



Role of gas chromatography–single quadrupole mass spectrometry in the identification of compounds migrating from polypropylene-based food contact plastics

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ARTICLE INFO

Keywords:

Food contact material
Non intentionally added substances (NIAS)
GC–MS screening
Migration studies
Polypropylene (PP)

ABSTRACT

The migration of volatile and semi-volatile substances from commercially available polypropylene-based food contact materials was studied. Both intentionally and non-intentionally added substances – among them degradation products and contaminants of common additives – were identified. The efficiency and the reliability of tentative identification with GC-EI-QMS measurements followed by NIST mass spectral library searches were also evaluated. In addition to the 24 migrated *n*-alkanes, 46 compounds were tentatively identified with GC-EI-QMS. Of these, 31 were confirmed with both GC-EI-TOFMS and analytical reference materials. In four cases, however, the tentative identification proved to be wrong. Two compounds were identified despite not being included in the library. Our results prove that GC-EI-QMS and the NIST mass spectral library combined are powerful in the identification of compounds migrating from food contact plastics. But these same results also prove that both reliability and productivity can be improved with GC-EI-TOFMS measurements and consideration of linear retention indices.

1. Introduction

Nowadays a significant part of food is packed in plastic materials due to their excellent properties (e.g. low price, quick and easy manufacturing, formability, cheap raw materials). The most commonly used plastics are polyolefins, i.e. polypropylene (PP), low-density polyethylene (LDPE) and high-density polyethylene (HDPE), all of which are also regular raw materials of the food packaging industry [1]. Even though one of the main roles of the packaging is the protection of the products they are also potential sources of chemical contaminants in food. Besides different plastic additives, such as antioxidants, plasticizers and UV stabilizers, which are added intentionally during manufacturing processes, food contact plastics (FCPs) may contain non intentionally added substances (NIAS) as well [2,3]. These can be formed by the degradation of polymers and plastic additives. Also, impurities of raw materials and additives are considered as NIAS [2,4].

Since the appearance of certain compounds in food may deteriorate food quality and/or pose risks to human health, the safety of FCPs cannot be ensured without the qualitative and quantitative determination of both intentionally added substances (IAS) and NIAS migrating from them. Due to the numerous functions of IAS and the diverse origin of NIAS these compounds have various chemical structures and thus deeply heterogeneous physical–chemical properties [2,5]. This makes the identification of unknown migrating compounds a difficult and most challenging analytical task. Generally, the first step is a migration experiment conducted in accordance with the relevant legislation, i.e. Commission Regulation (EU) 10/2011 of 14 January 2011 on “Plastic materials and articles intended to come into contact with food” [6]. This regulation specifies experimental conditions (e.g. temperature, contact time) as well as food simulants with regard to various probable applications of the FCP to be tested. The next step is usually sample preparation preferably including both sample clean up and enrichment.

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<https://doi.org/10.1016/j.microc.2022.107772>

Received 27 May 2022; Received in revised form 1 July 2022; Accepted 8 July 2022

Available online 15 July 2022

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Finally, the migrated compounds are identified and quantified using chromatography coupled with mass spectrometric detection (MS). This paper is focused on volatile and semi-volatile substances for which gas chromatography – mass spectrometry (GC–MS) is the typical choice, while liquid chromatography – mass spectrometry (LC-MS) is more suitable for the analysis of non-volatile, polar and heat-sensitive compounds.

Several articles [2,5,7] mention that the best choice for the non-target analysis of NIAS and other migrants are high-resolution mass spectrometry (e.g. MS with time-of-flight analyser) and hybrid techniques such as quadrupole-time-of-flight mass spectrometer (QTOF-MS) or Orbitrap MS. Beside the fragmentation pattern, these techniques provide accurate mass data which together with isotope patterns give information on the elemental composition of the detected compounds. The other key feature of a mass spectrometer with significant influence on the identification is the type of its ion source. In GC–MS the most commonly used ionization technique is electron impact ionisation (EI). It provides highly reproducible fragmentation mass spectra which help the identification of unknown compounds by enabling comparison with mass spectral libraries (e.g. NIST or WILEY mass spectral libraries). But this ionization technique can lead to low abundance or absence of the molecular ion, which otherwise could also provide relevant information for identification. Consequently, soft ionization techniques, such as chemical ionization (CI) or atmospheric pressure chemical ionization (APCI) may have an emerging role in the identification of NIAS [8–10]. Another solution could be the application of variable ionization energies in EI [11].

The chance of successful identification of the migrated compounds by mass spectrometry can considerably be improved by better (preferably baseline) separation of the compounds. The high peak capacity provided by comprehensive two-dimensional gas chromatography (GC × GC) proved to be rewarding in complex mixtures, including compounds originating from FCPs [12–14]. Therefore, GC × GC-EI-HRMS is a particularly powerful technique. However, there are two main factors preventing the GC-HRMS and GC × GC-HRMS systems from becoming widely spread: their purchase and operating costs are high and their use requires a high level of expertise.

Nowadays, the GC with single quadrupole (Q) MS is the workhorse in routine laboratories because of its easy operability and cost-efficiency. Hence GC-QMS is the most commonly used analytical technique for both the identification and quantification of small, volatile and semi-volatile compounds [2,15,16]. The identification of migrating compounds is often facilitated by commercially available mass spectral libraries, such as the NIST mass spectral library. This database contains the mass spectra of >200 000 compounds. All these spectra were obtained with electron impact ion source (EI) at 70 eV. The significant similarity of both m/z values and relative intensities in a recorded mass spectrum and in another included in the library is grounds for identification. It means that the searching algorithm of the library compares the measured mass spectra of an unknown compound with spectra from the database and generate a hit list. The quality of hits is ranked based on two parameters, the matching factor (MF) and the probability value. MF is a numerical value between 0 and 999 that indicates how close the peaks in the sample mass spectrum are to the peaks in the library mass spectrum based on mass-to-charge ratio and relative intensities [17]. The probability value is based on the matching factor together with the uniqueness of the mass spectrum [17].

NIST library guidelines define the following classes for interpreting the quality of mass spectral matching: $MF > 900$ is an excellent match, 800–900 is a good match, 700–800 is a fair match and MF less than 700 is a poor match [18]. Acceptance thresholds are sometimes not specified [19,20]. Many researchers accepted hits with $MF > 700$ [9,21,22], others required at least a good match ($MF > 800$ or 850) [23–25]. When instead of MF , probability values are applied the threshold also varies: Ubeda *et al.* [26] used 80%, the most common acceptance limit is 85% [27–29], but 90% is not rare either [30,31]. This diversity clearly shows

that even though the identification of unknown compounds is generally based on spectral library searches, there is no widely approved procedure for the acceptance of a hit.

We investigated IAS and NIAS compounds migrating from 53 commercially available polypropylene-based FCPs. Besides mass spectra measured with GC-EI-QMS we used GC-EI-TOFMS, linear retention indices and comparison with analytical reference materials for confirmation. Along with presenting the identified compounds, we aimed to evaluate the efficiency and the reliability of identifications based solely on GC-EI-QMS measurements followed by NIST mass spectral library searches.

