Non-target screening of (semi-)volatiles in food-grade polymers by comparison of atmospheric pressure gas chromatography quadrupole timeof-flight and electron ionization mass spectrometry

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ABSTRACT

Atmospheric pressure gas chromatography (APGC) coupled to quadrupole time-of-flight (QTOF) and electronionization mass spectrometry together with commercial library search are two complementary techniques for non-target screening of volatile and semi-volatile compounds. Optimization was first conducted to achieve easier search of correspondent peaks between the two systems. Analytical strategy for the determination of volatile and semi-volatile compound with different identification confidence levels was then proposed and applied to food contact grade polypropylene (PP) samples. Identification was found to be much easier and less time-consuming especially when correspondent peak was found in the two systems with the help of library search, exact mass of precursor and fragment ions as well as Kovats Index (KI). The behavior of APGC-QTOF-MS was also further investigated. Apart from the M+. ion and the well-known adduct [M+H]+ others such as [M-3H + O]+, [M-3H+2O]+ and [M-H+3O]+ were also observed for n-alkanes. Besides, new reaction products were found, formed by diol compounds (1-Monostearoylglycerol, 2-Monostearoylglycerol and NX 8000K) and silanediol dimethyl, which would be a transformation product of the silicone base septum or the methyl 5% phenyl polysiloxane based column. These new compounds were only detected in APGC-MS-QTOF as EI-GC-MS was not enough sensitive for this purpose

Keywords:
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1. Introduction

Food safety concerns arising from food contact materials (FCM)have attracted growing attention in recent years. Current legislations mainly focus on authorized substances and on those that could be present in specific foods. This is true in food [1] as well as FCM sector. In FCM, most of them are also known as intentionally added substances(IASs). Traditional targeted screening (TS) based on building ways to determine a list of known compounds [2], normally IASs, is a typical strategy to check FCM compliance. However, apart from IASs, there are also non-intentionally added substances (NIAS) coming from impurities of starting materials, degradation products from raw materials, unwanted side-products, and so on, which might endanger consumer health [3,4]. Hence, to give consumers higher level of security, NIAS should also be considered in FCM safety evaluation before being launched into the market. Target screening is therefore

insufficient, and generic analytical screening methods are required [5]. Non-target screening (NTS) is a very good idea in order to have a comprehensive understanding of FCMs; however, it is not so easy without knowing even the origin of the unknowns. Fortunately, the development of hybrid quadrupole high-resolution mass spectrometer (Q-HRMS) like quadrupole-time of flight mass spectrometry (Q-TOFMS) together with soft ionization techniques e.g. electron spray ionization (ESI) and atmospheric pressure chemical ionization (APCI) allow obtaining exact mass of the molecule. Also, high energy collision cell can provide structural information from accurate masses of fragmentions. Taking the advantage of HRMS, soft ionization, and collision fragmentation, elucidation of the molecular structure is available [6]. Liquid chromatography (LC) coupled to Q-HRMS have been successfully applied for NTS of non-volatile compounds in various matrices including wastewater [7], olive oil [8], food [1,9], FCM [10–13], and soon.

For volatile compounds, conventional GC-MS in electron ionization (EI) mode is a powerful tool for the identification as commercially available spectral libraries, such as NIST and Wiley, cover the spectra of several hundreds of thousands of compounds [14]. However, its shortage is also obvious when chemicals are not included in the library. In this situation, soft ionization mode together with HRMS are in high demand. APGC-QTOF-MS is the combination to meet this requirement, which is merely available in the market since 2008 [15]. Until now, it has been successfully employed to detect some specific classes of chemical sin different samples, for example, organophosphorus pesticides in fruits and vegetables [16], nitro-polyaromatic hydrocarbons in PM2.5 [17], nitro and oxo PAHs [18,19] and brominated flame retardant sin food [20]. To the best of our knowledge, it has not yet been widely used for (true) NTS. A non-target analytical strategy based on GC-(EI)TOF-MS and APGC-QTOF-MS was proposed y Cherta et al. [21].Library search of the GC-(EI)TOF-MS spectrum was first conducted to generate positive matches list (library match>700). Then both molecular ion and protonated molecule of those candidates were extracted from APGC-QTOF-MS chromatogram at similar retention time to confirm or reject candidates. It has been used for identification of potential migrants from 4 composite FCMs into isooctane and Tenax food simulants. The number of candidates were reduced by approximately half with the help of APGC-QTOF-MS. However, the methodology did not deal with the case where no candidate can be obtained with satisfied match. In this case, the chemical would probably not be present in the library, and we would have no idea about the possible molecular ion neither protonated molecule. Hence, the potential of APGC-QTOF-MS for unknown elucidation is limited. Onghena et al. [22] developed a strategy for elucidation of unknown migrants from plastic FCM (baby bottles) based on GC-MS, GC-(EI)TOF-MS, and APGC-QTOF-MS. Extracted mass of molecular ion and protonated molecule were carried out to search for correspondent peak in APGC-QTOF-MS spectrum as well. If no correspondence could be found by this way, APGC-QTOF-MS spectra was manually examined for possible molecular ion or protonated molecule at the expected retention time. However, how to do this was not clarified. In addition, retention time distinction between both systems was not well defined. APGC-QTOF-MS was said to have about2 min earlier retention time than GC-(EI)TOF-MS. However, the time difference is not fixed across the whole chromatogram. This would add difficulty in finding correspondent peak between both systems especially when the chromatogram is complicated. Furthermore, the two above mentioned studies mainly focused on the power of APGC-QTOFMS in non-target identification, but no effort have been made to see the difference between both systems. The objective of this article is to further explore the potential of APGC-QTOF-MS for NTS using conventional GC-MS together with commercial library search as a

