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# Optimization of pressurized liquid extraction (PLE) for rapid determination of mineral oil saturated (MOSH) and aromatic hydrocarbons (MOAH) in cardboard and paper intended for food contact

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ABSTRACT

Packaging can represent a primary source of food contamination with mineral oil saturated hydrocarbons (MOSH) and aromatic hydrocarbons (MOAH), especially when recycled cardboard or mineral oil based printing inks are used. A pressurized liquid extraction (PLE) method, followed by on-line LC–GC analysis, has been optimized for rapid mineral oil determination in cardboard and paper samples. The proposed method involves extraction with hexane (2 cycles) at 60 °C for 5 min, and allows for the processing of up to 6 samples in parallel with minimal sample manipulation and solvent consumption. It gave good repeatability (coefficient of variation lower than 5%) and practically quantitative extraction yield (less than 2% of the total contamination found in a third separate cycle). The method was applied to different cardboards and paper materials intended for food contact. Results obtained were similar to those obtained by applying classical solvent extraction with hexane/ethanol 1:1 (v/v) as described by Lorenzini et al. [20].

## 1. Introduction

Mineral oils are complex mixtures of saturated hydrocarbons (MOSH) comprising linear, branched and cyclic compounds, and variable amounts of aromatic hydrocarbons (MOAH), mainly alkylated. Food can be contaminated with mineral oils from different sources [1], the most important being food grade mineral oils (free from MOAH) widely used in the food industry, environmental contamination, and migration from packaging [1–3].

Although MOSH toxicity in humans has not been completely elucidated, it has been proven that saturated hydrocarbons from C16 to C35 can accumulate in the body [1–4]. Several MOAH have been shown to be potential carcinogens, including 3- and 4-ring constituents possibly migrating from printed cardboard [5].

Cardboard packaging represents an important source of food contamination with MOSH and MOAH, especially when recycled fibers or mineral oil based printing inks are used. Cardboard made with recycled fibers contains mineral oils from different routes such as newspaper and other printed paper entering the recycling process, adhesives and solvents used as carriers for binders and additives, and waxes added to improve water resistance [6]. Of particular concern are the offset printing inks used for newspapers, since they contain hydrocarbons of sufficient volatility ($<$C24) to be transferred via gas-phase [7]. The presence of a suitable barrier can limit migration [8].

First data on migration of mineral oil from printing ink and recycled cardboard were published in 1997 [9], but the issue became public only after the German Federal Institute for Risk Assessment (BfR) released its opinion (expressed in December 2009) stating that the migration of mineral oil from boxes of recycled cardboard into dry foods should urgently be reduced [10].

From 2009 to 2012 a number of papers, summarized in a review [5], have been published by Grob and co-workers on this topic. In 2011, a survey on 119 food samples from the German market [11] revealed high contamination levels of MOSH $<$C24 in cardboard packaging (on average 65 and 265 mg kg$^{-1}$ in virgin and recycled cardboard boxes, respectively) and in foods, as consequence of migration from the packaging (on average 10.9 mg kg$^{-1}$ for food packaged in recycled fibers). MOAH represented 10–20% of the total mineral oil contamination. Similar results were reported for recycled and virgin printed packaging materials in the recent survey of the UK Food Standard Agency

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(on average 160 mg $kg^{-1}$ of MOSH $<$ C24 and 31 mg $kg^{-1}$ of MOAH $<$ C24, respectively) [12].

Rapid MOSH and MOAH determination in packaging material is a useful tool for monitoring purposes and migration studies.

Mineral oil determination has been largely performed with on-line liquid chromatography–gas chromatography–flame ionization detector (LC–GC–FID) using different interfaces mainly based on the retention gap techniques [13,14], and, more recently, on the syringe-based programmed temperature vaporizer (PTV) interface [15,16]. By a careful optimization of the LC conditions, MOSH and MOAH can be separated on a silica column as described by Biedermann et al. [17]. MOSH and MOAH separation can also be achieved by off-line solid phase extraction (SPE)–GC-FID [18] exploiting the ability of silver silica to retain fat and efficiently separate the MOSH and the MOAH [18,19].

Extraction and sample preparation often represent the slowest stage of an analytical method. A method for MOSH and MOAH extraction from cardboard, based on classical solvent extraction, was recently developed [20]. According to this method, the cardboard is extracted with a mixture of hexane/ethanol (1:1 v/v), able to insure good extraction yields and a limited extraction of high-boiling material disturbing GC analysis. The ethanol is then separated by adding an appropriate amount of water, and the hexane phase is used for LC–GC analysis.

