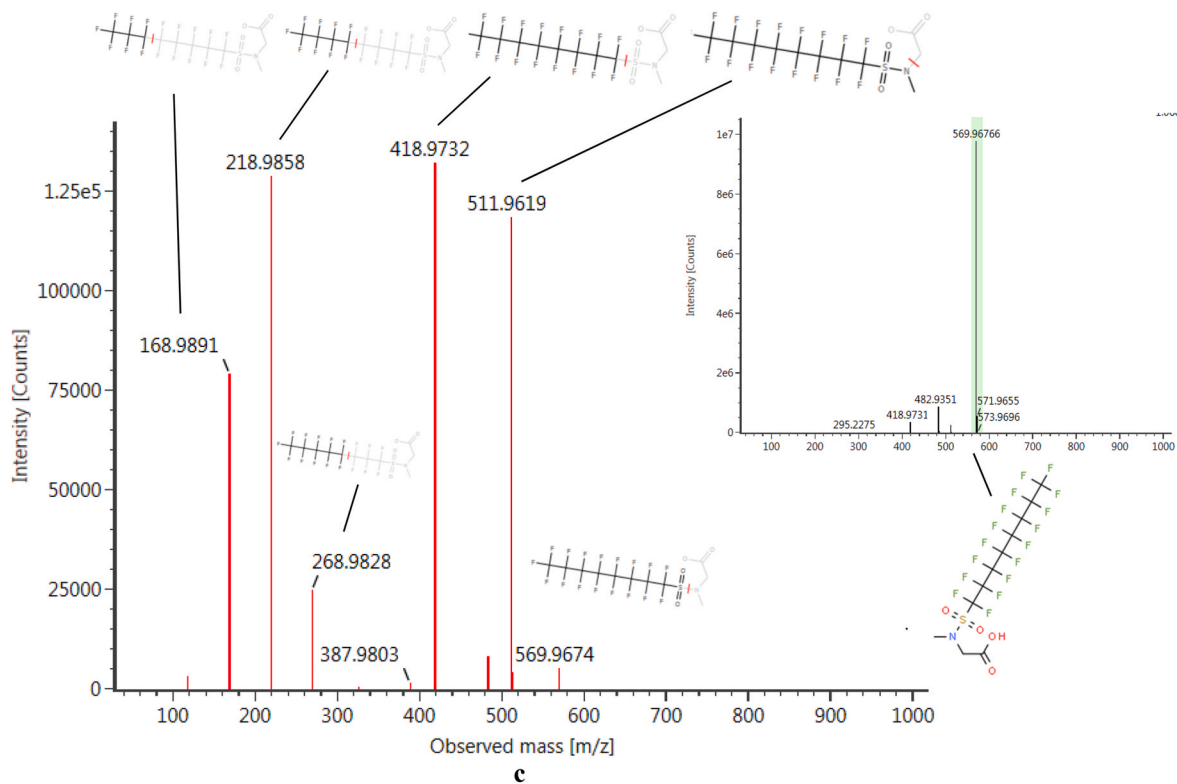
Fig. 2. (*continued*).

3.2. Migration results

Prior to performing the migration assays, the number of extractions for each compound from Tenax was optimized by spiking Tenax with the certified standards and the recoveries, quantitation parameters and limits of detection (LOD) and quantification (LOQ) obtained from this process are shown in Table 3. The values of LOD and LOQ were determined by considering the minimum amount of the analyte of interest that produces a chromatographic peak with a signal-to-noise (S/N) ratio of 3:1 and 10:1, respectively, in the presence of background signal noise [37].

Higher recoveries were obtained on using three consecutive extractions ranging between 77.5 ± 5.4% for 4:2 FTS and 119 ± 22% for PFBS. Very low limit of detections (ranging between 0.07 and 3.42 µg/kg) and good linearity ($R^2 > 0.99$) were obtained. Validation tests provided good results of these tested parameters. The sensitivity of the method was

Table 3

Calibration parameters, coefficient of correlation (R^2), limit of detection (LOD), limit of quantification (LOQ) and extraction recoveries (%) for the compounds analyzed.

