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Solid phase micro extraction arrow optimization for the screening of volatiles compounds in recycled plastics in GC/MS

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ABSTRACT

The aim of this work is to develop and optimize a non-targeted screening (NTS) method based on Arrow SPME for the characterization of volatile and semi-volatile compounds in recycled polyethylene terephthalate (PET) and polyolefins (POs). Both, solid materials and migration extracts obtained with food simulants (ethanol 10 %, ethanol 95 %, and acetic acid 3 %) were studied. The method development considered both headspace and direct immersion extraction modes to assess their relative performance and applicability depending on the sample type. To achieve robust optimization, a RSM based on CCD was employed, allowing the evaluation of the effects and interactions of key variables such as extraction time, temperature, and sample amount. Separate designs were constructed for each sample type, acknowledging their distinct behaviour and matrix effects. A mixture of 15 selected Food Contact Materials (FCM) analytes showed that SPME Arrow improved sensitivity, with response factors 7–14 % higher than traditional SPME. It also demonstrated superior linearity ($R^2 > 0.990$ for all analytes) and lower variability, whereas conventional SPME showed acceptable linearity for only a limited number of compounds.

1. Introduction

Food Contact Materials (FCMs) are materials and articles intended to come into contact with food during processing, packaging, storage, or consumption. These materials encompass a wide variety of types, including plastics, paper, metals, glass, and multilayer composites [1]. Among them, plastics are by far the most prevalent due to their versatility, low cost, barrier properties, and ability to be molded into a wide range of functional packaging formats. Within the plastic category, two families stand out: polyolefins (POs), such as polyethylene (PE) and polypropylene (PP), and polyethylene terephthalate (PET). These materials are widely used for applications ranging from films and trays to bottles and caps. Their widespread adoption is driven by their chemical stability, mechanical resistance, and suitability for both single-use and reusable packaging systems [2].

POs are valued for their low density, excellent moisture barrier, and chemical inertness. They are commonly used in applications requiring flexibility or heat resistance, such as microwaveable containers or sealing layers [3]. PET, on the other hand, is primarily used in the production of bottles and food trays due to its transparency, high strength, and effective barrier to gases [4]. Both of them play a crucial role in modern food packaging systems, including those that incorporate recycled content, which is increasingly encouraged under circular economy strategies in the European Union and beyond [5].

However, the widespread use of plastic materials in direct food contact raises concerns about the potential migration of chemical substances from the packaging into food [2,6–8]. These migrating substances can be intentionally added substances (IAS), such as monomers or additives, or non-intentionally added substances (NIAS), which include degradation products, reaction by-products, degradation additives and impurities [9]. Among the latter, volatile and semi-volatile compounds are of particular interest, as they may transfer more easily into food or food simulants under common usage conditions [10–12]. To ensure consumer safety, it is essential to monitor and control such migrations, particularly in light of increasingly stringent regulations [13].

Food safety authorities, including the European Food Safety Authority (EFSA), require that FCMs do not transfer their constituents to food in quantities that could endanger human health, cause unacceptable changes in food composition, or affect the organoleptic characteristics of food. In the European Union, the regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food establishes specific migration limits (SMLs) for many IAS, as well as

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specific migration limits (SMLs) for total extractables [13]. However, NIAS are not systematically regulated, and their identification and quantification pose a major analytical challenge due to their diversity and the lack of reference standards [14]. This creates a pressing need for powerful, sensitive, and non-targeted analytical methods that can provide a comprehensive chemical profile of migration extracts and packaging materials.

Solid-phase microextraction (SPME) has emerged as a solvent-free, efficient technique for the analysis of volatile and semi-volatile compounds in complex matrices [15–17]. The introduction of SPME Arrow fibers represents a significant advancement in this field [18]. These fibers offer a larger sorptive phase volume and greater mechanical robustness compared to conventional SPME fibers [19], leading to enhanced sensitivity, improved reproducibility,faster extraction and extended fiber lifespan. Arrow SPME fibers are particularly well suited for the analysis of complex matrices such as food packaging, where a wide range of volatile and semi-volatile compounds may be present at trace levels. Additionally, their compatibility with both headspace (HS) and direct immersion (DI) modes enables flexibility in addressing a variety of sample types, including solid plastics and migration simulants.

Despite their advantages, the analytical performance of Arrow SPME is highly dependent on the extraction conditions, including temperature, extraction time, and sample matrix characteristics [15,17]. Therefore, systematic optimization of the extraction parameters is essential to fully exploit the capabilities of these arrows. More broadly, it is important to emphasize that such optimization is not exclusive to SPME Arrow, but rather a fundamental principle applicable to all sample preparation and extraction techniques, which should always be tailored to the specific requirements of the analysis. Moreover, the comparison between HS and DI modes remains underexplored for complex matrices like recycled plastics and migration extracts, which often contain heterogeneous mixtures of unknown compounds. Such optimization is especially relevant in the context of evaluating recycled plastics, where potential degradation and contamination introduce additional variability in the chemical profile.

This work addresses current analytical challenges in the characterization of volatile and semi-volatile compounds in FCM, particularly in relation to NIAS and complex migration matrices. The main contribution lies in the systematic evaluation of SPME Arrow as an extraction approach for both solid polymers and migration extracts, including recycled polyolefins and PET. A structured workflow was established, encompassing fiber coating selection, comparison of headspace and direct immersion modes, and matrix-specific optimization under accelerated migration conditions. The study also defines, for the first time, the practical limitations associated with ethanol-rich simulants and direct immersion, clearly establishing the operational boundaries of the technique. Within this framework, the results demonstrate that SPME Arrow enables robust and sensitive multi-analyte quantification in representative FCM simulants, supporting its applicability to routine analysis. Therefore, the scope of this work extends beyond method optimization, providing a validated analytical strategy and practical guidance for the implementation of SPME Arrow in complex migration testing scenarios.

2. Material and methods

2.1. Chemicals and reagents

Absolute ethanol for UV, IR (HPLC grade) were obtained from Panreac (Barcelona, Spain) and methanol (LC-MS quality) were obtained from Honeywell (Germany). Glacial acetic acid CAS 64–19–7 (ACS reagent) were obtained from Honeywell (Germany)

Sodium hydroxide 0.25 mol/L standard volumetric solution were purchased from Sigma-Aldrich Quimica S.A. (Madrid, Spain). Sodium hydroxide was used for neutralization of the acetic acid extract.

Ultrapure water was produced using a Milli-Q Ecomatic Wasserlab GR 216,071 system (Madrid, Spain).

Analytical standards were acquired from Sigma-Aldrich and included acetophenone (99 %, liquid ReagentPlus), benzaldehyde (≥99 %, liquid, ReagentPlus), benzophenone (analytical standard), C7–C40 certified alkanes solution (certified reference material, 1000 μg/mL each component in hexane), 2,4-di-tert-butylphenol (solid 99 %), D-limonene (ReagentPlus®, 99 %), isophorone (liquid 97 %), methyl salicylate (ReagentPlus®, ≥99 % (GC)), naphthalene (analytical standard), nonanal (analytical standard), o-xylene (analytical standard), styrene (analytical standard), 2-tridecanone (solid 99 %), butylated hydroxytoluene (analytical standard), hexadecane (99 %, liquid, suitable for synthesis, ReagentPlus), and 2,6-diisopropylnaphthalene (analytical standard).