Pressurized Liquid Extraction (PLE), described for the first time in 1995 for the extraction of environmental contaminants from waste samples [21], and later for the extraction of contaminating hydrocarbons from soil [22], is a well-established sample preparation technique which uses high temperatures and high pressures for rapid and efficient analyte extraction from solid samples. The solvent is pumped into an extraction vessel containing the sample. The high pressure allows to maintain liquid the solvent at temperatures well above its atmospheric boiling point. As the temperature is increased, the viscosity of the solvent is reduced increasing its ability to wet the matrix and solubilize the analytes. Higher temperatures also cause a higher diffusion and desorption rate, increasing extraction efficiency [23,24].

The purpose of this study was to optimize a robust and efficient PLE method for rapid MOSH and MOAH extraction from cardboard and paper intended for food contact. The results obtained were compared with those obtained with the method developed by Lorenzini et al. at the Official Food Control Authority of Zürich [20], based on classical solvent extraction. The optimized PLE method was then used to analyze different cardboards and paper materials intended for food contact.

## 2. Experimental

### 2.1. Reagents and standards

Dichloromethane and *n*-hexane were purchased from Sigma-Aldrich (Milan, Italy) and distilled before use. Ethanol was of HPLC grade. Internal standards were all from Supelco (Milan, Italy). The working standard solution was obtained by mixing 5-α-cholestane (Cho, 0.6 mg $mL^{-1}$), *n*-C11 (0.3 mg $mL^{-1}$), *n*-C13 (0.15 mg $mL^{-1}$), cyclohexyl cyclohexane (CyCy, 0.3 mg $mL^{-1}$), n-pentyl benzene (5B, 0.30 mg $mL^{-1}$), 1-methyl naphthalene (1-MN, 0.30 mg $mL^{-1}$), 2-methylnaphthalene (2-MN, 0.30 mg $mL^{-1}$), tri-tert-butyl benzene (TBB, 0.3 mg $mL^{-1}$) and perylene (Per, 0.6 mg $mL^{-1}$) in toluene.

### 2.2. Samples

Cardboard samples (unprinted and printed recycled cardboards) used for method optimization were taken directly by producers. Cardboard boxes used in direct contact with foods (printed recycled and virgin cardboard) and other paper samples (paper bags used for bread, baking paper, baking cups, etc.) used for analysis and method comparison, were taken from the market.

### 2.3. Extraction

PLE was carried out using a SpeedExtractor E-916 (Buchi, Flawil, Switzerland) equipped with six 10-mL stainless steel extraction cells. Pre-washed cellulose filters were placed at the exit of the cells to prevent clogging of the metal frit. The sample (1 g for cardboard, 0.2–0.5 g for paper samples) was cut in strips (6 cm × 2–4 mm) and inserted into the cell containing two 2-mL stainless steel bars (expansion elements) to fill part of the void volume and reduce solvent consumption. Prior to extraction, a 20 μL of the internal standard working solution was added into the cell for quantification and to verify LC–GC performance and efficient MOSH and MOAH separation as described by Biedermann and Grob [13]. Alternatively the standard can be added in the collecting vial after the extraction. An aliquot of the extract collected in 60-mL glass vial (generally 60 μL) was directly injected into the LC–GC, but it could also be used for off-line SPE–GC as described by Moret et al. [18]. For PLE optimization, different solvents or mixtures (hexane, ethanol, hexane/ethanol), extraction temperature (from 30 to 70 °C), extraction times (5, 10 min) and number of extraction cycles (1-3), were tested. Optimized conditions including a two-cycle extraction, are reported in Table 1. Solvent consumption depends on the volume of the cell and the number of the extraction cycles. By using two 2-mL expansion elements the solvent consumption is reduced to about 15 mL per sample.

A tightness test is performed as default by the instrument before the first cycle to check leaks. During the “heat up” step the pressure inside the extraction cells is slowly increased to the set parameters of the extraction method. During the “hold time” period, these parameters remain constant (static extraction), followed by the “discharge” of the extract via pressure compensation and collection in the vials. No flush with solvent is performed after the two-cycle extraction. A flow of pressurized nitrogen is sent through the cell at the end of the extraction (after the last cycle) to purge residual solvent.