Compounds	Acronym	Calibration equation	R^2	LOD (µg/kg)	LOQ (µg/kg)	Linear range (µg/kg)	Recoveries (%) 2 extractions	Recoveries (%) 3 extractions
Perfluorobutanoic Acid	PFBA	y = 13.8x-80.7	0.9955	3.42	11.4	11.4–488	74.1 ± 2.2	80.7 ± 4.0
Perfluorohexanoic Acid	PFHxA	y = 161x-4064	0.9991	1.98	6.60	6.30–1070	79.3 ± 2.9	90.4 ± 6.1
Perfluorooctanoic Acid	PFOA	y = 401x+189	0.9950	0.89	2.58	2.98–1100	79.7 ± 5.6	89.0 ± 7.9
Perfluorodecanoic Acid	PFDA	y = 137x+3656	0.9934	0.44	1.47	1.47–1180	73.5 ± 2.9	83.7 ± 2.5
Perfluorododecanoic Acid	PFDoA	y = 325x+1825	0.9971	0.42	1.40	1.40–1130	99.1 ± 5.9	105 ± 12
Perfluorotetradecanoic Acid	PFTeDA	y = 335x-4610	0.9951	0.40	1.33	1.34–1181	74.6 ± 4.4	92.6 ± 6.5
Perfluorobutanesulfonic acid	PFBS	y = 9597x+5885	0.9978	0.40	1.33	1.33–26	84.7 ± 7.0	119 ± 22
Perfluorohexanesulfonic acid	PFHxS	y = 3415x+14321	0.9991	0.38	1.27	1.27–505	105 ± 16	104 ± 10
Perfluorooctanesulfonic acid	PFOS	y = 4161x+265	0.9991	0.41	1.39	1.39–110	81.5 ± 4.9	118 ± 11
N -methyl perfluorooctane sulfonamidoacetic acid	N-MeFOSAA	y = 3163x+6722	0.9959	0.06	0.20	0.19–400	54.1 ± 3.5	89.5 ± 3.5
N-ethyl perfluorooctane sulfonamidoacetic acid	N-EtFOSAA	y = 266x+3533	0.9963	0.07	0.23	0.25–1020	95 ± 7.6	103 ± 8.2
Sodium 1H,1H,2H,2H perfluoro-1,1-hexanesulfonate	4:2 FTS	y = 939x+4550	0.9963	0.37	1.23	1.23–250	65.5 ± 1.5	77.5 ± 5.4
Sodium 1H,1H,2H,2H perfluoro-1,1-decanesulfonate	8:2 FTS	y = 4751x+1645	0.9964	0.07	0.23	0.24–43	69.4 ± 4.1	99.3 ± 5.1
Sodium perfluoro-1-pentanesulfonate	PFPeS	y = 12279x+1813	0.9928	0.08	0.26	0.25–45	72.7 ± 11	103 ± 5.2

LOD: Limit of detection and LOQ: Limit of quantification.

mostly comparable to other methods based on UPLC-QTOF and UPLC-MS/MS as ythey provided lower values of detection limits due to its spectral cleaning capability [38–43].

The migration results are shown in Table 4. The migration of PFAS from most of the samples obtained from a local Spanish market (trays 1–6) was lower than the LODs of the method. However, for tray 2 and tray 4, which were made of recycled cardboard [44], the migration values of PFOA and PFOS were above the LOD. For tray 2 the levels of migration of PFOA and PFOS were found to be below their limit of quantifications (LOQs), at <2.58 µg/kg and <1.39 µg/kg, respectively. For tray 4 the levels of migration of PFOA and PFOS were found to be

3.15 ± 0.02 µg/kg and 2.22 ± 0.02 µg/kg, respectively.