complementary tool by analyzing the extractables from food contact grade PP. Adjustment of chromatographic conditions to make the two systems more comparable has been made. Struggle has been made to further understand the distinction between these two complementary platforms, especially the behavior of APGC, so that complementary information from both techniques can be realized to widen the scope and reduce the time of non-target volatile compounds screening.

2. Materials and methods

2.1. Reagents and samples

Dichloromethane (DCM) for GC residue analysis was bought from Scharlab (Barcelona, Spain). Ultra-pure water was obtained from a Wasserlab purification system (QUGR0011; Navarra, Spain). Standards used were purchased from various suppliers: C7–C40 saturated alkane standard from Supelco (49452-U; Pennsylvania, USA); didecyl phthalate (84-77-5) from Riedel-de Haen (Bucharest, Romania); benzene propanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester (6386-38-5) from Activate Scientific (Ely, UK); benzofuran (271-89-6) and silane, cyclohexyldimethoxymethyl- (17865-32-6) from Alfa Aesar (Heysham, UK); Tinuvin 326 (3896-11-5) and Irgafos 168 (31570-04-4) from Ciba-Geigy (Barcelona, Spain); tridecane (629-50- 5), octacosane (630-02-4), stearamide (124-26-5), palmitamide (629-54-9), benzaldehyde, 4-propyl- (28758-06-0), dioctyl phthalate (DOP; 117-81-7), butylhydroxytoluene (BHT; 128-37-0), 2,6-di-tert-butylbenzoquinone (719-22-2), 2,4-di-tert-butylphenol (96-76-4), 3,5-ditert-butyl-4-hydroxybenzaldehyde (1620-98-0), diisobutyl phthalate (DIBP; 84-69-5), dibutyl phthalate (DBP; 84-74-2), palmitic acid (57-10-3), stearic acid (57-11-4), tributyl acetylcitrate (77-90-7), 1-monostearolglycerol (123-94-4, abbreviated as 1-MSGC), 2-monostearolglycerol (621-61-4, abbreviated as 2-MSGC) and NX 8000K (882073-43-0) from Sigma-Aldrich (Madrid, Spain); Oxidized Irgafos 168 were self-manufactured in our lab. Two PP sheets intended for food contact use were supplied by an European company.

2.2. Solvent extraction from polypropylenes

PP samples were quickly cleaned with ethanol, dried in the air, and cut into small pieces (ca. 2mm×2 mm) with scissors. 1.00 g of sample was weighed into a 20 mL glass vial by a Mettler Toledo analytical balance (XS205; Ohio, USA). Three consecutive extractions with 2 mL DCM were applied in an ultrasonic bath for 1 h (Brasonic 3510-MTH; Connecticut, USA). The extract was collected and concentrated by a nitrogen concentrator (Techne DB-3; Staffordshire, UK) at 40 °C until ca. 1 mL and weighed. The concentrated extract was then filtered with a 0.2 μm Acodisc GHP syringe filter (Corporation, New York, USA), and injected in both GC-MS and APGC-QTOF-MS using the parameters described below. Three replicates were conducted for each sample. Also, two blank samples were prepared in the same manner as described above, with the exception that no sample was added.