2.2. Sample collection and treatment

Two types of recycled plastic materials have been used: polyethylene terephthalate (PET) and polyolefins (POs). Both materials studied were pellets provided by international recycling companies. Regarding PET, a total of six different recycled pellet samples were proportionally mixed to create a pooled PET sample. Two sample treatments were carried out for each sample, one for the direct analysis of the materials and other for migration tests.

For the direct analysis of the materials, pellets were cryogenically ground at 10,000 rpm while constantly adding liquid nitrogen in a RETSCH ZM200 Ultra Centrifugal Mill using a stainless-steel ring sieve with a pore size of 0.5 mm, resulting in a powder. This treatment not only ensures homogeneity of the sample without loss of volatiles but also increases the specific surface area of the material which leads to a higher release of potential migrants. Direct material testing is an interesting alternative to migration testing as it allows the detection of potential migrants without waiting for long material-food contact times.

Concerning migration tests, 35.5 g of ground pellets were immersed in 250 mL of food simulant covering the plastic cup with aluminum foil to avoid contamination. Food simulants used were ethanol 95 % v/v, ethanol 10 %v/v, and acetic acid 3 % w/v. Migration conditions were accelerated migration for 2 hours at 70°C as indicated in EU legislation [13]. It is important to notice that the legislative ratio of 6 dm^2/kg simulant is exceeded in order to enhance the release of compounds for optimize the method. Lastly, ground pellets and migrations extracts were used for the optimization of SPME. Blanks were simultaneously prepared for each simulant.

2.3. Gas chromatography-mass spectrometry

A PAL RSI 85 autosampler Series 2 was used with a gas chromatograph 8890 GC System coupled to a mass spectrometer (5977C GC/MSD) from Agilent Technologies (California, USA). Chromatographic separation was performed out using a DB-5 MS UI column from Agilent (5 % phenyl – 95 % dimethylpolysiloxane, 30 m x 0.25 mm i.d. and 0.25 μm film thickness). The inlet temperature was set at 250°C in splitless mode and ultra inert liners (2 mm id for SPME Arrow injection) were used with a fiber desorption time of 8 min. The oven temperature was as follows: 50°C hold for 5 min, raised to 300°C at 8°C/min, and held for 10 min from Su et al. [20]. High purity helium was the carrier gas at a constant flow rate of 1 mL/min. MS spectra were obtained by electron ionization (EI) at 70 eV in scan mode monitoring m/z between 45 to 700. Transfer line and ion source temperatures were both set at 250°C. Data acquisition was performed using Agilent MassHunter Acquisition software version 13.0.

2.4. Chromatographic data processing with MS-DIAL and candidate identification

Chromatographic data was processed using MS-DIAL software version 4.9 [21] in combination with the NIST 20 library for peak

deconvolution, alignment, and tentative identification. Software parameters were configured according to previously reported settings [22]. To improve the reliability of compound identification, both the mass spectra and retention indices (RIs) of all candidate compounds were manually evaluated. Identification levels were subsequently assigned to each compound in accordance with the criteria established [23].

2.5. Fiber coating

Five commercial SPME Arrow fibers (d = 1.1 mm) from Agilent were used to compare their performance: Polydimethylsiloxane 100 μm (PDMS), Polyacrylate 100 μm (PA), Carboxen/Polydimethylsiloxane 120 μm (CAR/PDMS), Divinylbenzene/Polydimethylsiloxane 120 μm (DVB/PDMS) and Divinylbenzene/Carboxen/Polydimethylsiloxane 120 μm (DVB/CAR/PDMS). All fibers were previously conditioned according to the manufacturer's recommendations before use. Additionally, conventional SPME fiber DVB/CAR/PDMS from Supelco was also used.

2.6. Final optimum SPME Arrow procedure

Based on the comprehensive optimization of extraction parameters, fiber coatings, and extraction modes across ground polymers and migration extracts, a final harmonized HS-SPME Arrow procedure was established to ensure robust, sensitive, and reproducible non-targeted analysis of volatile and semi-volatile compounds in food contact materials.

For ground polymer samples (rPOs and rPET), mixed-phase coatings demonstrated superior performance due to their ability to combine adsorption and absorption mechanisms across a wide polarity range. In particular, DVB/CAR/PDMS and DVB/PDMS fibers achieved the highest overall desirability and were selected as the most suitable coatings for comprehensive screening. The optimal extraction conditions consisted of a sample amount of approximately 2 g, elevated extraction temperatures (typically 120°C for DVB/CAR/PDMS and 60°C for DVB/PDMS), and long extraction times (up to 60 min). These conditions maximize analyte release and headspace enrichment without reaching saturation, while maintaining high reproducibility. Cryogenic grinding of the polymer prior to extraction is a critical step to enhance surface area and improve analyte availability.

For migration extracts, headspace SPME was confirmed as the only reliable extraction mode. Direct immersion was excluded due to fiber saturation and incompatibility with organic-rich matrices. Among the simulants evaluated, ethanol 10 % and acetic acid 3 % provided optimal conditions by ensuring a balanced partitioning between liquid phase, headspace, and fiber coating. Ethanol 95 % was discarded due to fiber swelling effects and poor partitioning behavior.

The optimized HS-SPME conditions for migration extracts were defined through DOE and RSM approaches. A high extraction temperature of 75°C was consistently optimal across all matrices, enhancing analyte volatilization and transfer into the headspace. Extraction time was matrix-dependent: 60 min for ethanol 10 % extracts (both PET and PO), and shorter times (approximately 20 min) for PET in acetic acid 3 %, reflecting faster equilibrium under acidic conditions. Sample volume also influenced extraction efficiency, with larger volumes (10 mL) preferred for ethanol 10 %, while acetic acid 3 % required matrix-specific adjustments (1 mL for PET and ~10 mL for PO).

Overall, the final optimized HS-SPME Arrow procedure combines: (i) the use of mixed-phase fibers (preferably DVB/CAR/PDMS), (ii) elevated extraction temperatures to promote volatilization, (iii) sufficiently long extraction times to reach equilibrium without saturation, and (iv) careful selection of simulant type and volume to maintain stable partitioning conditions. This unified methodology enables comprehensive, reproducible, and high-sensitivity screening of unknown migrants in food contact materials, supporting advanced non-targeted analysis workflows.

2.7. Experimental development

2.7.1. Relevant factors for the SPME optimization

One of the most fundamental elements to consider is the type of SPME fiber coating. Different coatings exhibit varying affinities for analytes based on their physicochemical properties such as polarity, volatility, and molecular weight. Each of the five SPME fibres was individually optimised once the critical factors were identified to ensure a reliable comparison between the fibres.