The levels of migration of PFAS from the samples obtained from a Chinese market (trays 7–12) were significantly elevated compared to the migration levels from the samples from the Spanish market. The only trays for which the level of migration of PFAS were below the LOD were trays 7 and 10. In the other samples from the Chinese market, the migration level of compounds belonging to the PFCA and PFSA classes were found to range between 1.55 and 22.3 µg/kg, with the highest concentrations determined for PFOA. It is worth noting that the level of migration of the compounds in these families decreased with the increasing length of the fluorinated chain [14]. Furthermore,

Table 4

Migration results to Tenax expressed as: µg of compound/kg of simulant.

Samples/Compounds	Tray 1	Tray 2	Tray 3	Tray 4	Tray 5	Tray 6	Tray 7	Tray 8	Tray 9	Tray 10	Tray 11	Tray 12	Coating T = 40 °C	Coating T = 175 °C
PFBA	<3.42	<3.42	<3.42	<3.42	<3.42	<3.42	<3.42	12.5 ± 1.0	16.3 ± 0.32	<3.42	<11.4	13.5 ± 1.1	<3.42	<3.42
PFHxA	<1.98	<1.98	<1.98	<1.98	<1.98	<1.98	<1.98	8.71 ± 0.43	11.9 ± 1.0	<1.98	<6.3	8.92 ± 0.80	<1.98	<1.98
PFOA	<0.89	<2.58	<0.89	3.15 ± 0.02	<0.89	<0.89	<0.89	9.58 ± 0.61	18.5 ± 0.9	<0.89	5.33 ± 0.21	22.3 ± 1.9	2.61 ± 0.34	4.12 ± 0.20
PFDA	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	<0.44	5.33 ± 0.47	7.55 ± 0.6	<0.44	<0.44	7.33 ± 0.58	<0.44	<0.44
PFDoA	<0.42	<0.42	<0.42	<0.42	<0.42	<0.42	<0.42	2.11 ± 0.10	4.23 ± 0.29	<0.42	<0.42	4.14 ± 0.37	<0.42	<0.42
PFTeDA	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	1.83 ± 0.09	<0.40	<0.40	2.12 ± 0.06	<0.40	<0.40
PFBS	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	<0.40	5.24 ± 0.41	3.18 ± 0.22	<0.40	<1.33	6.99 ± 0.35	<0.40	<0.40
PFHxS	<0.38	<0.38	<0.38	<0.38	<0.38	<0.38	<0.38	2.15 ± 0.19	1.55 ± 0.12	<0.38	<0.38	9.2 ± 0.6	<0.38	<0.38
PFOS	<0.41	<1.39	<0.41	2.22 ± 0.02	<0.41	<0.41	<0.41	7.33 ± 0.51	8.57 ± 0.77	<0.41	2.17 ± 0.10	15.3 ± 1.4	<0.41	<0.41
N-MeFOSAA	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	3.15 ± 0.28	<0.06	<0.06	2.15 ± 0.14	<0.06	<0.06
N-EtFOSAA	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	1.22 ± 0.06	<0.07	<0.07	0.86 ± 0.02	<0.07	<0.07
4:2 FTS	<0.37	<0.37	<0.37	<0.37	<0.37	<0.37	<0.37	<0.37	<0.37	<0.37	<0.37	<0.37	<0.37	<0.37
8:2 FTS	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
PFPeS	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08

compounds belonging to the FOSAA family (N-EtFOSAA and N-MeFO-SAA) were detected at concentrations ranging from 0.86 to 3.15 µg/kg for trays 9 and 12.

It is worth noting that no fluorotelomer sulfonates substances (FTS) and perfluoroalkanesulfonates substances (PFAS) were detected above the LOD in any of the tray samples. Only PFOA was found to migrate above the LOD from the Teflon-coated sample. The level of migration was found to increase with temperature even though the contact time at the higher temperature is significantly lower than that at the lower temperature [12]. This phenomenon can be explained by the concept of diffusion, which is the process where molecules move from areas of high concentration to areas of low concentration. Diffusion is driven by the kinetic energy of the molecules and is affected by various factors, including temperature. With an increase in temperature, the kinetic energy of molecules also increases, resulting in a higher diffusion rate. This implies that although the contact time between migrating molecules and their surroundings is shorter at higher temperatures, the increased diffusion rate allows for more molecules to migrate within that shorter time frame. Therefore, despite the shorter contact time, the net effect of temperature on migration can be an increase. Nevertheless, it is worth noting that other factors, such as the specific properties of the migrating molecules, can also influence migration.