2.3. GC-MS analysis

For GC-MS injection, a 7820 A gas chromatography equipped with a 7693 autosampler, coupled to a 5977B mass spectrometry detector from Agilent (California, USA) was used. HP-5 MS column (30m×0.25mm id, 0.25 μm film thicknesses) also from Agilent Technologies was employed. 2 μL injection volume was applied using splitless mode, and solvent delay was 3 min. Liner with 4mm internal diameter and 10 μL syringe were used in both systems. The inlet temperature was set at 250 °C. Helium (99.999%) was the carrier gas at a constant flow rate of 2.4 mL/min. In-line gas purifier (RMSH-2, Agilent)

was used to remove oxygen, water, and hydrocarbons from He before entering GC in both systems. The total flow, however, was evenly divided into 2 fractions: one went into the mass detector and the other went into an olfactory even though it was not used here. Scan mode with a mass range from 40 to 700 was applied. The temperature program was as follows: kept 50 °C for 3 min, increased to 300 °C at the rate of 10 °C/min, and held for 12 min.

2.4. APGC-QTOF-MS analysis

For APGC-QTOF-MS injection, an Agilent A7890 gas chromatography equipped with a PAL autosampler, coupled to a high-resolution mass spectrometer Xevo G2 QTOF (> 20000 FWHM at m/z 956 and >10000 FWHM at m/z 152) from Waters (Massachusetts, USA was employed. Atmospheric pressure chemical ionization APCI) was used to interface the GC and QTOF-MS, which allows obtaining precursor ions.

SPB 5 column, which has the same dimension (30m×0.25mm id, 0.25 μm film thickness) and stationary phase (methyl 5% phenyl polysiloxane) as HP 5 MS column was applied. The inlet temperature, oven temperature program and carrier gas were all as the same as that in GC-MS analysis. The flow rate here, however, was 3.5 mL/min. In this way, the chromatograms between GC-MS and APGC-QTOF-MS are more comparable. The heated transfer line temperature was set at 280 °C, and the auxiliary gas (N2) flow rate 300 L/h. 150 °C source temperature and 1.0 μA corona current were applied. No humidity modifier was used. Cone and desolvation gas (N2 99.999%) flow were 20 and 175 L/h, respectively. The scan mass range was also from 40 to 700. MSE acquisition mode which is designed for simultaneous acquisition of both precursor and fragmentation ions was used. Low energy (6 V) was set to keep more precursor ion while high energy (10–40 V) was applied in the collision cell to generate higher fragmentation. Positive ion mode was selected. Exact mass 281.0517 (C7H21O4Si4) from column bleed was used to correct the mass for every peak of interest after injection.

The mass accuracy of another column bleed ion 355.0705 (C9H27O5Si5) was checked after correction to ensure the quality of correction. Acceptable mass distinction here was set at 5 ppm. If the mass correction is not good, which happens sometimes when there is interference near the used mass, 355.0705 can be used for correcting mass, and check 281.0517. If interference happens in both ions, which should not be a common case, other column bleed ions for example, 207.0327 or 429.0893 can be considered as well. BHT was injected before and after the samples to make sure the equipment was in good condition.

2.5. Data processing

The workflow of identification using both GC-MS and APGC-QTOFMS is shown in Fig. 1. Identification confidence proposed by E. Schymanski et al. [23] was used here. It contains 5 levels. **Level 1: Confirmed structures** are those confirmed by a reference standard with MS, MS/MS and retention time match; **Level 2**: **Probable structure** indicates unambiguous spectrum-matching with library or literature information or diagnostic evidence including MS/MS fragments and/or ionization behavior, parent compound information and the experimental context; **Level 3: Tentative candidate(s)** describes that evidence exist for possible structures but no one specific structure can be concluded as for lacking of sufficient information, for instance, positional isomers; **Level 4: clear molecular formula** means only one formula can be undeniable assigned by spectral information, e.g., adduct, isotope, and/or fragment information, but no further information can be obtained; **Level 5: Exact mass (m/z)** of interest for the investigation can be measured, but no sufficient information exists to assign even one specific formula.