Extraction time and extraction temperature are pivotal parameters in SPME. Increasing the extraction temperature generally enhances analyte volatility and diffusion rates, improving mass transfer from sample to fiber. Extraction time should be determined experimentally to take into account the kinetics of analyte transfer. Additionally, pre-equilibrium time must be sufficient to reach equilibrium conditions setting it to 20 min [15,17]. Stirring rate was considered and set to 600 rpm to avoid direct contact between the fiber and the sample ensuring fiber integrity. When working in headspace mode, the sample quantity was additionally evaluated as a relevant parameter, as it increases the amount of analyte available, the same is true for direct immersion mode.

Regarding migration extracts, parameters such as pH and ionic strength are key parameters. Sample pH is particularly relevant for analytes that can exist in ionized and non-ionized forms. The pH should be adjusted relative to their pKa to favor the non-ionized form and extreme values should be avoided if fiber integrity or analyte stability were compromised. In the case of performing non-targeted screening, the identity of the overall analytes remains unknown so a pH = 7 was selected as the most suitable for migration extracts of recycled materials as explained in the literature [20]. Ionic strength was also studied by Su et al, demonstrating that the extraction efficiency was negatively impacted with a high increase of the chromatogram baseline. Therefore, no salt was used for the optimization, although acetic acid and sodium hydroxide alter the ionic strength of the sample solutions.

2.7.2. Response surface methodology

Knowing the relevant factors, a response surface methodology (RSM) was applied to optimize the experimental conditions for the extraction of volatiles using Arrow SPME fibers. The design and statistical analyses were carried out using Minitab ® (version 20.4). A Central Composite Design (CCD) was used for each of the three types of samples evaluated: solid, headspace, and direct immersion.

For the solid and headspace migration extracts, which shared the same design, three independent variables were studied: extraction time, extraction temperature, and sample amount. Sample amount is considered an optimization parameter in HS-SPME due to its direct influence on headspace volume and analyte partitioning. In DI-SPME, however, it is generally maintained above a minimum threshold to prevent depletion effects (situations in which the fiber extracts a significant fraction of the analyte, leading to a decrease in its concentration in the sample and a shift in the extraction equilibrium). Additionally, if the sample volume is too low, the fiber may not remain fully immersed in the liquid phase and can be partially exposed to the headspace, resulting in simultaneous contact with liquid and air. This introduces a mixed extraction regime with an additional equilibrium between fiber–liquid–air, which can compromise reproducibility. As a result, sample amount is less frequently treated as an optimization variable in DI-SPME, although it may still become relevant under conditions where sample volume is limited or analyte concentrations are low.

A blocked CCD was constructed with an axial distance (α) of 1, including 20 experiments divided into two blocks. For the direct immersion condition, only two factors were considered: extraction time and extraction temperature. In this case, a rotatable CCD was used with an axial distance (α = 1.414), consisting of 14 experiments arranged similarly in two blocks. The levels of each factor are summarized in Table 1. The use of different α values was necessary due to the fact that axial points of sample amount would be outside the natural experiment

Table 1
Coded and uncoded values of variables of CCD model for the optimization for migration extracts of recycled plastic in HS mode.

	Coded values		
	-1	0	1
		True values	
Extraction time, X_1 (min)	20	40	60
Extraction temperature, X_2 (°C)	60	90	120
Amount, X_3 (g)	1	2	3

range. For further information regarding the variables for the rest of CCD please check Tables S2 and S3.

All response optimization and model fitting were performed using Minitab's response surface platform, and model adequacy was assessed through analysis of variance (ANOVA), significance of regression coefficients (p-values), and coefficient of determination (R^2 adjusted and predicted). The desirability function was used to determine the optimal conditions for each sample type.

2.7.3. SPME Arrow sensitivity and linearity

Calibration capability of Arrow SPME fibers was studied with a mixture of 15 analytes found in food contact materials, particularly in recycled plastics. The detailed list can be found in Table S1. The larger sorption phase volume is suspected to not only improve the response [19] but also the linear range.

3. Results and discussion

3.1. Optimization of HS-Arrow SPME parameters for ground plastic

A critical aspect of implementing SPME effectively lies in the optimization of the extraction parameters which directly influence efficiency, selectivity and reproducibility of the method. For this reason, the temperature, extraction time and amount of sample were optimized as indicated in Table 1 and Tables S2 and S3. Fig. 1A shows how increasing the extraction temperature and time increases the number and the response of the compounds. However, this optimization process involves several interrelated factors, each of which must be carefully evaluated and adjusted according to the sample matrix. As shown in Fig. 1B, grinding the pellets with cryogenic liquid is essential to increase the number of compounds and the response as the specific surface area is increased. The baseline drift could be explained by the release of additional matrix components from the plastics as the temperature increases. This effect is minimal in blank chromatograms, suggesting that it does not significantly compromise sensitivity, since the blank signal will be subtracted during data processing.

Each fiber was optimized considering the total peak area of identified analytes by RSM methodology considering the critical parameters as extraction time, extraction temperature and sample amount. Optimization experiments design can be found in Table S4 and all identified compounds can be found in Table S8 (Up to 110 compounds identified in rPO and 27 in rPET). Fig. 2 shows the response surface methodology plots for all fibers for PET. A detailed analysis reveals several important trends governing the HS-SPME Arrow extraction efficiency. One of the most prominent effects is the strong influence of sample amount, which leads to an increase in response by approximately a factor of 3–4. This behavior can be attributed to the increased availability of analytes in the headspace as the sample mass increases. Under the studied conditions, headspace saturation is not reached, and therefore the system remains far from equilibrium limitations, particularly for coatings with significant adsorption capacity such as DVB/CAR/PDMS and DVB/PDMS.

In addition, clear interaction effects between variables are observed, reflecting the complex interplay between analyte release from the polymer matrix and mass transfer to the fiber coating. For instance, DVB/PDMS exhibits a positive interaction between extraction time and sample mass at lower temperatures, indicating that longer extraction times are required to compensate for slower diffusion processes. At higher temperatures, however, analyte transfer is enhanced, and the relative importance of extraction time and sample amount is reduced.

For several fibers, particularly DVB/PDMS and PA, a maximum in the response is observed as a function of extraction time. This behavior can be explained by the combined effect of equilibrium processes and competitive phenomena. At short extraction times, the response increases as analytes partition from the sample into the headspace and are subsequently extracted by the fiber. However, at longer extraction times, the system approaches equilibrium, and further extraction does not lead to increased uptake. Moreover, competitive displacement effects may occur, where more abundant or more strongly interacting compounds replace previously extracted analytes on the active sites of the coating. This is especially relevant for adsorption-based or partially adsorptive coatings. Additionally, prolonged exposure at elevated temperatures may promote thermal degradation or transformation of certain compounds, leading to a decrease in the overall signal. Back-diffusion from the fiber to the headspace may also contribute to this effect under extended extraction conditions.