For extraction with the method proposed by Lorenzini et al. [20], chopped cardboard (1 g) provided with internal standards (20 μL), was extracted at room temperature with 10 mL of hexane/ethanol 1/1 (v/v) for 2 h, applying magnetic stirring the first and the last 5 minutes. An aliquot of the extract (3 mL) was added with a double amount of water (6 mL) to remove the ethanol from the extract. After vortexing and centrifuging, the hexane phase was used for LC–GC analysis.

**Table 1**
Optimized extraction conditions.

| **Speed extractor E-916 (6 positions)** | |
|---|---|
| Temperature | 60 °C |
| Pressure | 100 bar |
| Cells (volume) | 10 mL |
| Solvent | hexane |
| Cycles (number) | 2 |
| −Heat up | 1 min |
| −Hold time | 5 min |
| −Discharge | 2 min |
| Flush with solvent | 0 min |
| Flush with gas (N2) | 1 min |
| Total extraction time | 30 min |

### 2.4. LC-GC analysis

The LC–GC instrument (LC–GC 9000, Brechbühler, Zurich, Switzerland) consisted of a PAL LHS2-xt Combi PAL autosampler (Zwingen, Switzerland), a Phoenix 40 three syringe LC pumps equipped with four switching valves (injection, backflush, transfer and additional valve) and a UV/VIS, UV-2070 Plus detector (Jasco, Japan). The LC column was a 25 cm × 2.1 mm i.d. LC column packed with Lichrospher Si 60, 5 μm (DGB, Schlossboeckelheim, Germany). The GC was a Trace GC Ultra from Thermo Scientific (Milan, Italy).

A gradient, starting with hexane (0.1 min) and reaching 30% of dichloromethane (at 300 μL/min) in 0.5 min, was used to elute the MOSH (from 2.0 to 3.5 min) and the MOAH (from 4 to 5.5 min) [18].

LC–GC transfer occurred by the retention gap technique and partially concurrent eluent evaporation through the *Y*-interface [25]. A 10 m × 0.53 mm i.d. uncoated, deactivated precolumn was followed by a steel T-piece union connected to the solvent vapor exit (SVE) and a 10 m × 0.25 mm i.d. separation column coated with a 0.15 μm film of PS-255 (1% Vinyl, 99% Methyl Polysiloxane) (Mega, Italy). A rapid oven gradient (40 °C/min) starting from 55 °C up to 350 °C was used for GC analysis. The FID and the SVE were heated at 360 °C and 140 °C, respectively. After the transfer, the LC column was backflushed (dichloromethane) and reconditioned prior to the subsequent injection.

Data were acquired and processed by the Exachrom software (Brechbuhler, Switzerland). The MOSH area was determined by the integration of the whole hump of largely unresolved peaks, comprised *n*-alkanes. All sharp peaks standing on the top of the MOAH hump were subtracted from the total area (sharp signals are unlikely to belong to the MOAH [5]). The quantification limit was around 2 mg kg$^{-1}$ (when processing 1 g of sample with PLE). A higher sensitivity could be reached by concentrating the sample extract before injection.

## 3. Results and discussion

### 3.1. Optimization of PLE

Development of a PLE method in general requires the optimization of a number of parameters such as the choice of the extraction solvent, number of extraction cycles, extraction temperature and extraction time.

Also the choice of the extraction cell and the filling procedure are important. To minimize solvent consumption, the size of the extraction cell should match the sample size and void volume should be avoided. The smallest available cell (10 mL) was used for this application.

Generally, a dispersing agent is mixed with the ground sample to increase the surface area exposed to the solvent and to fill void volume minimizing solvent consumption. In the case of cardboard, neither sample pre-treatment nor dispersing agent were required. The sample was simply cut in strips and inserted into a 10 mL cell containing two 2-mL expansion elements placed on the bottom to reduce solvent consumption (up to 3 expansion elements can be used per cell to further reduce solvent consumption).

PLE uses high pressure to maintain the solvent liquid at the operating temperature (above the solvent atmospheric boiling point) and to force it through the sample. Since pressure adjustments have in general a little impact on analyte recovery [24], a default value of 100 bar which guarantees the solvent remained liquid was selected for this application.

#### 3.1.1. Extraction solvent

The choice of the extraction solvent represents one of the most important parameters to optimize for a PLE method. For an efficient extraction, the solvent must be able to solubilize the target compounds limiting co-extraction of interferences. Generally, if a solvent or a solvent mixture works well with conventional extraction techniques, it will also work well using PLE. Compatibility with the post-extraction analytical technique should also be considered.