The first step was to pick out all peaks that had a Signal to Noise ratio higher than 10 in APGC-QTOF-MS by manually checking the total ion chromatogram (TIC) using Masslynx 4.1 from Waters. Peaks present also in blanks were excluded, except for the case where its height was over 10 times higher in samples than that in blanks [21]. The second step was to find out their correspondent peak in GC-MS chromatogram. To achieve this goal, the spectra of peaks that had closed retention time (less than 0.5 min) in GC-MS were compared to the APGC-QTOF-MS spectrum in low and high energy modes. The comparison of chromatograms of the same sample in GC-MS and APGCQTOF- MS were much easier when applying the optimized parameters described above, because of the smaller retention time difference between them. Automated Mass Spectral Deconvolution & Identification System (AMDIS) from National Institute of Standards and Technology (NIST; Maryland, USA) was employed for peak picking from GC-MS chromatogram. It was of great help to find out separate components by deconvoluting GC-MS file automatically even though some of them were very small or overlapped by others such as alkanes. In most cases, shared abundant ions were found in both systems which helped to find correspondence. However, there were also exceptions where the spectra in both systems were totally different as shown below (3.1.3) and also in a previous study by Onghena et al. [22]. In this case, exact mass of high match candidates from possible peaks were considered. By this way, correspondence could be found for most peaks. If neither shared abundant ion(s) nor high match candidates could be found, which would happen but might not be a common case, it would be difficult to know if they were correspondent or not. Of course, not all peaks had correspondence in GC-MS, because APGC-QTOF-MS has much higher sensitivity than GC-MS. What is more, the inherent property of the two ionization techniques is not the same. It is possible that some compounds could only be detected by one of these two techniques. The third step was to search candidates using NIST library once correspondence was found. When hits with both match and R. match higher than 700 were found, their exact mass were compared with the precursor ion obtained in APGC-QTOF-MS, considering the possible adducts, usually the molecular ion or the protonated ion (fourth step). Relatively low match value (700) was set here just to reduce false negative judgement, because it could be the result of relatively low concentration, peak overlap and so on. As additional confirmation, exact mass and Kovats Index (KI) match in the following steps were important to decrease false positive deduction. When the accurate mass error is lower than 5 ppm, KI was checked (< 30) as well if it existed (fifth step). This way, taking the advantage of library search as well as the exact mass of the precursor ion, the number of tentative candidates could be largely reduced. Then, reference standards were injected in APGC-QTOF-MS to confirm it, if available. If only one candidate matched spectral library, accurate mass and KI, it was set as probable structure even though no reference standard was available. When no correspondent peak was found in GC-MS, or all candidates were ruled out by KI, accurate mass or even library match, another process was applied. This process is much more effortful and difficult, posing a great challenge in analytical chemistry. It involves accurate mass of the precursor ion, element selection, adducts and isotopic fit [4]. Even though unambiguous molecular formula can be generated, there could be, in most cases, a lot of chemicals fit this formula, making the work imaginably huge, especially when the number of candidates is huge. In this sense, information from samples, literature search, and structure deduction from probable/confirmed chemicals are useful to narrow the range of candidates. MassFragment from Waters is a powerful tool to generate possible fragments from a given chemical based on the likelihood of breaking certain bonds [6]. Therefore, it allows us to evaluate if a candidate is good or not by comparing experimental spectrum with

MassFragment result. According to the extent we obtain, candidates can be assigned to various identification confidence levels, from level 1 to level 5 as shown in Fig. 1.

3. Results and discussion

3.1. Comparison between GC-MS and APGC-QTOF-MS

Soft ionization, in this case APCI, allows us to keep more precursor ions, while QHRMS helps to elucidate the structure of the molecular ion and/or protonated molecule. However, it is anyway difficult and timeconsuming, as there are still huge possibilities, even with an accurate mass. What is worse, there is no commercially available library for APGC-HRMS up to now. This means that every peak of interest obtained in APGC-HRMS chromatogram needs to be qualified using the structure elucidation, which makes the work imaginable huge and effortful. Combining APGC-QTOF-MS and GC-MS, the advantage of library search, precursor ions conservation as well as accurate mass, can be well integrated, making the structure elucidation of the peaks largely reduced. However, chromatograms between these two systems are not comparable because of their system distinctions. Optimization is therefore required.