These phenomena explain why, in the case of DVB/PDMS, higher temperatures combined with long extraction times may result in a decrease in response, and why PA exhibits a defined optimum despite its strong affinity for polar compounds. In contrast, DVB/CAR/PDMS does not show a decline within the experimental domain, suggesting that

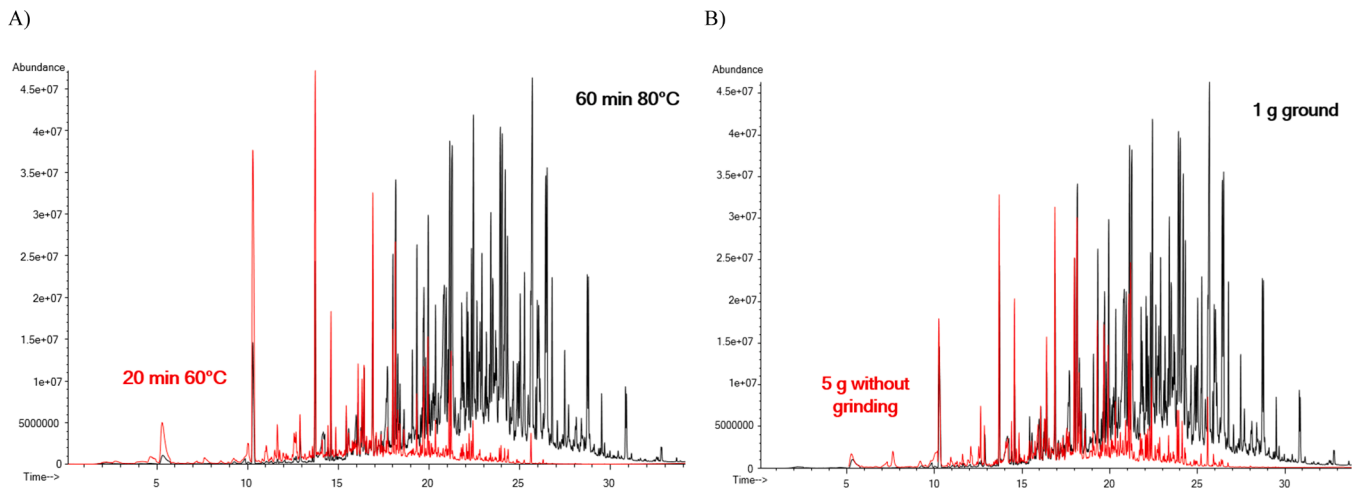

Fig. 1. Overlayed chromatograms of POs at different extraction temperature and time (A) and comparison of 1 g of ground POs with 5 g without grinding (B).

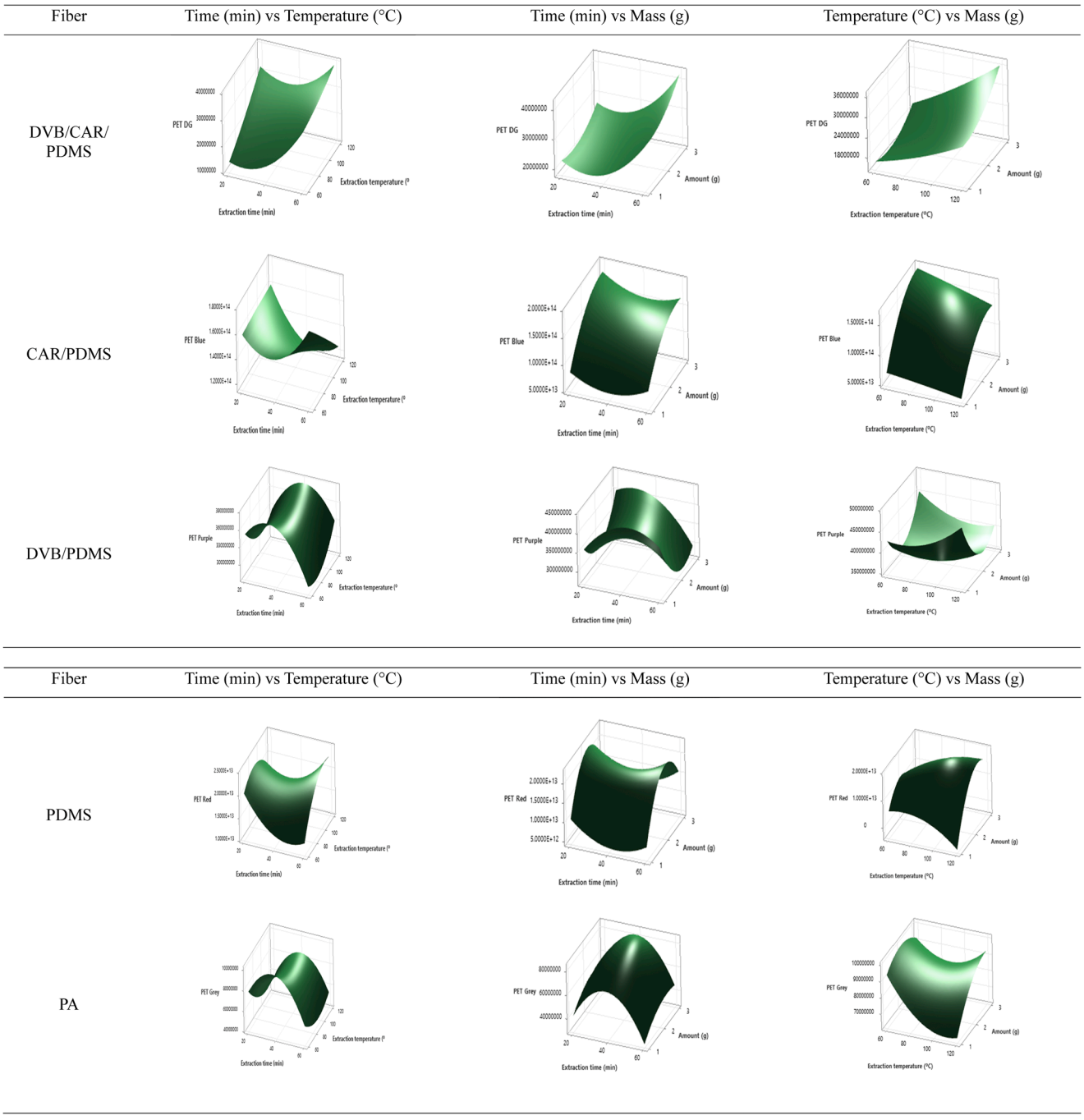

Fig. 2. RSM plots for HS optimization of recycled PET for each fiber.

equilibrium is not fully reached and that its mixed adsorption/absorption mechanism provides higher capacity and broader analyte coverage.

The influence of temperature is particularly pronounced for CAR/PDMS and PA, where extraction is primarily temperature-driven, consistent with their affinity for polar and semi-volatile compounds. Conversely, CAR/PDMS shows a relatively weak dependence on sample amount, indicating that headspace saturation may be approached more rapidly for this coating. PDMS displays a broad and gently sloping maximum, reflecting its absorption-based mechanism and resulting in a more robust performance across a wide range of conditions, with limited sensitivity to extreme extraction times.

Overall, these results highlight that coatings combining adsorption and absorption mechanisms, such as DVB/CAR/PDMS and DVB/PDMS, provide superior and more robust extraction performance across different polymer matrices. In contrast, more selective coatings such as PA, while effective for specific compound classes, are less suitable for comprehensive non-target screening of complex volatile profiles. Additional information regarding RSM plots for POs can be found in Figure S1.