2. Material and methods

2.1. Chemicals and materials

The analytical reference materials such as [2.2]paracyclophane (CAS: 1633-22-3), 1-stearoyl-*rac*-glycerol (CAS: 123-94-4), 2-(2*H*-benzotriazol-2-yl)-4,6-*bis*(1-methyl-1-phenylethyl)phenol (CAS: 70321-86-7), 2,4-*bis*(α,α -dimethylbenzyl)phenol (CAS: 2772-45-4), 2,5-*bis*(5-*tert*-butyl-2-benzoxazolyl)thiophene (CAS: 7128-64-5), 2,6-diisopropyl-naphthalene (CAS: 24157-81-1), 2,6-di-*tert*-butyl-1,4-benzoquinone (CAS: 719-22-2), 2,6-di-*tert*-butylphenol (CAS: 128-39-2), 2-palmitoyl-glycerol (CAS: 23470-00-0), 2-phenylpropane (CAS: 98-82-8), 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (CAS: 1620-98-0), 4-propyl-benzaldehyde (CAS: 28785-06-0), benzophenone (CAS: 119-61-9), decamethyl cyclopentasiloxane (CAS: 541-02-6), dibutyl phthalate (CAS: 84-74-2), diethyl phthalate (CAS: 84-66-2), di-*n*-octyl-phthalate (CAS: 117-84-0), *D*-limonene (CAS: 5989-27-5), dodecamethyl cyclohexasiloxane (CAS: 540-97-6), erucamide (CAS: 112-84-5), hexamethyl cyclotrisiloxane (CAS: 541-05-9), isopropyl myristate (CAS: 110-27-0), *meta*-tolualdehyde (CAS: 620-23-5), octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (CAS: 2082-79-3), octamethyl cyclotetrasiloxane (CAS: 556-67-2), oleamid (CAS: 301-02-0), *ortho*-tolualdehyde (CAS: 529-20-4), *para*-tolualdehyde (CAS: 104-87-0), squalene (CAS: 111-02-4), styrene (CAS: 100-42-5), toluene (CAS: 108-88-3), tributyl acetyl citrate (CAS: 77-90-7), trimethyl acetic anhydride (CAS: 1538-75-6), *tris*(2,4-di-*tert*-butylphenyl)phosphite (CAS: 31570-04-4), α -tocopherol (CAS: 59-02-9) and *n*-alkanes (standard mixture C₇–C₄₀) were purchased from Sigma Aldrich Co. (Budapest, Hungary). 2,4-di-*tert*-butylphenol (CAS: 96-76-4), 2,6-di-*tert*-butyl-4-methylphenol (CAS: 128-37-0), diisooctyl phthalate (CAS: 131-20-4) and tributyl citrate (CAS: 77-94-1) were bought from Alfa Aesar (Molar Chemicals, Budapest, Hungary). Hexadecane amid (CAS: 629-54-99), 1,1'-(1,3-propanediyl)*bis*-benzene (CAS: 1081-75-0), 7,9-di-*tert*-butyl-1-oxaspiro[4,5]deca-6,9-diene-2,8-dione (CAS: 82304-66-3) and *tris*(2,4-di-*tert*-butylphenyl) phosphate (CAS: 95906-11-9) were purchased from Toronto Research Chemicals Co. (RK Tech, Budapest, Hungary). *Bis*(2-ethylhexyl) phthalate (CAS: 117-81-7) and *tert*-butylbenzene (CAS: 98-06-6) were purchased from Honeywell Fluka (Thomasker Finechemicals Ltd, Budapest, Hungary). The GC grade 2,2,4-trimethylpentane (isooctane), *n*-hexane and acetone were supplied by LGC Standards GmbH (Budapest, Hungary). Silver nitrate (CAS: 7761-88-8) and sodium hydroxide (CAS: 1310-73-2) for synthesis of 2,6-di-*tert*-butyl-4-methylene-2,5-cyclohexadienone were bought from Sigma Aldrich Co. (Budapest, Hungary).

2.2. Food contact plastics

Twenty-one single-use and thirty-two reusable polypropylene (PP) food containers were examined. They were purchased from local supermarkets. Information on their composition and intended use are summarized in *Supp. Inf. Table 1*.

2.3. Migration tests and sample preparation

Migration experiments were performed in accordance with the

recommendations of Commission Regulation (EU) 10/2011 [6]. Isooctane (2,2,4-trimethylpentane) was used as food simulant. The food contact plastics were cut into 1.0 cm × 1.0 cm test specimen. For every plastic, 10 of these test species were placed in separate 40 cm³ glass vials. 6 cm³ of isooctane was added to each vial. Then, they were closed tightly and they were stored in a POL-EKO ST2 laboratory incubator (Pol-Eko-Aparatura, Wodzisław Śląski, Poland) at 60 °C for 10 days. Finally, after cooling the samples to room temperature, 5 cm³ aliquots of the liquid phase were combined from all 10 vials belonging to the same FCP sample. The combined solutions were evaporated under a gentle stream of 4.5 grade nitrogen (Messer Hungarogáz Kft., Budapest, Hungary) to a final volume of 1 cm³. These fifty-fold enriched samples were analysed with GC-EI-QMS and GC-EI-TOFMS.

2.4. GC-EI-QMS analysis

The separation of volatile and semi-volatile organic migrants was carried out with an Agilent 7890A gas chromatograph (Agilent Technologies, Santa Clara, California) which was coupled with an Agilent 5975C Inert XL MSD Mass Spectrometer with triple-axis detector (Agilent Technologies, Santa Clara, California).

The samples were injected in splitless mode at 300 °C with 1 min splitless time. The volume of the injected sample was 1 µL. The carrier gas was 5.0 grade helium (Messer Hungarogáz Kft., Budapest, Hungary) with a flow rate of 2.0 mL/min. The column was an Agilent J&W DB-5MS ultra inert capillary column (30 m × 0.25 mm i.d.; film thickness 0.25 µm). The oven temperature was initially 40 °C. This was held for 1 min, then it was increased to 320 °C at 25 °C/min heating rate and then held at this final temperature for 10 min. The mass spectrometer was equipped with an electron impact (EI) ion source and quadrupole analyser. The ionisation was achieved with 70 eV electron beam. The temperature of the ion source and the quadrupole were 230 °C and 150 °C, respectively. The MS was operated in scan mode in the *m/z* range of 50–700 AMU. The GC-MS was controlled with Agilent MSD ChemStation (E.02.02). The deconvolution and background subtraction of total ion chromatograms were performed with AMDIS (Automated Mass Spectral Deconvolution and Identification System) software. The identification of migrated compounds was aided with the NIST 17 mass spectral library (Version 2.2).