3.1.1. Alkanes in GC-MS and APGC-QTOF-MS

As can be seen in Fig. 2A and B, the chromatograms in APGC-QTOFMS and GC-MS differ a lot. There are humps in GC-MS chromatogram, the help of NIST library search, the humps were identified as alkanes, which are not of high interest in terms of safety of food contact materials. Alkane standard (C7–C40) was injected in both systems to see the differences. Compared to GC-MS, the peaks of alkanes in APGC-QTOFMS were relatively low, some of which were even invisible at the used concentration (10 μg/g) (Fig. S1 A). However, they were very high in GC-MS (Fig. S1 B). This phenomenon suggested that APGC is not good for alkane ionization under the used conditions but makes it easier to detect the components coming from the matrix. Fig. S2 A shows the spectrum of octacosane. In agreement with the research by Hourani et al. [24] where dry nitrogen gas source APCIQTOF- MS was used, [M-H]+ ion was observed. Besides, [M-H]+ was found in many studies using various reagents (dimethylether, methane, and nitric oxide) as Bell et al. summarized in the introduction as well as in their own study which used 63Ni as a reagent [25]. In addition, [M-3H + O]+, [M-3H+2O]+, and [M-H+3O]+ were monitored. These ions were previously found for n-tridecane, n-pentadecane, and nheptadecane using corona assisted direct analysis in real time (corona- DART) coupled to QTOF-MS [26]. The authors explained that they originated from hydride abstraction and oxidation reactions. Surprisingly, the relative intensity of [M-H]+ decreased while that of [M-3H + O]+ increased with the reduction of carbon number in alkanes. As shown in Fig. S2 B, [M-H]+ of tridecane (183 m/z) was hardly visible, but [M-3H + O]+, [M-3H+2O]+ were very high. This phenomenon could cause confusion when choosing the precursor ion for an unknown peak. Fortunately, there were common fragments (85.1014, 71.0857, 57.0698 and so on) in all alkanes, which would be of great help when we encounter this kind of situation. However, [M+N]+ mode was observed for alkanes in another research where much higher cone gas flow 150 L/h was applied while only 20 L/h herein [27]. The authors investigated the effect of various experimental parameters on the formation of [M+N]+ ion, and the result showed that [M+N]+ ion could not be seen when the cone gas flow below 150 L/h.

3.1.2. Retention time in GC-MS and APGC-QTOF-MS

From the same chart (Fig. 2), we can notice that GC-MS had a shorter retention time than APGC-QTOF-MS under the same chromatographic conditions, leading it relatively troublesome to compare the two chromatograms directly. It is well known that EI works in a high vacuum environment, while APGC works in atmosphere. The high vacuum may generate a pulling force at the end of the column, driving the compounds within the column moving faster. This could be one of the reasons why compounds in APGC-QTOF-MS had longer retention time. It is interesting that shorter retention time was observed in APGCQTOF- MS compared to GC-(EI)-TOF in previous studies (Cherta et al., 2015). In their studies, higher flow rate was applied in APGC-QTOF-MS than that in GC-(EI)-TOF (1.2 VS 1.0 mL/min). Longer retention time in APGC-QTOF-MS, however, can be overcome by its ability to have higher flow rate than the usual level applied in EI source [28]. In order to make the two chromatograms more comparable, six standards (benzofuran, BHT, DOP, Tinuvin 326, didecyl phthalate and Irgafos 168) covering various molecular mass and retention times were injected under different flow rates (1.2, 1.5, 2.0, 2.5, 3.0, 3.5 mL/min) in APGC-QTOF-MS while 2.4 mL/min was kept in GC-MS. As can be seen in Fig. S3, when the flow rate in APGC-QTOF-MS reached 3.5 mL/ min, the retention time difference of all the six chemicals in the two systems is less than 0.5 min. This way, it is more convenient to find correspondent peaks in the two systems.

3.1.3. Spectra in GC-MS and APGC-QTOF-MS

Same compound could show totally distinct fragmentation behavior under EI and APGC ionization because the precursor ion to be fragmented is an odd electron radical ion in EI, while in APGC is an even electron protonated ion. Hence, fragmentation pathways as well as product ions are usually different. Even so, in most cases, same fragmentation ions could still be found in these two systems as shown in Table 1, regarding those high abundant ions. These shared fragmentation ions together with close retention time could be helpful when finding corresponding peak between these two systems. However, there are components that have totally distinct fragmentation behaviors in these two systems, which would add difficulty to find corresponding peak. 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione (RT 19.90 min in APGC-QTOF-MS in Table 1) is one of these exceptions. Its spectra in APGC-QTOF-MS low energy, high energy, and in GC-MS are shown in Fig. S4. The spectrum in GC-MS (C) looked totally different from that found in APGC-QTOF-MS, at both low and high energies (A and B). Therefore, adjusting gas flow rate in APGC-QTOF-MS to make them the same retention time is of great help.