Table 2 summarizes the optimal HS condition for the analysis of ground POs and PET. The optimization revealed that DVB/CAR/PDMS and DVB/PDMS fibers achieved the highest composite desirability (1.0), under conditions of long extraction times (60 min), though with markedly different extraction temperatures (120°C vs. 60°C, respectively). CAR/PDMS also performed very well (0.97), requiring shorter extraction time (47.5 min) but still at elevated temperature (120°C). In contrast, PDMS reached a similar performance (0.96) under milder conditions (60°C, 36.97 min, 1.95 g), while PA exhibited the lowest

Table 2
Optimal HS conditions for the analysis of volatiles in ground PET for five SPME Arrow fiber coatings.

Ground PET	Extraction time (min)	Extraction temperature (°C)	Sample amount (g)	Composite desirability
DVB/ CAR/ PDMS	60.0	120	3.00	1
CAR/ PDMS	47.5	120	1.00	0.97
DVB/ PDMS	60.0	60	2.86	1
PDMS	37.0	60	1.95	0.96
PA	60.0	120	2.52	0.815

composite desirability (0.815), despite requiring long extraction time (60 min) and high temperature (120°C). These results highlight those mixed coatings combining adsorption and absorption mechanisms (DVB/CAR/PDMS and DVB/PDMS) provide the most robust performance across polymers, whereas PA is less efficient for the broad volatile profile.

3.2. Selection of SPME fiber

One of the most fundamental elements to consider is the type of SPME fiber coating. Different coatings exhibit varying affinities for analytes based on their physicochemical properties such as polarity, volatility, and molecular weight [24]. For instance, PDMS is a non-polar coating ideal for the extraction of volatile, non-polar compounds such as hydrocarbons, while coatings such as CAR/PDMS are more effective for capturing small, volatile polar compounds due to their microporous structure. Other coatings like DVB/PDMS or PA are suited for semi-volatile and polar analytes, respectively. The selection of the fiber coating must therefore be aligned with the chemical characteristics of the target analytes to ensure optimal extraction performance. This is particularly critical in the field of FCM where non-targeted screening analysis are mandatory due to the unknown identity of the majority of compounds that may migrate to the food in the first place.

The observed differences in extraction performance can be directly correlated with the polarity of both the fibers and the analytes. The DVB/CAR/PDMS fiber, combining non-polar PDMS, semi-polar DVB, and microporous CAR, covers a broad polarity range, enabling efficient extraction of volatiles with diverse physicochemical properties, which explains the dense and complex TIC. CAR/PDMS, with CAR favoring small polar compounds and PDMS non-polar volatiles, provides extensive but slightly less intense peak coverage. In contrast, DVB/PDMS and PDMS fibers preferentially extract semi-volatile and non-polar compounds, resulting in fewer but highly intense peaks, while the polar PA fiber shows limited efficiency for the primarily non-polar polyolefin-derived volatiles. This correlation confirms that fiber polarity critically governs extraction selectivity and efficiency, supporting the use of mixed-phase fibers for comprehensive non-targeted screening in FCM migration studies.

Considering this, each fiber type was tested in the optimized conditions of Section 0. Fig. 3 presents the overlaid total ion chromatograms (TICs) of ground POs obtained using the five different HS-SPME Arrow fiber coatings. The DVB/CAR/PDMS fiber produced the most complex chromatographic profile, with a high density of peaks across the entire retention time window, indicating its superior capability to extract a wide range of volatiles with diverse physicochemical properties. CAR/PDMS also displayed extensive peak coverage, though with slightly lower intensities compared to DVB/CAR/PDMS. In contrast, DVB/PDMS and PDMS generated chromatograms dominated by fewer, highly intense peaks, suggesting a preferential enrichment of specific volatile classes rather than broad-spectrum extraction. The PA fiber exhibited the lowest response, with limited peak abundance and diversity, highlighting its lower efficiency for polyolefin-derived volatiles under the tested conditions. Overall, the chromatographic profiles corroborate the optimization results, confirming that mixed-phase sorbents such as DVB/CAR/PDMS provide the most comprehensive volatile profile.

3.3. Optimized SPME Arrow conditions for migration extracts

When the Arrow fiber is immersed directly into EtOH 10 % or HAc 3 %, the extraction phase rapidly saturates. This behaviour can be attributed to high matrix–fiber affinity for mid-polarity compounds. In both EtOH 10 % and HAc 3 %, many migrating species display moderate

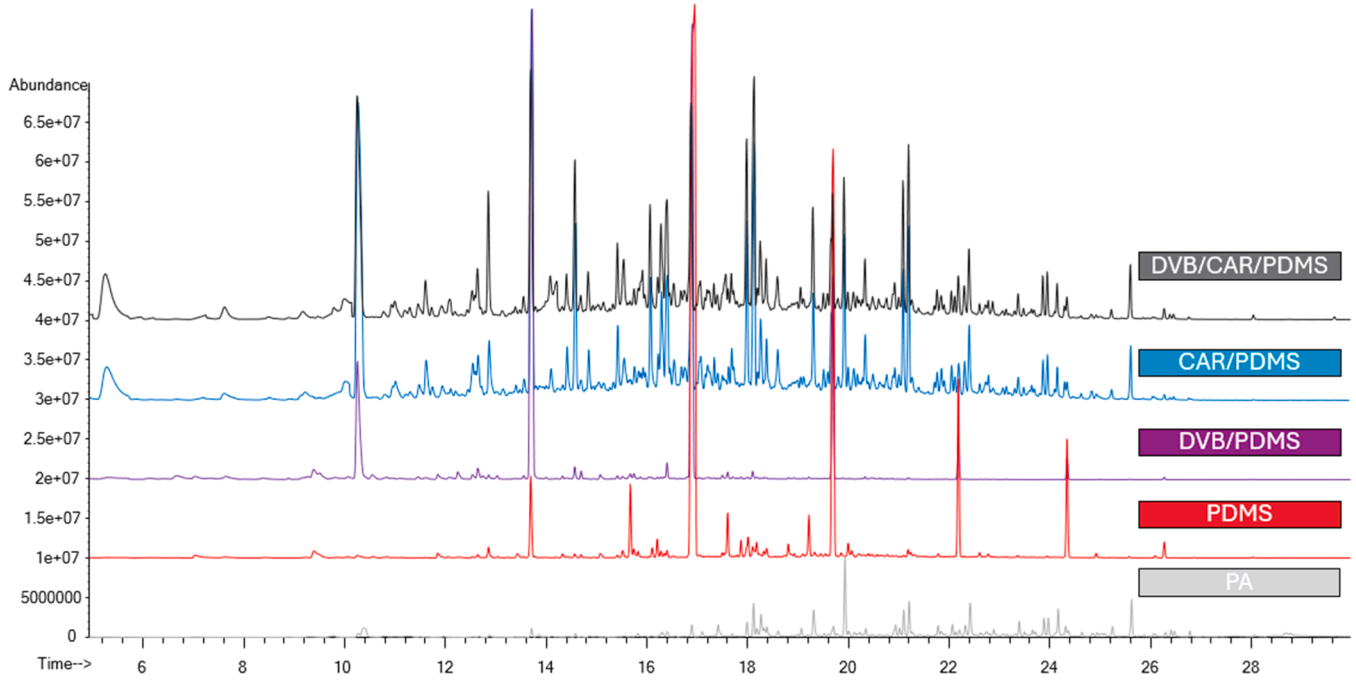

Fig. 3. Overlayed chromatograms of ground POs analyzed for each fiber in optimized conditions by HS-SPME-Arrow-GC–MS.

polarity. These matrices therefore promote strong partitioning toward the Arrow coating. The driving force for adsorption is high, and high-capacity Arrow phases can become saturated quickly because the analyte load in solution is relatively large compared to the coating volume.