2.5. GC-EI-TOFMS analysis

GC-EI-TOFMS analysis was performed with an Agilent 7890B gas chromatograph coupled with a JEOL AccuTOF GC-X time-of-flight mass spectrometer (JEOL USA, Inc., Pleasanton, California). The chromatographic separation was carried out on an RTX-5MS capillary column (15 m × 0.25 mm i.d. × 0.25 µm film thickness). The carrier gas was 5.0 grade helium (Messer Hungarogáz Kft., Budapest, Hungary) at a constant flow rate of 2.0 mL/min. The samples were injected in split mode with 1:50 split ratio. The temperature of the inlet was held at 250 °C. The initial temperature of the oven was kept at 50 °C for 1.5 min, then increased to 320 °C at a rate of 30 °C/min. This final temperature was held for 3 min. The electron impact (EI) ionisation was operated at 70 eV in positive ion mode. The data acquisition was performed in scan mode with an *m/z* range of 50–700 AMU. Perfluorotributylamine (PFTBA) was used for the mass calibration. Drift correction was performed for every peak primarily using *m/z* 281.0511 coming from the GC column bleeding. In case of any interferences, causing inadequate mass correction, *m/z* 207.0324 was used.

2.6. Qualitative analysis of migrated chemical compounds

Total ion chromatograms (TIC) recorded by GC-EI-QMS were evaluated with MSD ChemStation and AMDIS softwares. After deconvolution, the tentative identification of the detected compounds was based on a search in the NIST spectral library. The hits were then considered

based on either the matching factor or the probability value. All hits with a matching factor above 700 were considered for confirmation. If no hits reached this limit, then the hit with the best matching factor was considered especially when it suggested compounds that are known to be used in the production of FCPs or that are known degradation products or contaminants of such compounds.

The GC-EI-TOFMS confirmation of the tentative identification was accepted if the mass difference between the measured and calculated exact mass was below 5 ppm. For confirmation with analytical reference materials, both retention times and the fragmentation pattern were considered. The comparison of retention times measured at different times was enabled by the use of *Van den Dool* and *Kratz* linear retention indices (*LRI*s). Under temperature-programmed gas chromatographic conditions (See section 2.4.) the *LRI*s can be calculated with the following formula (Eq. (1)) [32]:

$$LRI = 100 \cdot z + 100 \cdot \left[\frac{(t_{R,X} - t_{R,Z})}{(t_{R,Z+1} - t_{R,Z})} \right] \quad (1)$$

where *t_{R,X}* is the retention time of the target compound, *t_{R,Z}* and *t_{R,Z+1}* are the retention time of the reference *n*-alkane compounds eluting immediately before and after the target compound and *z* is the number of carbon atoms in the smaller *n*-alkane of the two. If analytical reference material was not available for the confirmation of the tentatively identified compound, then the measured *LRI* value was compared with *LRI* values from the NIST retention index library [33]. The tentative identification was considered confirmed if the absolute value of the difference between the measured and library *LRI* values ($|\Delta LRI|$) was less than 10 units.

2.7. Synthesis of 2,6-di-*tert*-butyl-4-methylene-2,5-cyclohexadienone

2,6-di-*tert*-butyl-4-methylene-2,5-cyclohexadienone (BHT-QM) was synthesized by oxidation of 2,6-di-*tert*-butyl-4-methylphenol (BHT) with freshly prepared silver oxide following the method described by Kupfer *et al* [34]. Silver oxide was prepared by the addition of 2 mol·dm⁻³ sodium hydroxide solution to 1.0 g silver nitrate in 10 cm³ water until no further precipitation occurred. The solid substance was filtrated by vacuum filtration system, and it was washed with water and acetone. The washed silver oxide was dried 48 h under high vacuum. 380 mg of freshly prepared silver oxide and 25 mg of BHT were added to 100 cm³ *n*-hexane. The mixture was stirred for two hours at 25 °C. The formation of BHT-QM was confirmed with ¹H-NMR. Purity was estimated to be 52%. Based on the relative peak areas in the total ion chromatogram measured with the GC-EI-QMS method described in Section 2.4.

3. Results and discussion

In addition to *n*-alkanes, 45 volatile and semi-volatile compounds were identified from 21 single-use and 32 reusable commercially available PP-based FCPs after migration tests (at 60 °C for 10 days) in isooctane. Table 1 lists these compounds along with those 4 that were misidentified in the tentative identification step (based solely on the GC-EI-QMS measurements). Because of multiple occurrences, the 45 identified, non-alkane compounds belonged to 364 peaks in the initial 53 GC-EI-QMS chromatograms. Fig. 1 shows an example (PP-09) where along with the peaks of the almost always present Irgafos 168 and its degradation products [2,4-di-*tert*-butylphenol and *tris*(2,4-di-*tert*-butylphenyl)phosphate], also the peaks of a non-phthalate type plasticizer (tributyl acetyl citrate) and its degradation product (tributyl prop-1-ene-1,2,3-tricarboxylate) are present. Moreover, the chromatogram of PP-09 extract shows the peak of octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (Irganox 1076) and its precursor compound [methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate, Metilox]. The characteristic peak pattern of the homologous series of *n*-alkanes shown in Fig. 2 was observed in the chromatograms of several food contact

Table 1

Compounds classified as IAS or NIAS migrated into isooctane from PP samples stored in isooctane at 60 °C for 10 days.