According to Regulation (EU) 2020/784, the maximum concentration for PFOA and its salts should be 0.025 mg/kg with a maximum concentration of 1 mg/kg for a combination of PFOA-related compounds. It can be seen in Table 4 that the migration level of all compounds studied here were below these limits.

4. Conclusions

A method has been developed to analyze PFAS compounds migrating from various materials, including trays made from virgin and recycled cardboards, biopolymers, papers and Teflon, sourced from different markets. These materials are commonly used as food contact materials and are believed to contain PFAS to enhance their water-repellent and oleophobic properties. The UPLC-IMS-QTOF system has proven to be a powerful tool, enabling the creation of a PFAS target list with CCS values for subsequent screening analysis. The addition of CCS as a screening parameter increases the levels of confidence in the compound assignments and reduces the number of false positives, thereby enabling increased accuracy in quantitation. The optimized extraction procedure for the Tenax migration assays produced recoveries in the range 77.5–119% with good repeatability.

A total of eleven PFAS compounds were detected with higher levels of migration observed in trays obtained from a Chinese market. In this respect, a significant difference between the Spanish and Chinese trays was found, with only two compounds were detected at levels very close to their LODs in the Spanish samples.

The compounds detected belong to the PFCAs, PFSAs and FOSAAs classes. The compound found to have the highest level of migration was PFOA with migration values between 3.15 and 22.3 µg/kg. The concentrations of the other compounds considered in the migration experiments, were found to decrease with increasing chain length for each of the compound classes.

Overall, the migration values were found to be between 0.86 and 22.3 µg/kg, below the limits set by the EU Regulation for PFOA-related compounds (25 µg/kg). Therefore all of the packaging materials tested in this study comply with the current legislation.

Credit author statement

Paula Vera: Conceptualization, Methodology, Validation, Investigation, Data Curation, Formal analysis, Writing - Original Draft, Writing - Review & Editing. Elena Canellas: Conceptualization, Validation, Data Curation, Writing. Cristina Nerín: Conceptualization, Resources, Review, Supervision, project administration, funding acquisition. Nicola

Dreolin Original Draft Review, project administration and funding acquisition. Jeff Goshawk project administration and funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

[1] X.X. Liang, X.Y. Yang, W.Q. Jiao, J. Zhou, L.Y. Zhu, Simulation modelling the structure related bioaccumulation and biomagnification of per- and polyfluoroalkyl substances in aquatic food web, Sci. Total Environ. 838 (2022).

[2] L.J.L. Espartero, M. Yamada, J. Ford, G. Owens, T. Prow, A. Juhasz, Health-related toxicity of emerging per- and polyfluoroalkyl substances: comparison to legacy PFOS and PFOA, Environ. Res. 212 (2022).

[3] R.A. Dickman, D.S. Aga, A review of recent studies on toxicity, sequestration, and degradation of per- and polyfluoroalkyl substances (PFAS), J. Hazard Mater. 436 (2022).

[4] M.A. Khan, S.M. Wabaidur, M.R. Siddiqui, A.A. Alqadami, A.H. Khan, Silico-manganese fumes waste encapsulated cryogenic alginate beads for aqueous environment de-colorization, J. Clean. Prod. 244 (2020).

[5] Z.A. Alothman, A.H. Bahkali, M.A. Khiyami, S.M. Alfadul, S.M. Wabaidur, M. Alam, B.Z. Alfarhan, Low cost biosorbents from fungi for heavy metals removal from wastewater, Separ. Sci. Technol. 55 (10) (2020) 1766–1775.