As a result, DI-SPME in EtOH 10 % and HAc 3 % produced chromatograms with broadened peaks, plateaued total area responses, and replication issues characteristic of fiber saturation as shown in Fig. 4.

Ethanol 95 % was not evaluated in direct immersion because such a high organic content is incompatible with DI-SPME when using polymeric Arrow coatings. At this solvent strength, ethanol can severely swell the polymeric extraction phase, reducing its selectivity and potentially causing irreversible damage. In addition, the partition coefficients of analytes shift strongly toward the bulk solution in nearly pure organic media, making enrichment onto the fiber highly inefficient. The combination of coating swelling, loss of partitioning efficiency, and the risk of fiber degradation leads to extremely poor reproducibility.

In headspace mode, ethanol 95 % caused saturation of the Arrow coating due to its exceptionally high vapour pressure. Under these conditions, the headspace becomes dominated by ethanol vapour, which rapidly occupies the sorption sites of the coating and competes strongly with target analytes. As a result, the fiber becomes saturated primarily with solvent instead of analytes, leading to suppressed extraction efficiency, distorted chromatographic baselines, and unstable responses. Furthermore, the reduced volatility of many semi-volatile compounds in a nearly pure ethanol matrix limits their transfer into the headspace, further diminishing extraction performance.

Among all matrices evaluated, only ethanol 10 % and acetic acid 3 % provided conditions compatible with reliable headspace extraction. These solvents offer a balanced volatility profile that allows efficient transfer of analytes into the headspace without overwhelming the fiber with solvent vapours. The resulting partitioning between the liquid phase, headspace, and fiber remains stable, leading to selective adsorption of the compounds of interest and minimal competitive displacement. This favourable equilibrium ensures clean chromatographic profiles, consistent peak areas, and reproducible performance, confirming that HS-SPME is the most suitable extraction mode for EtOH 10 % and HAc 3 %. All identified compounds can be found in Table S8 where a total of 121 compounds were identified in ethanol 10 % and 162 in acetic acid 3 % for in rPET samples, while 178 were for both ethanol 10 % and acetic acid 3 % extracts of rPOs.Given their suitability in headspace mode, ethanol 10 % and acetic acid 3 % were selected for full optimization using a Design of Experiments (DOE) approach followed by Response Surface Methodology (RSM). This strategy enabled the systematic evaluation of key extraction parameters as extraction time, extraction temperature and simulant volume used. Fig. 5shows the RSM plots for HS optimization of PET migration extracts ethanol 10 % and acetic acid 3 %.

The optimization of HS-SPME conditions for all matrices and simulants demonstrated clear trends driven by the interplay between extraction temperature, extraction time, and sample volume as shown in Table 3.

Across all PET and PO extracts, a high extraction temperature of 75°C consistently maximized the analytical response, confirming that elevated temperatures enhance analyte transfer into the headspace and improve partitioning towards the Arrow fiber. The optimal extraction time, however, varied depending on the matrix. For ethanol 10 %, both PET and PO materials required the longest extraction time evaluated (60 min), indicating that the gradual release and volatilization of semi-volatile oligomers and NIAS in this simulant benefit from prolonged exposure to the headspace. In contrast, PET extracted in acetic acid 3 % reached its maximum response at a much shorter extraction time of 20 min, suggesting faster equilibrium under acidic conditions.

Sample volume (simulant amount) also played a key role. The highest desirability values for ethanol 10 % were obtained with 10 mL of simulant, both for PET (0.996) and PO (0.991), showing that larger volumes favor a stable headspace environment and sustained analyte release. For acetic acid 3 %, the optimal volumes were substantially lower, 1 mL for PET and 9.9 mL for PO, reflecting matrix-dependent differences in analyte solubility, volatility, and release kinetics. PET in acetic acid 3 % produced a remarkably high desirability (0.982) despite the small sample volume, whereas the PO/acetic acid 3 % combination showed a significantly lower overall desirability (0.82), indicating reduced extraction efficiency under acidic conditions for polyolefins.

3.4. SPME Arrow sensitivity and linearity results

To validate the optimized HS-SPME conditions, a mixture of 15 representative analytes commonly detected in food contact materials was prepared and analysed under the selected parameters. The evaluation focused on sensitivity and linearity, comparing the performance of Arrow SPME against traditional SPME fibers in the two most suitable simulants identified previously: ethanol 10 % and acetic acid 3 %.

Sensitivity was evaluated by comparing the response factors obtained for each analyte using Arrow SPME and conventional SPME under identical analytical conditions. In both simulants, Arrow SPME provided consistently higher response factors, with increases ranging from 7 % to 14 % depending on the analyte, which is consistent with other publications [19]. This improvement can be attributed to the

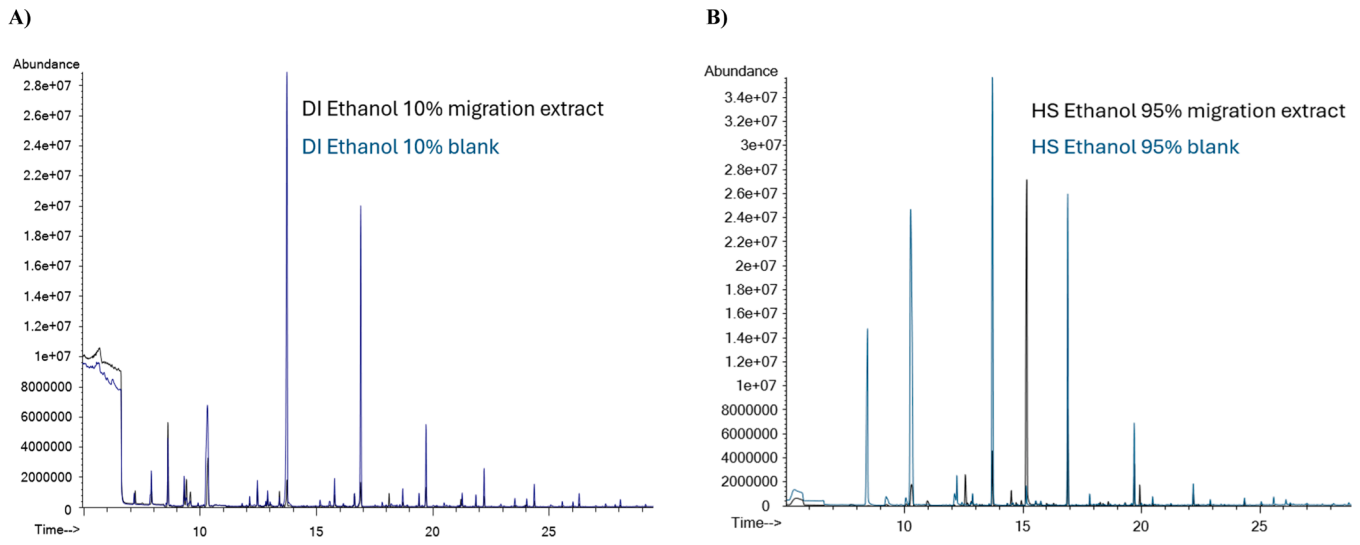

Fig. 4. Overlayed chromatograms of ethanol 10 % in DI mode (A) and ethanol 95 % in HS mode (B).