3.2. Non-target screening of volatile and semi-volatile compounds from PP extracts

Using the method established above, the extracts from two PP samples used for food contact purpose were screened. The chemicals found in the samples with different identification confidence level are shown in Table 1. A total of 27 compounds were found in all samples. They are ordered according to their retention time. Nine of them were detected only by APGC-QTOF-MS, probably due to the higher sensitivity in APGC-QTOF-MS than in GC-MS or their different ionization pattern. Thirteen of them were confirmed by reference standards. They are antioxidants, lubricants, catalysts as well as their transformation products. Besides, 2 of them were set to have one probable structure, 5 of them were assigned to have tentative structures, and 7 of them were only found to have clear molecular formula. Case studies below will explain how the proposed strategy works in detail.

3.2.1. Reducing the number of candidates with the help of APGC-QTOF-MS

The peak with RT 19.37 min (unless otherwise specified, RT refers to retention time in APGC-QTOF-MS) was buried in the TIC chromatogram as shown in Fig. 3 A. Its spectrum is shown in Fig. S5 using also hidden in TIC mode GC-MS chromatogram, was clearly found in GC-MS (Fig. 3 B) thanks to AMDIS. However, there were quite a lot of candidates with match even higher than 850 (Fig. S6), which would cause trouble in identification. Fortunately, most of the candidates could be ruled out with the help of APGC-QTOF-MS. As can be seen in Fig. S5, precursor ion 279.1589 was observed in APGC-QTOF-MS, which suggested that the molecular weight could be 279 (M+**.**) or 278 ([M+H]+) considering two very common adduct modes. Finally, only 4 isomers (diisobutyl phthalate, 1-butyl 2-isobutyl phthalate, dibutyl phthalate, and di-sec-butyl phthalate) out of more than 30 candidates matched the exact mass. Dibutyl phthalate was then rejected by KI. The rest are displacement isomers. Diisobutyl phthalate reference standard was then injected, and it matched very well the retention time and spectrum in APGC-QTOF-MS. For the others, no standards were available in our lab. However, considering that diisobutyl phthalate had a higher match in NIST search and it was more frequent detected in FCM in the literature, this peak was confirmed as diisobutyl phthalate with high reliability. The other two were set as "non-confirmed" because there are displacement isomers which could have exactly the same retention time and spectra as those indicated for 1-monostearoylglycerol and 2-monostearoylglycerol below (3.2.3). If this phenomenon happens, the peak could be one of them or the mix of them. That is why they cannot be directly ruled out without the injection of reference standards but only "non-confirmed". The same rule was applied for the peaks RT 15.25 min and RT 18.27 min, which were confirmed as 2,4-ditert- butylphenol and 3,5-di-tert-butyl-4-hydroxybenzaldehyde, respectively, but the rest as "non-confirmed".

3.2.2. Molecular formula selection with the aid of GC-MS

It is well known that different adduct modes could be obtained in precursor ion when applying soft ionization like APGC, which would add difficulty in deducting molecular formula; while molecular ion rather than other adducts would exist in EI spectrum if it is not too fragile to break down totally. In this respect, once correspondence is found in GC-MS, effort could be made to find out the molecular ion if it exists. In many cases, it would be very small even hardly visible. However, APGC-QTOF-MS spectrum could be a good reference telling us where to find it. This step is of great help, especially when correspondence is found but no acceptable candidates can be obtained in GCMS. Correspondence was found for the peak (RT 14.02 min), and 26 candidates were listed with match higher than 700. However, all of them were rejected by exact mass as well as KI telling that it would not be present in the NIST library. Precursor ion 163.1123 m/z was obtained in APGC-QTOF-MS. It is worth to mention that odd electron should be selected in Elemental Composition Experiment (ECE) when assuming the precursor ion is M+**.** and the returned formula is exactly the MF. Whereas even electron should be used when it is assumed as a protonated ion or other adducts, the molecular formula (MF) is the returned formula minus the fixed formula, usually H, in APGC-QTOFMS. 163 m/z was clearly found in the right end of the GC-MS spectrum (Fig. 4) telling that 163.1123 was the mass of the molecule and C7H18NOP was generated as the MF by ECE. It is worth mentioning that except for C, H, O, N, which are common elements in polymer compositions, Si and P were chosen as well when conducting ECE. The reason is that these two elements were found in some confirmed components, and some of those unknowns could be related to them, for example reaction products from them. There were 3 and 11 hits in Chemspider and SciFinder, respectively. Most of them were found in the

list of Precursor Chemicals of the Chemical Weapons Convention, and they were then rejected. One of them, 1-propanamine, 3-[(2-methylpropyl) phosphinyl]-, was found to be a starting material of azaphospholanes, which are lubricating oil antioxidants or flame retardants in plastic, and no relevant information was found for the others. Unfortunately, there was no commercial standard available and it was then set as tentative. When looking at RT 11.32 min, 173.1355 m/z was regarded as a protonated precursor ion because 172 m/z was monitored unambiguously in the GC-MS spectrum (Fig. S7).