According to Lorenzini et al. [20], with respect to hexane, ethanol more efficiently extracts the low molecular mass hydrocarbons (probably due to its ability to swell cellulose), but has a limited extracting power towards higher molecular weight hydrocarbons (particularly *n*-alkanes). It also allows to discriminate against high molecular mass hydrocarbons, such as resins, waxes and hot melts, which can accumulate in the retention gap causing peak broadening. A mixture hexane/ethanol 1:1 (v/v) combines the advantages of the two solvents but complicates the sample post-treatment since a washing step with water (to separate ethanol), followed by centrifugation, is required.

Extraction performance of hexane, ethanol and the mixture ethanol/hexane 1:1 (v/v), were compared using PLE (60 °C for 5 min, 1 cycle). Fig. 1 histograms show, MOSH and MOAH results (minimum, maximum and average of 2 replicates) from C10 to C24 (relevant for migration) and from C10 to C35 (relevant from a toxicological point of view and which could migrate under wet-contact condition) for two different recycled cardboards.

No appreciable differences were observed between the 3 different solvents for both MOSH and MOAH. A slightly higher extraction yield of high boiling compounds was observed in one case for hexane.

As the optimized method uses a two-cycle extraction, as described later, a comparison between hexane and the mixture hexane/ethanol 1:1 (v/v) was also performed on two samples of

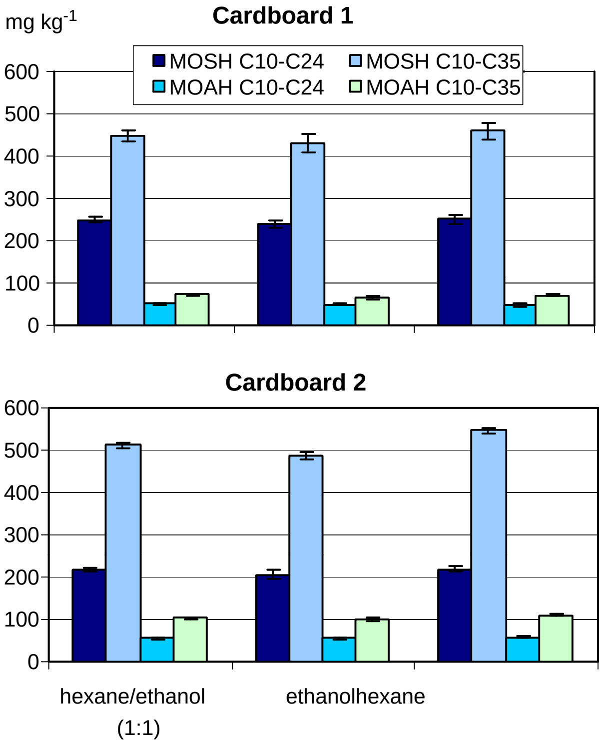

**Fig. 1.** Comparison of PLE (1 cycle at 60 °C for 5 min) results (mg kg$^{-1}$) obtained using different extraction solvents (hexane, ethanol, ethanol/hexane 1:1). Bars represent the average of two replicates, while vertical lines represent minimum and maximum values.

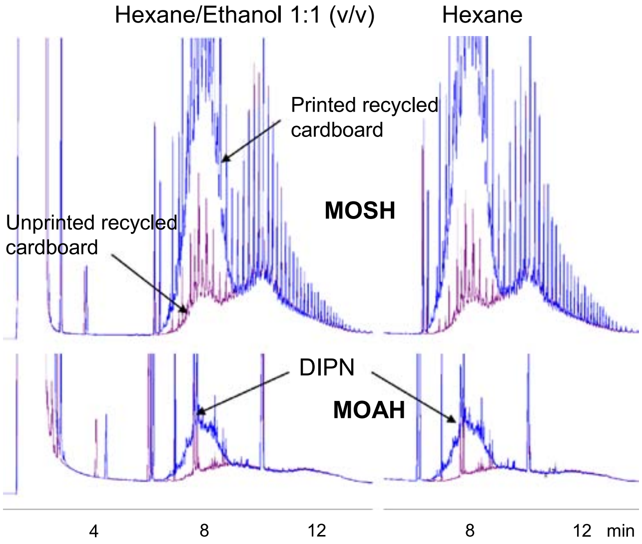

**Fig. 2.** Overlay of LC–GC traces obtained for a recycled cardboard available with and without printing (with mineral oil based ink) and extracted with PLE using hexane or the mixture hexane/ethanol (1:1). DIPN: diisopropyl naphthalenes.

the same recycled cardboard, one printed with an offset ink containing mineral oil and the other unprinted. Since printed cardboards showed a heterogeneous distribution of the contamination, probably related to the different amount of ink applied in different printed areas, the same printed area was sampled from different sheets.