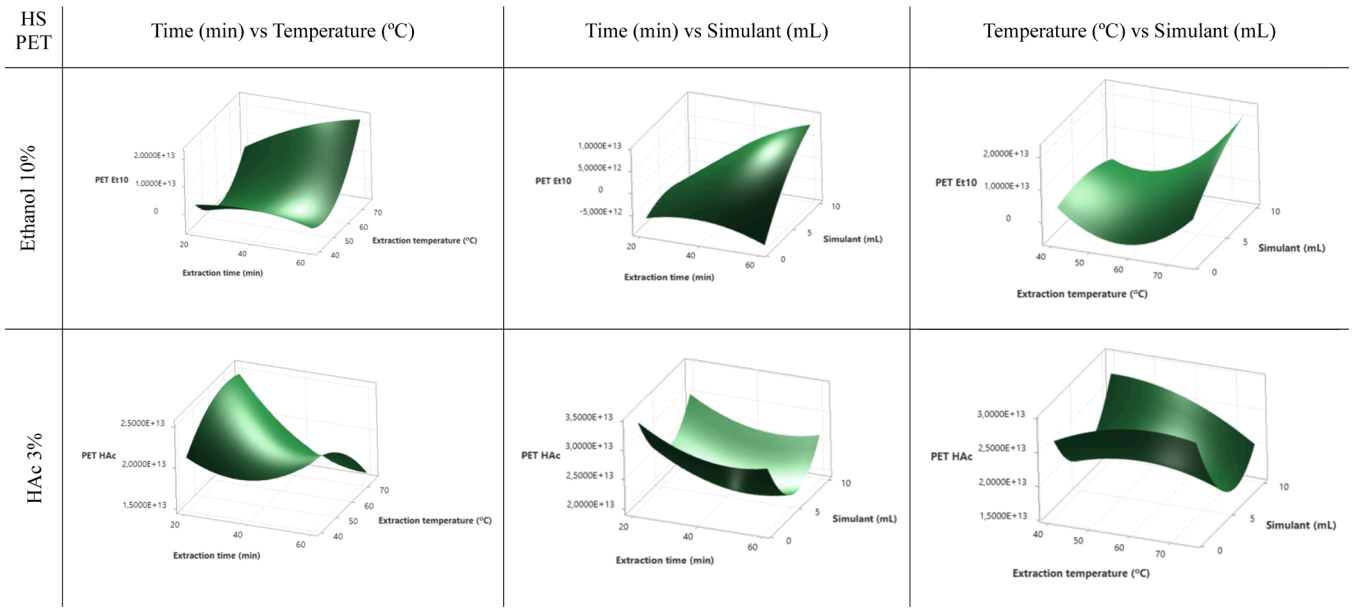

Fig. 5. RSM plots for HS optimization of PET migration extracts ethanol 10 % and acetic acid 3 %.

Table 3
Optimized conditions for DVB/CAR/PDMS Arrow fiber in DI mode for PET and POs in ethanol 10 % and acetic acid 3 %.

HS	Extraction time (min)	Extraction temperature (°C)	Simulant (mL)	Composite desirability
PET Ethanol 10 %	60	75	10	0.996
PET Acetic acid 3 %	20	75	1	0.982
POs Ethanol 10 %	60	75	10	0.991
POs Acetic acid 3 %	60	75	9.9	0.82

larger sorbent volume and enhanced extraction capacity of the Arrow format, which allows greater enrichment of semi-volatile and moderately polar migrants. The enhancement was systematic across the full panel of 15 compounds, demonstrating that Arrow SPME delivers a meaningful gain in sensitivity for the broad range of analytes typically encountered in FCM extracts.

A full 15-point calibration curve was constructed to assess the linearity of the method with all analytes analysed simultaneously. All calibration solutions were prepared gravimetrically to ensure high accuracy and reproducibility. Individual stock solutions of each analyte were first prepared separately in an acetonitrile/methanol mixture. These stock solutions were then used to prepare working solutions.

A multi-analyte calibration mixture containing all 15 target compounds was initially prepared and used to build a calibration curve covering a wide concentration range (approximately 20 ng/kg to 20 µg/kg) with 15 calibration levels. This approach allowed evaluation of the capability of SPME Arrow for simultaneous multi-analyte quantification.

To further assess potential matrix effects, competition, or saturation phenomena, two additional calibration sets were prepared by splitting the analytes into two groups (7 and 8 compounds, respectively), which were calibrated independently under the same experimental conditions. Arrow SPME showed excellent linearity across the entire concentration range for all 15 analytes, enabling reliable quantitative evaluation. In contrast, traditional SPME exhibited acceptable linearity for only five analytes, as shown in Fig. 6, while the remaining compounds showed deviations from linear behaviour, most likely due to limitations in sorbent capacity, lower extraction efficiency, and increased susceptibility to competitive effects in multi-analyte mixtures.

The validation of the 15-analyte mixture using SPME Arrow demonstrated strong sensitivity, linearity, and precision in both ethanol 10 % and acetic acid 3 %, as summarized in Table 4. In ethanol 10 %, the method achieved very low LODs (0.007–0.047 µg/kg), reflecting

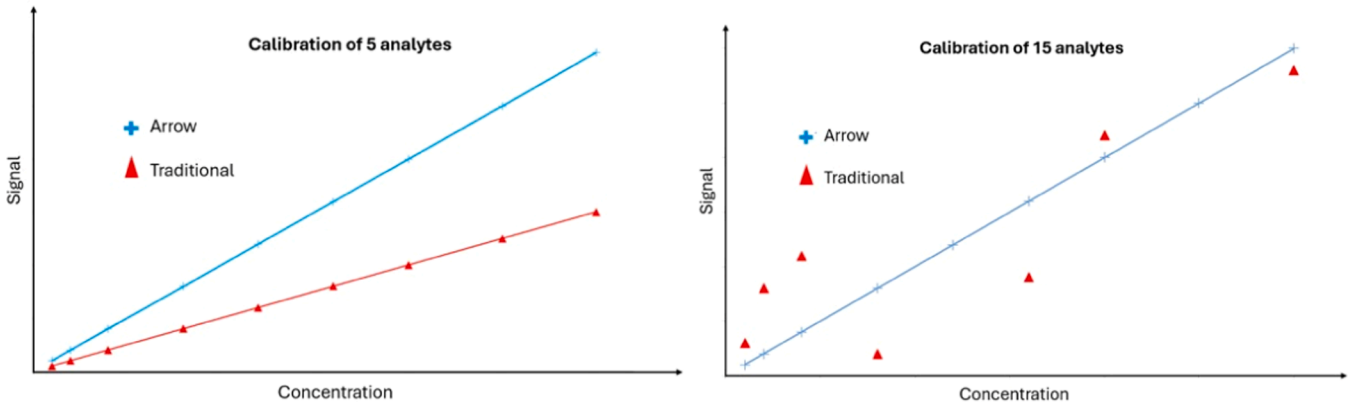

Fig. 6. Conceptualization of the linearity results of Arrow and traditional SPME.