[6] A. Mittal, M. Naushad, G. Sharma, Z.A. Alothman, S.M. Wabaidur, M. Alam, Fabrication of MWCNTs/ThO2 nanocomposite and its adsorption behavior for the removal of Pb(II) metal from aqueous medium, Desalination Water Treat. 57 (46) (2016) 21863–21869.

[7] E.R. Kenawy, A.A. Ghfar, S.M. Wabaidur, M.A. Khan, M.R. Siddiqui, Z. A. Alothman, A.A. Alqadami, M. Hamid, Cetyltrimethylammonium bromide intercalated and branched polyhydroxystyrene functionalized montmorillonite clay to sequester cationic dyes, J. Environ. Manag. 219 (2018) 285–293.

[8] S.M. Wabaidur, M.A. Khan, M.R. Siddiqui, M. Otero, B.H. Jeon, Z.A. Alothman, A. H. Hakami, Oxygenated functionalities enriched MWCNTs decorated with silica coated spinel ferrite - a nanocomposite for potentially rapid and efficient de-colorization of aquatic environment, J. Mol. Liq. 317 (2020).

[9] M. Lerch, K.H. Nguyen, K. Granby, Is the use of paper food contact materials treated with per- and polyfluorinated alkyl substances safe for high-temperature applications? - migration study in real food and food simulants, Food Chem. 393 (2022).

[10] H. Choi, I.A. Bae, J.C. Choi, S.J. Park, M. Kim, Perfluorinated compounds in food simulants after migration from fluorocarbon resin-coated frying pans, baking utensils, and non-stick baking papers on the Korean market, Food Addit. Contam. Part B-Surveillance 11 (4) (2018) 264–272.

[11] Commission delegated Regulation, Eu, April 2020 Amending Annex I to Regulation (EU) 2019/1021 of the European Parliament and of the Council as Regards the Listing of Perfluorooctanoic Acid (PFOA), its Salts and PFOA-Related Compounds, 2020/784 of 8.

[12] M.P. Elizalde, S. Gomez-Lavin, A.M. Urtiaga, Migration of perfluorinated compounds from paperbag to Tenax (R) and lyophilised milk at different temperatures, Int. J. Environ. Anal. Chem. 98 (15) (2018) 1423–1433.

[13] Commission Recommendation, Eu, On a Coordinated Control Plan with a View to Establishing the Prevalence of Certain Substances Migrating from Materials and Articles Intended to Come into Contact with Food (Notified under Document C (2019) 3519) (Text with EEA Relevance, 2019/794 of 15 May 2019.

[14] A.R. Carnero, A. Lestido-Cardama, P.V. Loureiro, L. Barbosa-Pereira, A.R.B. de Quiros, R. Sendon, Presence of perfluoroalkyl and polyfluoroalkyl substances (PFAS) in food contact materials (FCM) and its migration to food, Foods 10 (7) (2021).

[15] N.K. Li, X.C. Song, P. Shen, C. Zhao, Rapid determination of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in vegetables by on-line solid-phase extraction (SPE) with ultra-high-performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS), Anal. Lett. 55 (14) (2022) 2227–2238.

[16] L. Serrano, L.M. Iribarne-Duran, B. Suarez, F. Artacho-Cordon, F. Vela-Soria, M. Pena-Caballero, J.A. Hurtado, N. Olea, M.F. Fernandez, C. Freire,

Concentrations of perfluoroalkyl substances in donor breast milk in Southern Spain and their potential determinants, Int. J. Hyg Environ. Health 236 (2021).

[17] X. Trier, K. Granby, J.H. Christensen, Polyfluorinated surfactants (PFS) in paper and board coatings for food packaging, Environ. Sci. Pollut. Control Ser. 18 (7) (2011) 1108–1120.

[18] W. Xu, X. Wang, Z. Cai, Analytical chemistry of the persistent organic pollutants identified in the Stockholm Convention: a review, Anal. Chim. Acta 790 (2013) 1–13.

[19] M. Alikord, A. Mohammadi, M. Kamankesh, N. Shariatifar, Food safety and quality assessment: comprehensive review and recent trends in the applications of ion mobility spectrometry (IMS), Crit. Rev. Food Sci. Nutr. 62 (8) (2022) 4833–4866.