Fig. 2 displays an overlay of the LC–GC traces obtained for both the unprinted and the printed cardboards. Also in this case the 2 solvents demonstrated to have similar extraction power and selectivity.

The unprinted cardboard (213 mg kg$^{-1}$ and 56 mg kg$^{-1}$ of MOSH and MOAH up to C24, respectively) shows the typical MOSH pattern of a recycled cardboard characterized by a large hump from about C15 to over C40 (in this case centered on C28) with long-chain *n*-alkanes on the top (waxes) and a narrower hump ranging from C14 to C20 and centered on C17, coming from newspaper inks present in recycled fibers [5]. With respect to the unprinted cardboard, the printed cardboard shows an increased MOSH and MOAH content (in the range C13–C23) due to the printing ink (1277 mg kg$^{-1}$ and 189 mg kg$^{-1}$ of MOSH and MOAH up to C24, respectively). In the MOAH traces are well visible the diisopropyl naphthalenes (DIPN) peaks that are excellent markers for the migration from recycled paper and board (they only originate from carbonless copy paper) [5].

In conclusion, the lower extraction power towards low molecular weight hydrocarbons, observed for hexane at ambient condition [20], was not observed under PLE condition. This led us to choose hexane as extraction solvent avoiding any sample post-treatment. No performance problems due to the introduction of high boiling material into the retention gap were observed, also after more than 300 injections with the same retention gap.

### 3.1.2. *Extraction temperature and time*

Different extraction temperatures (from 30 °C to 70 °C) were tested in duplicate on an unprinted recycled cardboard performing a one-cycle extraction with hexane and using the extraction conditions reported in Table 1.

Although most of the MOSH and the MOAH up to C35 were already extracted at 30 °C (about 80% of those extracted at 60 °C), improved extraction was obtained at higher temperature (60 °C). No appreciable differences were observed when increasing the temperature from 60 °C to 70 °C.

Since a single extraction cycle was not sufficient to guarantee quantitative extraction yield for all samples, as discussed in the next paragraph, a prolonged extraction time (10 min) was also tested. No differences were observed when increasing the extraction time from 5 min to 10 min.

### 3.1.3. *Number of cycles and extraction yield*

Depending on the matrix and its interactions with the analytes, one or more extraction cycles are usually necessary to obtain quantitative extraction yields with PLE [23,24].

Extraction yields, calculated comparing the response obtained (from duplicate analyses) with 1 or 2 cycles were assessed on 4 different cardboards. Recoveries ranging from 76% to 100% for both MOSH and MOAH up to C35 were obtained with a 1-cycle extraction, while a 2-cycle extraction always gave quantitative yields (less than 2% of the total contamination found in a third separate cycle). One-cycle extraction yield was also influenced by cardboard thickness. Two cardboards of the same type but different thickness (210 and 350 g/m$^2$) gave, for MOSH up to C35, different extraction yields with a one-cycle extraction (76 and 90%, respectively), but quantitative extraction yields with a two-cycle extraction.

Fig. 3 shows an overlay of the LC–GC traces of an unprinted cardboard, obtained performing a one-cycle extraction followed by a second cycle (collected in a separate vial), or a two-cycle extraction followed by a separate third cycle. The effect of a wash (with 5 mL of hexane) after a one-cycle extraction was also tested to verify if a second cycle could be avoided. The results obtained were similar to those obtained with a 1-cycle extraction. It was concluded that a two-cycle extraction is needed to assure complete recovery, independently of the cardboard type.