3.2.3. New reaction products in APGC-QTOF-MS

As shown in Table 1, for the compound with RT 26.71 min, correspondence was set at RT 26.42 min in GC-MS because high match candidates (1-MSGC and 2-MSGC) have molecular weight 358.3083, which suggested that 359.3153 m/z could be a protonated precursor ion. Besides, similar fragment 267 m/z was also observed in both systems. The fragment ion 267.2686 m/z in APGC-QTOF-MS corresponded to the formula C18H35O (267.2688 m/z) which is a common fragment from the candidates 1-MSGC and 2-MSGC. Both standards (100 μg/g) were then injected in APGC-QTOF-MS. However, surprisingly, the two standards had exactly the same RT as well as spectra in both systems. Their GC-EI-MS spectra matched very good the library, confirming that those two standards were good. However, in APGCQTOF- MS, instead of matching RT 26.71 min, they matched RT 26.54 min and had the precursor ion 415.3234 m/z rather than 359.3153 m/z (Fig. 5A). This phenomenon was quite unexpected and unusual. It was believed that 415.3234 m/z (RT 26.54 min) might not be the precursor ion of 1-MSGC nor 2-MSGC because no correspondence could be found for that big peak (APGC-QTOF-MS RT 26.71 min, 359.3153 m/z) in the sample GC-MS chromatogram (Fig. 5) if it was. There was no suspected peak at the near right side of the peak (RT 26.42 min) in the GC-MS chromatogram of the sample (Fig. 5B). It is noteworthy that the peak (RT 26.42 min in GC-MS) in the sample was much higher than that in the standards (100 μg/g), suggesting that its concentration in the sample could be very high. Therefore, this unusual phenomenon was suspected to be related to the high concentration. To further understand the phenomenon, higher concentration (200 μg/g 2-MSGC) of the standard was injected. Fig. 6 illustrates that extracted mass 359.3161 was totally absent in 100 μg/g (A) but obviously present in 200 μg/g (B) standard chromatograms. As the concentration increased, extracted mass 359.3161 appeared. It suggested that 359.3161 (RT 26.71 min) could be the protonated ion of the standard, and 415.3234 could be a reaction product related to the standard. The reason for missing 359.3161 ion in 100 μg/g standard could be that all standards entering the column were totally consumed to produce a new product that had 415.3234 precursor ion. Hence, no protonated standard appeared in the chromatograms. When the concentration increased to 200 μg/g, the chemical that reacted with the standard was finished, so the rest of standard could be eluted out and protonated under APGC. Finally, RT 26.71 min was confirmed as 1- MSGC and 2-MSGC and had a correspondence with RT 26.42 min in GCMS. To better understand the confusing peak that had a precursor ion 415.3234 (RT 26.54 min), ECE was then conducted and C23H47O4Si was unequivocally generated. The distinction between the generated formula and the standards is C2H5Si. It was interesting that silanediol, dimethyl (CAS 1066-42-8, MF C2H8O2Si), which could be a transformation product of the silicone base septum or the methyl 5% phenyl polysiloxane based column, was witnessed in many of our daily injections in GC-EI-MS. This substance could react with the two near hydroxyl groups by losing two H2O under certain conditions. Taking 1-MSGC as an example, the possible reaction is shown in Fig. 7. The reaction product (MF C23H46O4Si) was then protonated and detected by the detector. The absence of this reaction product in GC-MS

chromatograms is possibly due to either the high electronic ionization energy breaking down the reaction product totally and/or the lower sensitivity of quadrupole mass spectrometer. In addition, similar columns were used in both systems though, their amount of column bleed could be a little different depending on their usage. Same phenomenon was witnessed for NX 8000K (MF C29H40O6, 484.2825). Consequently, 485.2911 (RT 34.53 min) was set as its protonated molecular ions and 541.2986 (RT 34.12 min, MF C31H45O6Si) as its protonated reaction product ion. For the peak with RT 24.83 min in GC-MS, 1-monohexadecanoylglycerol and/or 2-monohexadecanoylglycerol (MF C19H38O4, 330.2770) were found to be candidates with high match (both match and R. match higher than 900). Finally, 331.2848 (RT 25.03 min) was set as its protonated ion and 387.2929 (RT 24.87 min, MF C21H43O4Si) was set as its protonated reaction product ion, even though no standard was available in our lab because they have very similar structure with 1-MSGC, 2-MSGC and NX 8000K (Fig. 8). They all have two hydroxyl groups near to each other which would allow them to react with silanediol dimethyl in a same manner.