[20] A.J. Midey, A. Camacho, J. Sampathkumaran, C.A. Krueger, M.A. Osgood, C. Wu, High-performance ion mobility spectrometry with direct electrospray ionization (ESI-HPIMS) for the detection of additives and contaminants in food, Anal. Chim. Acta 804 (2013) 197–206.

[21] A. Schweighuber, J. Fischer, W. Buchberger, Differentiation of polyamide 6, 6.6, and 12 contaminations in polyolefin-recyclates using HPLC coupled to drift-tube ion-mobility quadrupole time-of-flight mass spectrometry, Polymers 13 (12) (2021).

[22] P. Vera, E. Canellas, G. Barknowitz, J. Goshawk, C. Nerin, Ion-mobility quadrupole time-of-flight mass spectrometry: a novel technique applied to migration of nonintentionally added substances from polyethylene films intended for use as food packaging, Anal. Chem. 91 (20) (2019) 12741–12751.

[23] P. Vera, E. Canellas, C. Nerin, N. Dreolin, J. Goshawk, The migration of NIAS from ethylene-vinyl acetate corks and their identification using gas chromatography mass spectrometry and liquid chromatography ion mobility quadrupole time-of-flight mass spectrometry, Food Chem. 366 (2022).

[24] E. Canellas, P. Vera, C. Nerin, Ion mobility quadrupole time-of-flight mass spectrometry for the identification of non-intentionally added substances in UV varnishes applied on food contact materials. A safety by design study, Talanta 205 (2019).

[25] E. Canellas, P. Vera, C. Nerin, N. Dreolin, J. Goshawk, Ion mobility quadrupole time-of-flight high resolution mass spectrometry coupled to ultra-high pressure liquid chromatography for identification of non-intentionally added substances migrating from food cans, J. Chromatogr. A 1616 (2020).

[26] E. Canellas, P. Vera, C. Nerin, J. Goshawk, N. Dreolin, The application of ion mobility time of flight mass spectrometry to elucidate neo-formed compounds derived from polyurethane adhesives used in champagne cork stoppers, Talanta 234 (2021).

[27] Y. Lai, R. Lin, Q.M. Dong, Z.P. Huang, X.P. Tu, W.J. Lin, W.J. Sun, Determination of the migration of methyl methacrylate in food contact materials by high field asymmetric waveform ion mobility spectrometry technology, Chemical Journal of Chinese Universities-Chinese 39 (4) (2018) 660–666.

[28] J.N. Dodds, Z.R. Hopkins, D.R.U. Knappe, E.S. Baker, Rapid characterization of per- and polyfluoroalkyl substances (PFAS) by ion mobility spectrometry-mass spectrometry (IMS-MS), Anal. Chem. 92 (6) (2020) 4427–4435.

[29] N.A. Aly, J.N. Dodds, Y.S. Luo, F.A. Grimm, M. Foster, I. Rusyn, E.S. Baker, Utilizing ion mobility spectrometry-mass spectrometry for the characterization and detection of persistent organic pollutants and their metabolites, Anal. Bioanal. Chem. 414 (3) (2022) 1245–1258.

[30] M. Foster, M. Rainey, C. Watson, J.N. Dodds, K.I. Kirkwood, F.M. Fernandez, E.S. Baker, Uncovering PFAS and other xenobiotics in the dark metabolome using ion

mobility spectrometry, mass defect analysis, and machine learning, Environ. Sci. Technol. 56 (12) (2022) 9133–9143.

[31] Y.S. Luo, N.A. Aly, J. McCord, M.J. Strynar, W.A. Chiu, J.N. Dodds, E.S. Baker, I. Rusyn, Rapid characterization of emerging per- and polyfluoroalkyl substances in aqueous film-forming foams using ion mobility spectrometry-mass spectrometry, Environ. Sci. Technol. 54 (23) (2020) 15024–15034.