| Function | Name of migrated compound | CAS number | IAS or NIAS | Matching factor | | Probability (%) | | GC-EI-TOF-MS | Analytical reference material | Linear retention index | |
|--|--|------------|-------------|-----------------|------|-----------------|------------------------|-----------------------------------|-------------------------------|------------------------|-------------------|
| | | | | Min. | Max. | Min. | Max. | | | M ¹ | D.B. ² |
| MATCHING FACTOR ABOVE 700 WITH SUCCESSFUL CONFIRMATION | | | | | | | | | | | |
| Antioxidants and their degradation products | 2,4-Di- <i>tert</i> -butylphenol | 96-76-4 | NIAS | 716 | 913 | 2.37 | 62.6 | Confirmed (-1.261 ppm) | Confirmed | 1508 | 1512 |
| | 2,5-Bis(5- <i>tert</i> -butyl-2-benzoxazolyl)thiophene [BBOT] | 7128-64-5 | IAS | 851 | 867 | 97.6 | 98.5 | Confirmed (3.022 ppm) | Confirmed | 3895 | 3750 |
| | 2,6-Di- <i>tert</i> -butyl-1,4-benzoquinone | 719-22-2 | NIAS | 703 | 847 | 38.1 | 82.0 | Confirmed (0.591 ppm) | Confirmed | 1472 | 1472 |
| | 2,6-Di- <i>tert</i> -butyl-4-methylphenol [BHT] | 128-37-0 | IAS | 786 | 945 | 39.8 | 74.3 | Confirmed (-1.953 ppm) | Confirmed | 1510 | 1514 |
| | 2,6-Di- <i>tert</i> -butylphenol | 128-39-2 | NIAS | 911 | 930 | 58.8 | 68.4 | Confirmed (-2.668 ppm) | Confirmed | 1443 | 1443 |
| | 3,5-Di- <i>tert</i> -butyl-4-hydroxybenzaldehyde [BHA] | 1620-98-0 | IAS | 754 | 947 | 8.43 | 60.2 | Confirmed (1.367 ppm) | Confirmed | 1771 | 1774 |
| | 7,9-Di- <i>tert</i> -butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione | 82304-66-3 | NIAS | 700 | 889 | 81.4 | 95.3 | Confirmed (1.448 ppm) | Confirmed | 1916 | 1917 |
| | <i>Tert</i> -butylbenzene | 98-06-6 | NIAS | 771 | 915 | 34.5 | 62.7 | Confirmed (1.193 ppm) | Confirmed | 996 | 992 |
| | <i>Tris</i> (2,4-di- <i>tert</i> -butylphenyl)phosphate | 95906-11-9 | NIAS | 781 | 930 | 95.1 | 98.4 | Confirmed (-0.946 ppm) | Confirmed | 3577 | 3582 |
| | <i>Tris</i> (2,4-di- <i>tert</i> -butyl-phenyl)phosphite [Irgafos 168] | 31570-04-4 | IAS | 860 | 899 | 94.3 | 96.8 | Confirmed (-1.238 ppm) | Confirmed | 3400 | 3397 |
| Plasticizers | Dibutyl phthalate | 84-74-2 | IAS | 816 | 892 | 8.30 | 10.6 | M ⁺ was not detectable | Confirmed | 1962 | 1964 |
| | Diethyl phthalate | 84-66-2 | NIAS | 753 | 883 | 29.8 | 68.3 | M ⁺ was not detectable | Confirmed | 1594 | 1595 |
| | Di- <i>n</i> -octyl-phthalate | 117-84-0 | NIAS | 833 | 871 | 33.1 | 62.7 | M ⁺ was not detectable | Confirmed | 2735 | 2741 |
| Slip agents | 1-Stearoyl- <i>rac</i> -glycerol | 123-94-4 | IAS | 751 | 888 | 57.8 | 86.5 | Confirmed (-0.893 ppm) | Confirmed | 2736 | 2681 ³ |
| | Hexadecanamide | 629-54-9 | NIAS | 835 | 835 | 69.9 | 69.9 | Confirmed (3.643 ppm) | Confirmed | 2190 | 2186 |
| | Isopropyl myristate | 110-27-0 | NIAS | 735 | 918 | 79.7 | 91.7 | Confirmed (3.700 ppm) | Confirmed | 1822 | 1826 |
| | Oleamid | 301-02-0 | IAS | 771 | 780 | 25.6 | 79.6 | Confirmed (-0.512 ppm) | Confirmed | 2367 | 2375 |
| Other migrated compounds | (1-methylethyl)-Benzene | 98-82-8 | NIAS | 709 | 709 | 20.7 | 20.7 | Confirmed (0.999 ppm) | Confirmed | 931 | 930 |
| | 1,1'-(1,3-propanediyl)bis-Benzene | 1081-75-0 | NIAS | 843 | 930 | 91.3 | 93.7 | Confirmed (1.071 ppm) | Confirmed | 1680 | 1633 |
| | 2,6-Diisopropyl-naphthalene | 24157-81-1 | NIAS | 713 | 812 | 28.2 | 65.5 | Confirmed (0.514 ppm) | Confirmed | 1743 | 1736 |
| | 4-Propyl-benzaldehyde | 28785-06-0 | NIAS | 885 | 928 | 62.7 | 67.4 | Confirmed (-4.794 ppm) | Confirmed | 1286 | 1294 |
| | Benzophenone | 119-61-9 | IAS | 946 | 946 | 82.1 | 82.1 | Confirmed (-1.483 ppm) | Confirmed | 1649 | 1644 |
| | Decamethyl cyclopentasiloxane | 541-02-6 | NIAS | 819 | 819 | 58.6 | 58.6 | M ⁺ was not detectable | Confirmed | 1127 | 1161 |
| | <i>D</i> -Limonene | 5989-27-5 | NIAS | 865 | 907 | 21.5 | 36.2 | Confirmed (-1.469 ppm) | Confirmed | 1035 | 1034 |
| | Dodecamethyl cyclohexasiloxane | 540-97-6 | NIAS | 743 | 806 | 90.9 | 97.5 | M ⁺ was not detectable | Confirmed | 1298 | – |
| | Hexamethyl cyclotrisiloxane | 541-05-9 | NIAS | 843 | 915 | 17.3 | 80.7 | M ⁺ was not detectable | Confirmed | 815 | – |
| | Octamethyl cyclotetrasiloxane | 556-67-2 | NIAS | 796 | 926 | 9.14 | 59.0 | M ⁺ was not detectable | Confirmed | 975 | 994 |
| | Tolualdehyde | 529-20-4 | NIAS | 797 | 917 | 14.4 | 36.6 | Confirmed (2.915 ppm) | Confirmed | 1075 | 1067 |
| | Styrene | 100-42-5 | IAS | 841 | 947 | 36.2 | 45.2 | Confirmed (2.595 ppm) | Confirmed | 901 | 900 |
| | Toluene | 108-88-3 | NIAS | 735 | 909 | 20.1 | 55.2 | Confirmed (1.086 ppm) | Confirmed | 779 | 776 |
| 2,4-Bis(α,α-dimethylbenzyl)phenol | 2772-45-4 | NIAS | 917 | 917 | 96.1 | 96.1 | Confirmed (-1.423 ppm) | Confirmed | 2481 | 2488 | |

(continued on next page)

Table 1 (continued)