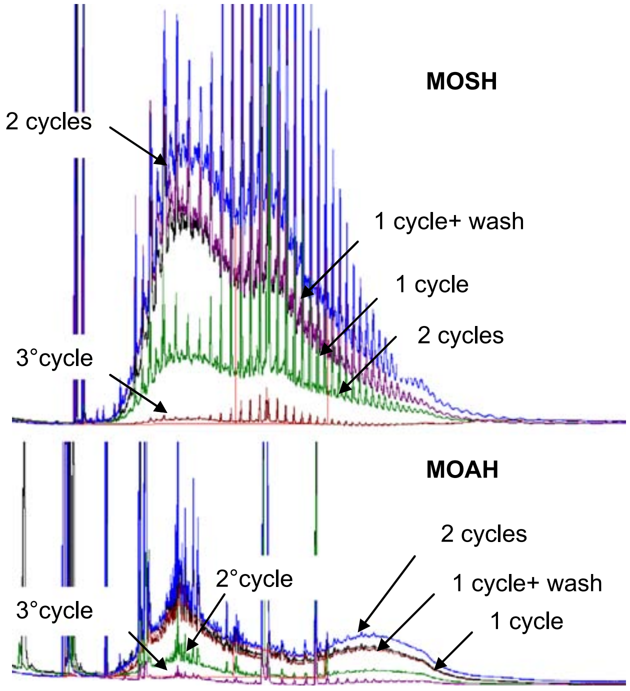

**Fig. 3.** Overlay of the LC–GC traces (MOSH and MOAH) of an unprinted cardboard, obtained performing a one-cycle extraction (1 cycle) followed by a second cycle (2° cycle), a two-cycle extraction (2 cycles) followed by a separate third cycle (3° cycle), and a 1 cycle+wash.

### *3.1.4. Recovery of volatile internal standards*

Quantification of mineral oil, as well as performance verification of the LC-GC analysis, are based on volatile internal standards (C11, CyCy C13, TBB, 1-MN, 2-MN). Recovery tests were carried out to assess possible losses of volatiles due to the purge with nitrogen (1 min) carried out at the end of the cycle to eliminate residual solvent.

For this purpose, single extraction cycles with hexane (using the conditions reported in Table 1) were performed on cells added with a known amount of internal standards (20 μL of the internal standard working solution), applying a 1-min nitrogen purge at the end of the cycle. The extracts obtained were adjusted to 10-mL with hexane and injected into the LC–GC. Also for the most volatile compounds, the chromatographic areas (mean of two replicates) obtained after a 1-minute purge, resulted comparable to those obtained by direct injection of the same internal standard solution (20 μL diluted to 10-mL with hexane) into the LC–GC instruments (Fig. 4). No losses were observed also when using a prolonged purge time of 2 min.

### *3.1.5. Repeatability and method comparison*

Repeatability of the PLE method was assessed by performing 8 replicate extractions (in two different days), followed by on-line LC–GC analysis, on different aliquots of the same unprinted recycled cardboard using optimized conditions reported in Table 1. Residual standard deviation lower than 5% were found in both cases.

Fig. 5 displays an overlay of the LC–GC traces (MOSH and MOAH) obtained with the optimized PLE method and the method developed by Lorenzini et al. [20]. The samples extract were in this case adjusted to the same final volume before sample injection.

As visible in Fig. 5, LC–GC profiles obtained with PLE agree well with those obtained with the reference method, indicating that the two methods have similar extraction efficiency. For some samples taken from the market, PLE showed a slightly increased extraction efficiency towards *n*-alkanes over C35.

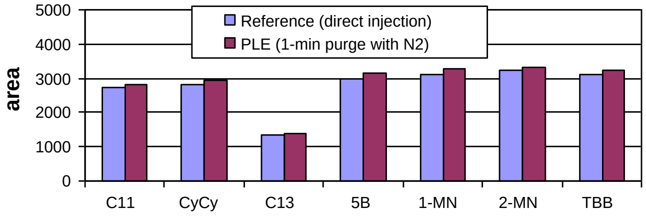

**Fig. 4.** Effect of PLE with a 1 min nitrogen purge on volatile internal standards.

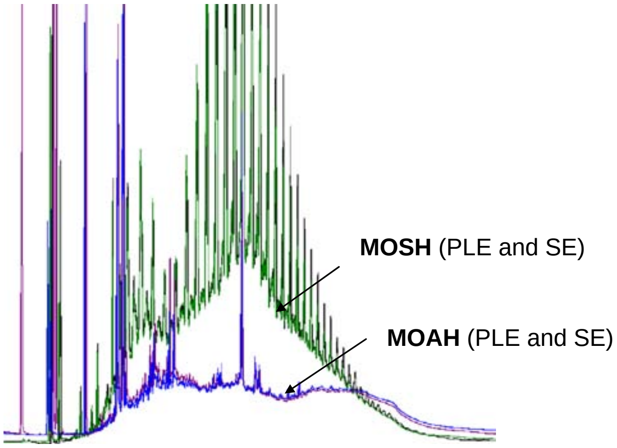

**Fig. 5.** Overlay of LC–GC traces (MOSH and MOAH) obtained with the optimized PLE method and with the method based on classical solvent extraction.