[32] A. Valdiviezo, N.A. Aly, Y.S. Luo, A. Cordova, G. Casillas, M. Foster, E.S. Baker, I. Rusyn, Analysis of per- and polyfluoroalkyl substances in Houston Ship Channel and Galveston Bay following a large-scale industrial fire using ion-mobility-spectrometry-mass spectrometry, J. Environ. Sci. 115 (2022) 350–362.

[33] R. Guo, Q.F. Zhou, Y.Q. Cai, G.B. Jiang, Determination of perfluorooctanesulfonate and perfluorooctanoic acid in sewage sludge samples using liquid chromatography/quadrupole time-of-flight mass spectrometry, Talanta 75 (5) (2008) 1394–1399.

[34] J.Y. Moisan, Diffusion of polyethylene additives .1. Effect of nature of diffusion agent, Eur. Polym. J. 16 (10) (1980) 979–987.

[35] P. Vera, M. Aznar, P. Mercea, C. Nerin, Study of hotmelt adhesives used in food packaging multilayer laminates. Evaluation of the main factors affecting migration to food, J. Mater. Chem. 21 (2) (2011) 420–431.

[36] UNE-EN 14338, Papel y cartón para contacto alimentario. Condiciones para la determinación de la migración en papel y cartón utilizando óxido de polifenileno modificado (MPPO) como simulante., UNE-EN 14338:2004. Papel y cartón para contacto alimentario. Condiciones para la determinación de la migración en papel y cartón utilizando óxido de polifenileno modificado (MPPO) como simulante, 2004.

[37] S.M. Wabaidur, A. AlAmmari, A. Aqel, S.A. Al-Tamrah, Z.A. Alothman, A. Ahmed, Determination of free fatty acids in olive oils by UPHLC-MS, J. Chromatogr., B: Anal. Technol. Biomed. Life Sci. 1031 (2016) 109–115.

[38] C. Moreta, M.T. Tena, Fast determination of perfluorocompounds in packaging by focused ultrasound solid-liquid extraction and liquid chromatography coupled to quadrupole-time of flight mass spectrometry, J. Chromatogr. A 1302 (2013) 88–94.

[39] C. Moreta, M.T. Tena, Determination of perfluorinated alkyl acids in corn, popcorn and popcorn bags before and after cooking by focused ultrasound solid-liquid extraction, liquid chromatography and quadrupole-time of flight mass spectrometry, J. Chromatogr. A 1355 (2014) 211–218.

[40] T.H. Kim, S. Yu, Y. Choi, T.Y. Jeong, S.D. Kim, Profiling the decomposition products of perfluorooctane sulfonate (PFOS) irradiated using an electron beam, Sci. Total Environ. 631–632 (2018) 1295–1303.

[41] T. Schwichtenberg, D. Bogdan, C.E. Schaefer, J. Stults, J.A. Field, Per- and Polyfluoroalkyl Substances Enrichment in the Surface Microlayer of a Freshwater System Impacted by Aqueous Film- Forming Foams, Acs Es&T Water, 2023.

[42] J.L. He, T. Peng, J. Xie, X.Y. Hu, Q.Y. Chang, H. Chen, C.L. Fan, C. Li, Determination of 16 perfluorinated alkyl substances in food packaging materials by solid phase extraction-liquid chromatography-tandem mass spectrometry, Chin. J. Chromatogr. 34 (7) (2016) 708–714.

[43] M.M. Yan, M. Chen, X.S. Meng, X.Y. Guo, H. Bai, Q. Ma, P.L. Wang, H.M. Lei, Determination of migration of perfluorooctanoic acid and perfluorooctane sulfonic acid from food contact materials by ionic liquid-based dispersive liquid-liquid microextraction and ultra-performance liquid chromatography-tandem mass spectrometry, Chin. J. Chromatogr. 36 (8) (2018) 738–744.

[44] G.W. Curtzwiler, P. Silva, A. Hall, A. Ivey, K. Vorst, Significance of perfluoroalkyl substances (PFAS) in food packaging, Integrated Environ. Assess. Manag. 17 (1) (2021) 7–12.