Table 4
Calibration analytes along with the retention time (RT in min), retention index (RI), CAS number, formula, limit of detection (LOD), linear range, R^2, and repeatability (% RSD, n = 3) in simulants ethanol 10 % and acetic acid 3 %.

N	RT (min)	RI	*m/z*	Compound	CAS	Formula	Ethanol 10 %				Acetic Acid 3 %			
							LOD (µg/kg)	Linear range (µg/kg)	R^2	%RSD	LOD (µg/kg)	Linear range (µg/kg)	R^2	%RSD
1	7.27	890	91	o-Xylene	95–47–6	C_8H_{10}	0.038	0.125 - 15.89	0.997	13.90	-	-	-	-
2	7.28	890	104	Styrene	100–42–5	C_8H_8	0.009	0.030 - 17.97	0.998	9.45	0.009	0.030 - 1.42	0.995	4.98
3	9.24	962	106	Benzaldehyde	100–52–7	C_7H_6O	0.009	0.031 - 18.85	0.997	6.65	0.045	0.148 - 18.85	0.992	4.92
4	10.94	1030	68	D-Limonene	5989–27–5	$C_{10}H_{16}$	0.016	0.052 - 31.93	0.999	13.31	0.228	0.753 - 31.93	0.989	13.56
5	11.85	1069	105	Acetophenone	98–86–2	C_8H_8O	0.009	0.030 - 18.50	0.995	15.30	0.018	0.060 - 18.50	0.997	6.99
6	12.65	1104	57	Nonanal	124–19–6	$C_9H_{18}O$	0.039	0.130 - 1.32	0.984	10.88	0.008	0.027 - 16.62	0.997	8.70
7	13.04	1124	82	Isophorone	78–59–1	$C_9H_{14}O$	0.007	0.024 - 14.59	0.992	17.16	0.014	0.047 - 14.59	0.999	10.59
8	14.32	1187	128	Naphthalene	91–20–3	$C_{10}H_8$	0.010	0.032 - 19.78	0.995	14.44	0.019	0.064 - 8.32	0.992	9.45
9	14.54	1198	120	Methyl salycilate	6934–03–8	$C_{12}H_{16}O_3$	0.008	0.025 - 15.07	0.999	13.32	0.036	0.118 - 3.21	0.993	13.22
10	19.65	1496	58	2-Tridecanone	593–08–8	$C_{13}H_{26}O$	0.007	0.023 - 14.16	0.976	14.41	0.007	0.023 - 14.16	0.985	6.35
11	19.91	1514	191	2,4-di-tert-butyl phenol	96–76–4	$C_{14}H_{22}O$	0.047	0.156 - 1.58	0.993	13.52	0.020	0.065 - 8.39	0.994	4.86
12	19.99	1519	205	Butylated Hydroxytoluene	128–37–0	$C_{15}H_{24}O$	0.008	0.025 - 3.27	0.990	11.66	0.008	0.025 - 0.47	0.992	13.09
13	21.18	1600	57	Hexadecane	544–76–3	$C_{16}H_{34}$	0.009	0.031 - 18.57	0.996	12.26	0.018	0.060 - 3.95	0.992	11.40
14	21.77	1640	105	Benzophenone	119–61–9	$C_{13}H_{10}O$	0.007	0.023 - 13.70	0.999	13.04	0.007	0.023 - 0.54	0.987	10.74
15	23.12	1737	197	2,6-Diisopropylnaphthalene	24,157-81-1	$C_{16}H_{20}$	0.009	0.031 - 18.91	0.995	16.35	0.009	0.031 - 4.02	0.997	7.03

excellent extraction efficiency across a broad chemical space, particularly for semi-volatile and mid-polarity analytes such as isophorone, 2-tridecanone, benzophenone, and BHT. In acetic acid 3 %, LODs were generally higher, especially for hydrophobic compounds like limonene and naphthalene, consistent with reduced partitioning of non-polar analytes into the headspace in acidic aqueous matrices. Nevertheless, several analytes still displayed LODs below 0.01 µg/kg, confirming that Arrow SPME retains strong sensitivity even under less favourable extraction conditions.

Linearity was excellent in both simulants, with R^2 values typically $\geq$ 0.990, demonstrating the robust quantitative capabilities of the Arrow format. Ethanol 10 % provided the strongest linear behaviour (up to R^2 = 0.999), while acetic acid 3 % also delivered high-quality calibration fits (R^2 = 0.985–0.999). The linear ranges were consistently broad enough to cover concentration levels relevant to FCM migration studies, and they remained stable across chemically diverse analytes.

Precision was satisfactory under both conditions. In ethanol 10 %, most %RSD values fell between 6 % and 17 %, with some compounds achieving exceptionally good repeatability (e.g., nonanal, 2,4-di-tert-butylphenol). In acetic acid 3 %, precision tended to improve, with several analytes showing %RSD values near or below 5 %, indicating more stable extraction equilibria in the acidic matrix.

4. Conclusions

This study confirms the strong analytical performance of SPME Arrow fibers, particularly DVB/CAR/PDMS, for the analysis of volatile and semi-volatile compounds in FCMs. Among the five coatings evaluated, DVB/CAR/PDMS showed the highest extraction efficiency and reproducibility, making it the optimal choice.

HS extraction proved to be the only suitable mode, as DI led to fiber saturation and poor reproducibility, especially in ethanol-rich matrices. Ethanol 95 % was excluded due to complete signal suppression, while ethanol 10 % and acetic acid 3 % allowed effective HS extraction, although with different optimal conditions. Overall, optimized HS conditions provided good performance for both simulants.

Method evaluation with 15 analytes showed that SPME Arrow improved sensitivity, with response factors 7–14 % higher than traditional SPME. It also demonstrated superior linearity ($R^2 > 0.990$ for all analytes) and lower variability, whereas conventional SPME showed acceptable linearity for only a limited number of compounds.

Overall, SPME Arrow proved to be a more robust, sensitive, and reliable approach for multi-analyte quantification in FCM migration studies.

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CRediT authorship contribution statement

Carlos Estremera: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Pilar Alfaro:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Investigation, Formal analysis. **Cristina Nerín:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Funding acquisition. **Celia Domeño:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Methodology, Formal analysis, Conceptualization.

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.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2026.466946.

Data availability

Data will be made available on request.

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