| Function | Name of migrated compound | CAS number | IAS or NIAS | Matching factor | | Probability (%) | | GC-EI-TOF-MS | Analytical reference material | Linear retention index | |
|--|---|-------------|-------------|-----------------|------|-----------------|------------------------|-----------------------------------|-------------------------------|------------------------|-------------------|
| | | | | Min. | Max. | Min. | Max. | | | M ¹ | D.B. ² |
| FALSE HITS WITH MATCHING FACTOR ABOVE 700 | | | | | | | | | | | |
| Other migrated compounds | 2- <i>Tert</i> -butyl-5-(2-methylprop-2-en-1-yl)cyclohexa-2,5-diene-1,4-dione | n.d. | – | 729 | 780 | 5.40 | 20.1 | Not confirmed (164.8 ppm) | No standard, not confirmed | – | n.d. |
| | 2,2-Dimethylpropanoic anhydride | 1538-75-6 | – | 901 | 902 | 40.8 | 40.9 | Not confirmed (203.6 ppm) | Not confirmed | 1066 | 1053 |
| | [2.2]Paracyclophane | 1633-22-3 | – | 835 | 859 | 26.2 | 82.3 | Not confirmed (-246.1 ppm) | Not confirmed | 1821 | 1853 |
| | Diisooctyl phthalate | 131-20-4 | – | 827 | 844 | 28.7 | 57.4 | M ⁺ was not detectable | No standard, not confirmed | 2540 | 2525 |
| | <i>Bis</i> (2-ethylhexyl) phthalate | 117-81-7 | IAS | 787 | 792 | 24.3 | 35.7 | M ⁺ was not detectable | Confirmed | 2540 | 2544 |
| MATCHING FACTOR ABOVE 700, BUT NO ANALYTICAL REFERENCE MATERIAL IS AVAILABLE | | | | | | | | | | | |
| Other migrated compounds | 2,4- <i>Bis</i> (dimethylbenzyl)-6- <i>tert</i> -butylphenol | 244080-16-8 | NIAS | 935 | 935 | 97.8 | 97.8 | Confirmed (2.654 ppm) | No standard | 2528 | 2528 |
| | 2,6-Di- <i>tert</i> -butyl-4-(2-phenylpropan-2-yl)phenol | 34624-81-2 | NIAS | 929 | 929 | 89.9 | 89.9 | Confirmed (1.943 ppm) | No standard | 2086 | 2083 |
| | 2- <i>Tert</i> -butyl-4-(2-phenylpropan-2-yl)phenol | 56187-92-9 | NIAS | 848 | 848 | 82.9 | 82.9 | Confirmed (2.014 ppm) | No standard | 2119 | 2128 ³ |
| | 1-Propene-1,2,3-tricarboxylic acid, tributyl ester | 7568-58-3 | NIAS | 817 | 842 | 65.4 | 98.5 | Confirmed (1.373 ppm) | No standard | 2153 | 2297 ³ |
| | Methyl 3-(3,5-di- <i>tert</i> -butyl-4-hydroxyphenyl)propionate | 6386-38-5 | NIAS | 735 | 857 | 69.8 | 98.3 | Confirmed (-0.998 ppm) | No standard | 1944 | 1943 |
| MATCHING FACTOR UNDER 700 | | | | | | | | | | | |
| Slip agents, antioxidants, plasticizers | 2-Palmitoylglycerol | 23470-00-0 | NIAS | 477 | 917 | 44.9 | 81.7 | M ⁺ was not detectable | Confirmed | 2516 | 2519 |
| | Erucamide | 112-84-5 | IAS | 684 | 725 | 63.2 | 70.5 | Confirmed (-1.408 ppm) | Confirmed | 2788 | 2625 |
| | Squalene | 111-02-4 | NIAS | 585 | 915 | 12.8 | 77.9 | Confirmed (2.656 ppm) | Confirmed | 2819 | 2819 |
| | Octadecyl 3-(3,5-di- <i>tert</i> -butyl-4-hydroxyphenyl)propionate | 2082-79-3 | IAS | 341 | 919 | 3.71 | 98.9 | Confirmed (-3.648 ppm) | Confirmed | 3604 | 3823 ³ |
| | α -Tocopherol | 59-02-9 | IAS | 668 | 901 | 53.7 | 75.4 | Confirmed (3.114 ppm) | Confirmed | 3147 | 3149 |
| Tributyl acetyl citrate [TBAC] | 77-90-7 | IAS | 609 | 907 | 77.1 | 96.4 | Confirmed (-0.970 ppm) | Confirmed | 2244 | 2250 | |
| COMPOUNDS THAT COULD BE IDENTIFIED WITHOUT ANY HITS FROM NIST MASS SPECTRA LIBRARY | | | | | | | | | | | |
| UV stabilizer and other migrated compound | 2-(2H-Benzotriazol-2-yl)-4,6- <i>bis</i> (1-methyl-1-phenylethyl)phenol | 70321-86-7 | IAS | – | – | – | – | Confirmed (0.402 ppm) | Confirmed | 3664 | n.d. |
| | 2,6-Di- <i>tert</i> -butyl-4-methylene-2,5-cyclohexadienone [BHT-QM] | 2607-52-5 | NIAS | – | – | – | – | Confirmed (-2.017 ppm) | Confirmed | 1487 | n.d. |

n.d.: no available data

¹: measured linear retention index.²: linear retention index from NIST retention index library.³: estimated retention index from NIST retention index library.

plastics (PP-22, PP-23, PP-41, PP-48, PP-50, PP-53). These compounds were confirmed by an *n*-alkanes standard mixture (from *n*-C₆H₁₆ to *n*-C₄₀H₈₂). The biggest number of the *n*-alkanes was identified in the extract of the PP-23 sample, with a total of 24 *n*-alkanes, covering the C₆–C₄₀ boiling point range. These alkane compounds may originated from machine oil, lubricants, waxes and plasticizers of petroleum series or their derivatives.

As we mentioned in the introduction, using 85% probability as a threshold for the identification of compounds in GC-EI-QMS measurements is a common practice. Applying this to our results would have disqualified 30 compounds for all their occurrences (detailed results can be seen in [Supp. Inf. Table 2](#)) without even considering their retention data. Lowering the threshold to 80% would lower the number of disqualified compounds to 25. In other words, only half or less of the peaks in a chromatogram could be identified with a probability value of 85%

and 80%. Toluolaldehyde is one of the compounds that had a very low probability (14.4%–36.6%) whenever it was detected. In all occurrences, it was tentatively identified as *ortho*-toluolaldehyde with high *MF* (797–917). Toluolaldehyde has three regioisomers which means that the isomers have the same functional group, but this group is located at different positions (*ortho*, *meta*, *para*) on the aromatic ring. The resulting lack of uniqueness of the mass spectra always lead to low probability values independent from the quality of the measured mass spectrum. Likewise, several other compounds (e.g. 2,4-di-*tert*-butylphenol and 2,6-di-*tert*-butylphenol) are destined to have low probability values. Therefore, we suggest evaluation based on *MF*s instead.

NIST suggests that *MF* above 800 is a good match and from 700 to 800 it is a fair match. Using 700 as an acceptance limit for identifications based solely on GC-EI-QMS measurements instead of the protocol described in the first paragraph of [Section 2.6](#) would slightly decrease

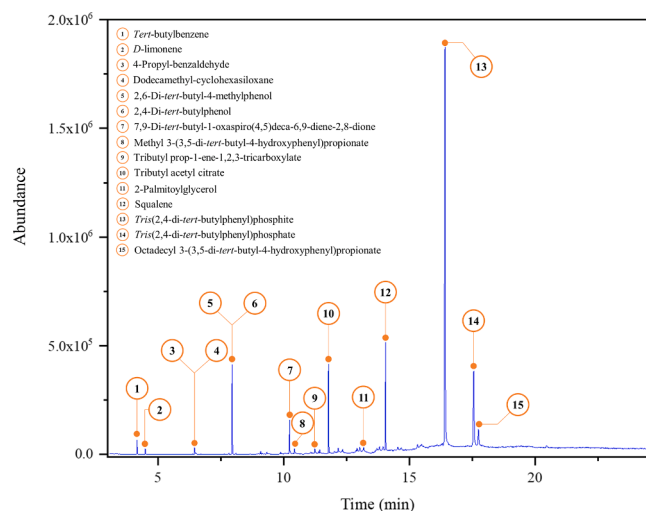


Fig. 1. Chromatogram of PP-09 sample.