**Table 2**
Comparison between MOSH and MOAH results obtained with pressurized liquid extraction (PLE) and classical solvent extraction (SE) on an unprinted recycled cardboard. Results (mg kg$^{-1}$) are expressed as average values ± SD.

| | PLE ($n$=8) | SE ($n$=4) |
|---|---|---|
| MOSH C10-C24 | 241 ± 5 | 238 ± 10 |
| MOSH C10-C35 | 622 ± 22 | 643 ± 28 |
| MOAH C10-C24 | 32 ± 1 | 34 ± 2 |
| MOAH C10-C35 | 59 ± 3 | 64 ± 3 |

Table 2 reports average contents (mg kg$^{-1}$) and standard deviations of MOSH and MOAH from C10 to C24 and from C10 to C35 obtained from the 8 replicate analyses with the optimized PLE method (performed in two different days) and the 4 replicate analyses with the methods based on classical solvent extraction (SE).

### *3.2. Application to different cardboard and paper used or intended for food contact*

The PLE method was then applied to recycled and virgin cardboard boxes from the market as well as paper used or intended for food contact such as baking paper, baking cups, paper bags, etc. Table 3 displays the results obtained. For some of the samples, results obtained with the method based on classical solvent extraction are also reported.

As expected, recycled cardboard boxes presented higher contamination level with respect to virgin cardboard boxes. The presence/absence of the DIPN was used to confirm if the sample was made with recycled or virgin fibers. For recycled cardboards a large part of the contamination below C24 was probably already migrated into the food before the analysis. Of the 6 printed cardboard packaging, all except one (cardboard box 4) were printed with mineral-oil-free or low-migration inks. The absence of mineral-oil-based inks was verified by comparing the contamination level of two different areas printed more or less intensely: when no differences were found, it was concluded that a mineral-oil-free printing ink was used. Following the recommendation of the European Carton Makers Association (ECMA) to use low migration inks for food packaging [26], packaging converters are slowly phasing out mineral oils in inks used for food packaging [27].

The two bread paper bags (one printed, the other not) showed similar LC–GC traces with a relatively low MOSH contamination (maximum 33 mg kg$^{-1}$ of MOSH up to C35) mainly due to *n*-alkanes from C20 to about C45 (with a maximum on C29).

Fig. 6 shows the LC–GC traces (MOSH) of some of the paper samples intended for food contact at high temperature. Considering the high temperature of use and the nature of the food usually cooked in contact with these materials (high fat content), high migration rate can be expected from the paper into the food, also for less volatile hydrocarbons (migration under wet-contact condition).

Baking paper (in roll) of different brands showed similar MOSH levels (22–25 mg kg$^{-1}$ of MOSH up to C35). Most of the contamination was in the range C10-C24 with a maximum centered on C18, as typical of contamination transferred from recycled printed cardboard to food via gas-phase. Since the baking paper was packaged in recycled cardboard, it can not be ruled out that at least part of the contamination came from the packaging.

**Table 3**
MOSH and MOAH content (mg kg$^{-1}$) of different cardboards packaging and paper materials intended for food contact and purchased from the Italian market.