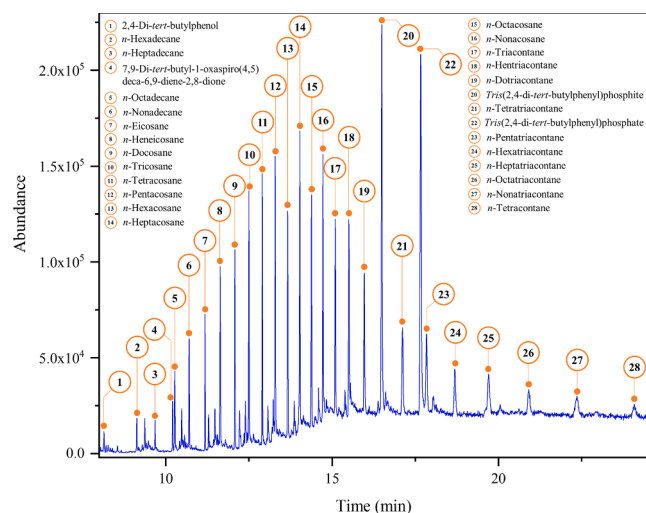


Fig. 2. Normal alkane (*n*-alkane) homologue series in GC-EI-QMS total ion chromatogram of PP-23 samples.

the number of identified peaks (from 364 to 349). Increasing the acceptance limit of the *MF* value (from 700 to 850) notably increases the number of peaks excluded from tentative identification. On the other hand, with *MF* acceptance value of 700 false tentative identification occurred for only four compounds. Based on all this, we decided to consider all hits with a matching factor above 700 for confirmation. If no hits reached this limit, then the hit with the best matching factor was considered. Especially when it suggested compounds that are known to be used in the production of FCPs or that are known decomposition products or contaminants of such compounds. In our workflow we met 4 distinguished scenarios (see more results in [Supp. Inf. Table 3](#)):

- the *MF* was above 700 and the tentative identification was confirmed by analytical reference material (31 compounds);
- the *MF* was above 700, but the tentative identification proved to be wrong (4 compounds);
- the *MF* was above 700, but analytical reference material was not available for the confirmation analysis (5 compounds);
- the *MF* was under 700 for either all or some occurrences still the tentatively identified compound was confirmed. (6 compounds);
- compounds that could be identified without any hits from NIST mass spectra library (2 compounds).

3.1. Matching factor above 700 with successful confirmation

Out of the 45 identified, non-alkane compounds, 31 have an *MF* value above 700 for all of its occurrences and all of these occurrences were confirmed with analytical reference material. For these 31 compounds, the GC-EI-TOFMS measurements either provided confirmation or could give no further information because of the lack of a detectable molecular ion.

The most frequently migrating compound was *tris*(2,4-di-*tert*-butylphenyl)phosphite (Irgafos 168), which appeared in the chromatograms of all, except seven of the tested PP samples (PP-24, PP-31, PP-32, PP-36, PP-41, PP-48 and PP-50). It is a common trisarylphosphite-type processing stabilizer and antioxidant in the polyolefin industry. It is also used as flame retardant with much lower environmental toxic effect than brominated flame retardants [35,36]. It is important to note, that the molecular mass of Irgafos 168 is relatively high (646.45148 Da), and in preliminary experiments, its molecular ion proved to be critical in the identification. Using the widely applied 50–500 AMU scan range, the library search gave either 2,4-di-*tert*-butylphenol (2,4-DTBP) or 4,4'-methylene-*bis*(2,6-di-*tert*-butylphenol) as best hits. However, based on the *LRI*s these hits are obvious misidentifications despite their high *MF* values. Consequently, we decided to use a wider scan range (50–700 AMU) for all our measurements. The oxidized form of Irgafos 168 was found in all PP samples that contained Irgafos 168. 2,4-DTBP, one of the degradation products of Irgafos 168 was also detected in 40 investigated samples, in three cases (PP-11, PP-24 and PP-52) along with its constitutional isomer, 2,6-DTBP. These two compounds and oxidized Irgafos 168 are both NIAS.

The migration of other antioxidants from the tested polypropylene-based FCPs was also observed. In some cases, α -tocopherol, a natural antioxidant was observed but the occurrence of synthetic phenolic antioxidants was much more common. One of them was 2,6-di-*tert*-butyl-4-methylphenol which is usually called butylated hydroxytoluene (BHT). This additive is also used in food and cosmetics as preservatives to prevent the oxidation of their fat and oil content [37]. We found BHT in nine PP samples with matching factors ranging from 786 to 945, even though its probability factor never reached 80% (its maximum probability factor was 74.3%). Furthermore, we could detect the migration of degradation products of BHT and other synthetic phenolic antioxidants (e.g., Irganox 1076, Irganox 1010) such as 2,6-di-*tert*-butyl-1,4-benzoquinone, 2,6-di-*tert*-butylphenol and *tert*-butylbenzene on multiple occasions. Since the positive list of Commission Regulation (EU) 10/2011 [6] does not include these compounds, they are NIAS, just like 7,9-di-*tert*-butyl-1-oxaspiro(4,5)-deca-6,9-diene-2,8-dione. This compound – a by-product of Irganox 1076 production [24] – was identified in 23 samples. An other antioxidant similar to BHT, 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (BHA) was identified in three samples.

The durability and flexibility of plastic products are facilitated by plasticizers [3]. Nowadays, phthalate-based plasticizers are still widely used in the plastics industry, but increasing efforts are being made to replace them. From our PP samples the migration of diethyl phthalate (from PP-10, PP-12, PP-13), dibutyl phthalate (from PP-27 and PP-42) and di-*n*-octyl phthalate (from PP-14, PP-22, PP-39 and PP-48) was detected with good *MF* each time. Phthalates in general pose a serious health risk for people because of their reprotoxic, carcinogenic and mutagenic effects [38]. Therefore, alternatives such as citrates, adipates and trimellitates are increasingly used.

2,4-*bis*(α,α -dimethylbenzyl)phenol was detected in one sample (PP-53) but with excellent *MF* (917). Its tentative identification was confirmed by both analytical reference material and exact mass measurement with GC-EI-TOFMS. This compound is a degradation product of 2-(2*H*-benzotriazol-2-yl)-4,6-*bis*(1-methyl-1-phenylethyl)phenol (Tinuvin 900), which is a benzotriazole-type UV absorber. The benzotriazole group can be cleaved from the Tinuvin 900 molecule with the appropriate wavelength of UV light [39]. The presence of this degradation product induced a search for the signs of Tinuvin 900. As a result,

Tinuvin 900 was indeed identified in the chromatogram of this sample using analytical reference material. This compound could have easily been missed as its EI mass spectrum is not included in our used version of the NIST mass spectral library.

3.2. False hits with matching factor above 700

The tentative identification based on *MF* value yielded false hits in a total of 14 cases. These 14 cases belonged to four compounds. Almost every sample (exceptions being PP-9 and PP-43) that released BHT also released a compound for which the best matching hit of the NIST library search was always 2-*tert*-butyl-5-(2-methylprop-2-en-1-yl)cyclohexa-2,5-diene-1,4-dione (729 < *MF* < 780). Its structure and library spectrum are shown in Fig. 3.A. The recorded low-resolution mass spectrum is shown in Fig. 3.B. However, this suggestion was rebutted by the GC-EI-TOFMS measurement (See mass spectrum in Fig. 3.C.) Still, the acceptable match of the measured and the library spectra indicate structural similarity. The investigation of the structure and exact mass of potential degradation products of BHT led to 2,6-di-*tert*-butyl-4-methylene-2,5-cyclohexadienone (BHT-QM), a compound that is not included in the NIST 17 mass spectral library (Version 2.2). (See structure and measured spectra in Fig. 3.B and C.) Unfortunately, BHT-QM was not commercially available, so confirmation with retention data (*LRI* = 1487) was enabled by its synthesis based on the oxidation of BHT with freshly prepared silver oxide.

Diisooctyl phthalate was tentatively identified in the chromatograms of two samples (PP-32 and PP-50), in both cases with *MF* values over 800. However, the *LRI* of the tentatively identified compound was 2540, while the *LRI* of diisooctyl phthalate – under the same chromatographic

conditions – was 2525. Meaning that the difference was out of the confirmation range ($\Delta LRI < 10$). Based on the recorded EI-MS spectrum, which contains the characteristic peaks (e.g. *m/z* 149) of phthalates, it was assumed that it was indeed a phthalate-type compound. The identification of the compound was aided by the fact that *bis*(2-ethylhexyl) phthalate – which was included in the NIST hit list (but not as the first hit) – has an *LRI* value of 2544 in the NIST retention index library [33] and our measured *LRI* value was 2540. These two *LRI* values are close to each other, so it can be assumed that the compound suggested by the NIST retention index library [33] is the same as the migrated compound. The *LRI* measurement using analytical reference material has also confirmed that the observed peak belongs to *bis*(2-ethylhexyl) phthalate instead of diisooctyl phthalate.

In two chromatograms 2,2-dimethylpropanoic anhydride (PP-08; PP-10) and in three (PP-24; PP-31; PP-36) other ones [2.2]paracyclophane were observed. In all cases, the matching factor was high (above 800). However, the *LRI* values found in the NIST retention index library [33] for these compounds were far from the measured *LRI* values, with a ΔLRI of 13 in the case of 2,2-dimethylpropanoic anhydride and 32 in the case of [2.2]paracyclophane. Furthermore, GC-EI-TOFMS measurements did not confirm the results of the tentative identifications either.

3.3. Matching factor above 700, but no analytical reference material is available

For five tentatively identified compounds, the matching factors were above 700, however, no analytical reference material was available to confirm their identification. So, in these cases confirmation was based

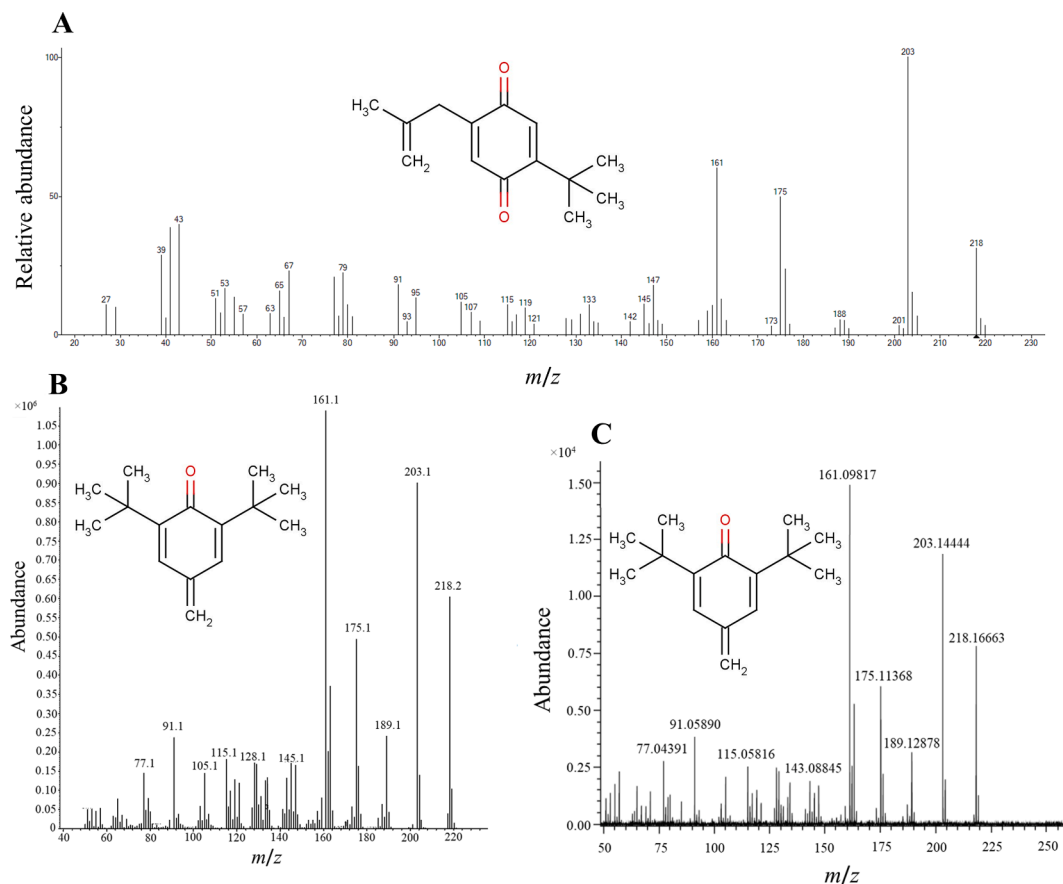


Fig. 3. Comparison of different EI mass spectra of 2-*tert*-butyl-5-(2-methylprop-2-en-1-yl)cyclohexa-2,5-diene-1,4-dione and 2,6-di-*tert*-butyl-4-methylene-2,5-cyclohexadienone (BHT-QM). **A)** Low resolution EI mass spectrum of 2-*tert*-butyl-5-(2-methylprop-2-en-1-yl)cyclohexa-2,5-diene-1,4-dione from NIST mass spectral library. **B)** The measured low resolution EI mass spectrum of BHT-QM. **C)** The measured high resolution EI mass spectrum of BHT-QM.

on the results of GC-EI-TOFMS measurements and *LRI* values obtained from the NIST reference index library. All five compounds are considered NIAS since the positive list of Commission Regulation (EU) 10/2011 [6] does not include neither of them. 2-*tert*-butyl-4-(2-phenylpropan-2-yl)phenol, 2,4-*bis*(dimethylbenzyl)-6-*tert*-butylphenol and 2,6-di-*tert*-butyl-4-(2-phenylpropan-2-yl)phenol migrated only from one FCP sample (PP-53). They were detected with good (848) and excellent (935 and 929) *MF*, respectively. The measured exact mass of the molecular ion for all of them showed less than 3 ppm deviation from the theoretical value. The measured *LRI* values were acceptably close to the values obtained from the NIST retention index library for all of them, even though for 2-*tert*-butyl-4-(2-phenylpropan-2-yl)phenol only an estimated *LRI* was available in the database.