| Sample | Packaging | | Extraction method | MOSH (mg kg$^{-1}$) | | MOAH (mg kg$^{-1}$) | |
|---|---|---|---|---|---|---|---|
| | | | | C10-C24 | C10-C35 | C10-C24 | C10-C35 |
| Cardboard box 1 | virgin | printed | PLE | 20 | 26 | < 2 | < 2 |
| | | | SE | 22 | 29 | < 2 | < 2 |
| Cardboard box 2 | virgin | printed | PLE | 16 | 36 | < 2 | < 2 |
| | | | SE | 15 | 37 | < 2 | < 2 |
| Cardboard box 3 | recycled | printed | PLE | 136 | 545 | 32 | 72 |
| | | | SE | 135 | 561 | 28 | 66 |
| Cardboard box 4 | recycled | printed | PLE | 354 | 538 | 99 | 155 |
| | | | SE | 358 | 548 | 108 | 170 |
| Cardboard pastry tray | virgin/recycled | unprinted | PLE | 89 | 276 | 51 | 103 |
| | | | SE | 86 | 270 | 46 | 95 |
| Cardboard cake box | virgin/recycled | printed | PLE | 120 | 288 | 25 | 450 |
| Cardboard egg box | recycled | printed | PLE | 188 | 503 | 40 | 124 |
| Pizza box | virgin | printed | PLE | 2 | 7 | < 2 | < 2 |
| Bread paper bag 1 | recycled | printed | PLE | 13 | 33 | < 2 | < 2 |
| Bread paper bag 2 | recycled | printed | PLE | 8 | 19 | < 2 | < 2 |
| Oven bag | virgin | printed | PLE | 8 | 15 | < 2 | < 2 |
| Baking cup 1 | virgin | printed | PLE | 76 | 854 | < 2 | < 2 |
| | | | SE | 75 | 851 | < 2 | < 2 |
| Baking cups 2 | virgin | unprinted | PLE | 69 | 430 | < 2 | < 2 |
| | | | SE | 75 | 445 | < 2 | < 2 |
| Baking cups 3 | virgin | printed | PLE | 39 | 46 | 5 | < 2 |
| | | | SE | 40 | 45 | 7 | < 2 |
| Oven paper 1 | virgin | unprinted | PLE | 22 | 25 | 2 | < 2 |
| | | | SE | 20 | 23 | 2 | < 2 |
| Oven paper 2 | virgin | unprinted | PLE | 18 | 22 | < 2 | < 2 |
| Oven paper 3 | virgin | printed | PLE | 23 | 28 | 2 | 2 |

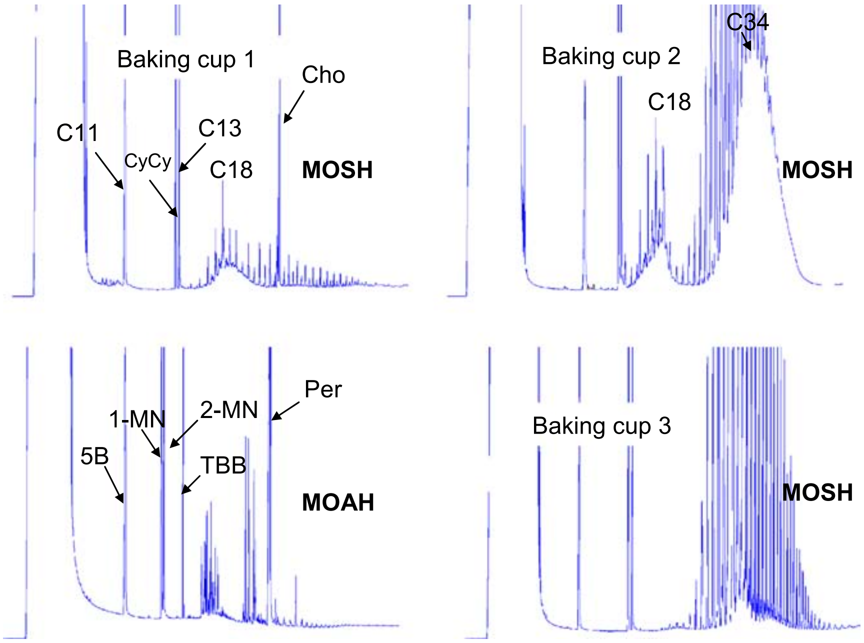

**Fig. 6.** LC–GC traces (MOSH) of some of the paper samples intended for food contact at high temperature. CyCy: cyclohexyl cyclohexane; Cho: 5-α-cholestane; 5B: n-pentyl benzene; 1-MN: 1-methyl naphthalene; 2-MN: 2-methylnaphthalene; TBB: tri-tert-butyl benzene; Per: perylene.

Baking cups of different brands had different LC–GC profiles (figure 7) and variable MOSH content (45–850 mg kg$^{-1}$ of MOSH up to C35). Sample 1 showed a contamination similar to that reported for oven paper (from C15 to C25, centered on C18), sample 2 had most of the contamination centered on C34, while sample 3 was contaminated with *n*-alkanes (waxes) from C21 to over 35.

## 4. Conclusion

A PLE method for rapid and efficient extraction of MOSH and MOAH from cardboard and paper material, using hexane as extraction solvent, has been set up. It delivered results similar to those obtained with the method based on classical solvent extraction (using hexane/ethanol 1:1, v/v), developed by Lorenzini et al. [20], with a great advantage in terms of sample manipulation and time savings. Six samples can be processed in parallel in less than 30 min compared to a processing time of 3 h with classical solvent extraction. The extracts obtained do not require any treatment prior to injection.

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