In extracts of PP-9, PP-17 and PP-24 samples, tributyl prop-1-ene-1,2,3-tricarboxylate was tentatively identified. In all three cases its *MF* was above 800. GC-EI-TOFMS measurements confirmed the tentative confirmation. However, analytical reference material was not available for the retention time-based identification. For this compound the NIST retention index library [33] contains only an estimated *LRI* value (2297), which is 144 units lower than the one we measured. Nevertheless, even this considerable ΔLRI value does not warrant the rejection of the tentative identification, since the estimated *LRI* values are often far from the real ones. Acceptance of the tentative identification is further supported by the fact that tributyl prop-1-ene-1,2,3-tricarboxylate can originate from TBAC – a common non-phthalate plasticizer – with the loss of acetic acid.

In 12 of the extracts from the 53 PP-based samples investigated, Metilox was identified with a matching factor between 735 and 857. Confirmation based on both GC-EI-TOFMS and *LRI* was successful. This compound is considered as NIAS. However, observing the structural formula of the molecule, one can see similarities with the structural formula of several phenolic antioxidants. This is because Metilox is used as a precursor in the manufacture of many phenolic antioxidants (e.g. Irganox 1076), which is probably why it is also found in polyolefin plastics. Thus the fact that Metilox and Irganox 1076 occurred together in 9 of the chromatograms of 12 extracts, also supports this identification.

3.4. Matching factor below 700

Six compounds were identified despite having an *MF* below 700 in at least one of its occurrences. The identification of all these compounds was supported by comparison with analytical reference materials. Out of the six only 2-palmitoylglycerol – which is migrated from almost half of the investigated plastic samples – could not be confirmed with GC-EI-TOFMS due to the lack of the molecular ion in its spectrum. This compound is applied as a slip agent to help the manufacturing process of the plastic. For the other five compounds – including erucamide, another slip agent – GC-EI-TOFMS measurement confirmed the tentative identification.

The *MF* value of Irganox 1076, which is an antioxidant, was below 700 five times out of 14 hits. In all these five cases, a highly probable cause for the low *MF* value was the low intensity of the chromatographic peak. The same may apply to the other compounds of this group. Hits of Irganox 1076 were successfully confirmed with GC-EI-TOFMS. Still, measuring retention with analytical reference material for further confirmation was also very reassuring, as comparison of the *LRI* of the peak in the samples' chromatogram to that in the NIST retention library [33] lead to a mismatch. The reason may be that only estimated *LRI* value was available in the library. (Just like for tributyl prop-1-ene-1,2,3-tricarboxylate discussed previously.) All this shows that caution should be exercised when confirming with *LRI* values taken from a database. The *LRI* values of a compound may differ depending on the gas chromatographic measurement conditions, and even more remarkable differences may occur when the *LRI* is determined theoretically.

In addition to 2-palmitoylglycerol, erucamide and Irganox 1076,

squalene was tentatively identified three times out of six hits, α -tocopherol one time out of three hits, and tributyl acetyl citrate (TBAC) three times out of 11 hits with a matching factor below 700. These compounds are applied as slip agent, antioxidant, oxygen-scavenging agent and plasticizer, respectively. Enabling the identification of TBAC – even though it tends to have low *MF* – is important as it is an emerging plasticizer due to having more favourable human and environmental toxicological properties than phthalates.

4. Conclusion

In our study, we performed migration studies with 21 single-use and 32 reusable polypropylene-based FCPs at 60 °C for 10 days in isooctane food simulant. Tentative identification of migrated chemical compounds from the extracts was performed with GC-EI-QMS and mass spectral library search. In addition to the 24 *n*-alkanes, 46 compounds were tentatively identified with this method. Of these, 31 were confirmed by both GC-EI-TOFMS and analytical reference materials. Five migrated compounds were confirmed by GC-EI-TOFMS and comparison of the measured *LRI* values with that from the NIST retention index library [33] since no analytical reference materials were available for these compounds.

In 4 cases the tentative identification gave unsatisfactory results, the hits of the mass spectral library search were false. Instead, *bis*(2-ethylhexyl) phthalate was identified with the help of the retention index library and confirmed successfully with analytical reference material. BHT-QM, which to the best of our knowledge – has been identified for the first time as a migrant from PP, was not available commercially, so confirmation with retention data was enabled by its synthesis based on the oxidation of BHT with freshly prepared silver oxide. Naturally, this confirmation had to be preceded by a tentative identification. As the NIST mass spectra library does not include the mass spectrum of this compound, the tentative identification was based on similarity of carbon skeleton to that of the hits of mass spectral library search and possible degradation pathways. Last, but not least, two other compounds suggested by the mass spectral library search remained unidentified despite their high matching factors, because their GC-EI-TOFMS measurements showed big deviation in the measured and calculated mass values.

For six migrants, identification was achieved despite matching factors below 700. For each of these compounds, confirmation was successfully performed by GC-EI-TOFMS measurements and/or analytical reference materials.

As a result, a total of 45 non-alkane compounds were identified and confirmed from the extracts of 53 plastic food contact material samples. Of these 45 migrated compounds, only 15 are included in the positive list of Commission Regulation (EU) 10/2011 [6]. The other 30 compounds must all be considered NIAS. They may originate from degradation of plastic additives and other sources such as contaminants of technological substances and cross-contaminations by plastic manufacturing processes. The fact that the number of the identified NIAS in this study is more than two times bigger than that of the IAS, highlights the importance of reliable untargeted analysis of the migrating compounds.

Our results prove that GC-EI-QMS followed by evaluation with AMDIS and NIST mass spectral library is a powerful tool in the non-target analysis of compounds migrating from plastic food contact materials. But these same results also prove that both reliability and productivity can be increased. The number of false identifications can be decreased both by measuring with GC-EI-TOFMS and using retention data. The latter is more powerful if it is measured in the same laboratory with the same analytical method, but using a retention index database can also be beneficial. Productivity (i.e. the number of identified compounds) can, however be improved mainly through expertise. Knowledge on materials used in plastic production, including their degradation products and typical contaminants may help to identify compounds with low *MF* values as well as identifying the ones for which

the tentative identification – based mainly on the NIST mass spectral library search – proved to be false.

CRedit authorship contribution statement

Csaba Kirckeszner: Conceptualization, Formal analysis, Visualization, Writing – original draft. **Noémi Petrovics:** Conceptualization, Writing – review & editing. **Zoltán Nyíri:** Conceptualization, Writing – review & editing. **Bálint Sámuel Szabó:** Conceptualization, Writing – review & editing. **Zsuzsanna Eke:** Conceptualization, Funding acquisition, Supervision, Writing – review & editing.

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.

Acknowledgement

We are thankful to Wessling Nonprofit Ltd. for providing financial support, laboratory equipment and materials for our research. The authors gratefully acknowledge Servier Hungary Ltd. for providing the opportunity to measure on the GC-EL-TOFMS instrument. This research program has been implemented with support provided from the National Research, Development and Innovation Fund of Hungary, financed under project No. 128440 of the FK18 funding scheme and New National Excellence Program (ÚNKP-17-3) of the Ministry of Human Capacities.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.microc.2022.107772>.

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