4. Conclusions

A non-target screening strategy using APGC-QTOF-MS and GC-EIMS as complementary techniques has been established and successfully applied for the identification of two PP extracts. The methodology could be used in many other research fields regarding non-target screening of volatile compounds. Besides, comprehensive comparison of the two systems has been conducted which would be helpful when using these two techniques. [M+H]+ or M+. are two common precursor ions in APGC-QTOF-MS. However, [M-H]+, [M-3H + O]+, [M- 3H+2O]+, and [M-H+3O]+ precursor ions were found for alkanes depending on the number of carbons. This phenomenon could add difficulty in deducing molecular formula. It is still unclear that if chemicals that have similar properties to alkanes would have similar ionization modes or not, so caution should be paid when deducing MF. Furthermore, new reaction products formed by diol compounds and silanediol dimethyl, which would be a transformation product of the silicone base septum or the methyl 5% phenyl polysiloxane based column, were found. It was quite unusual and has caused confusion during the identification process. In summary, APGC-QTOF-MS is a powerful tool for volatile chemicals identification. However, caution must be paid to avoid mistaken identification.

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Figures

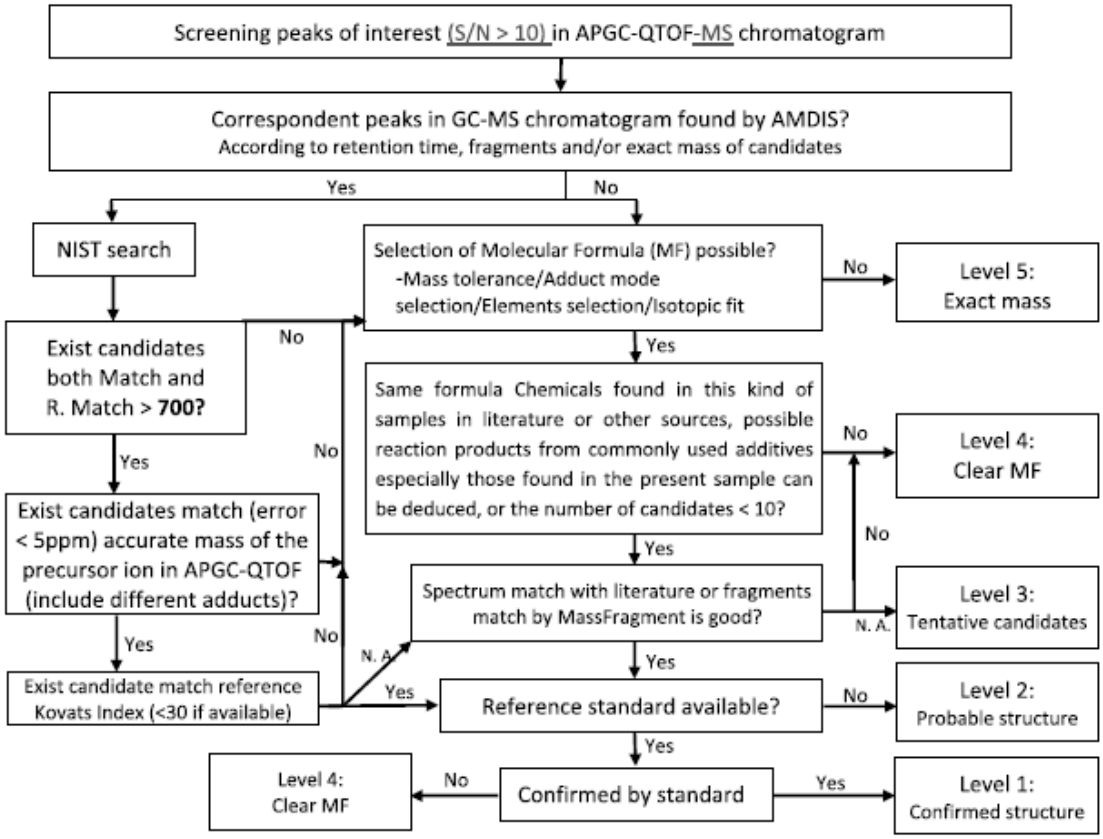

Fig. 1. Flow chart non-target screening of volatile and semi-volatile compounds by combing APGC-QTOF-MS and GC-MS.

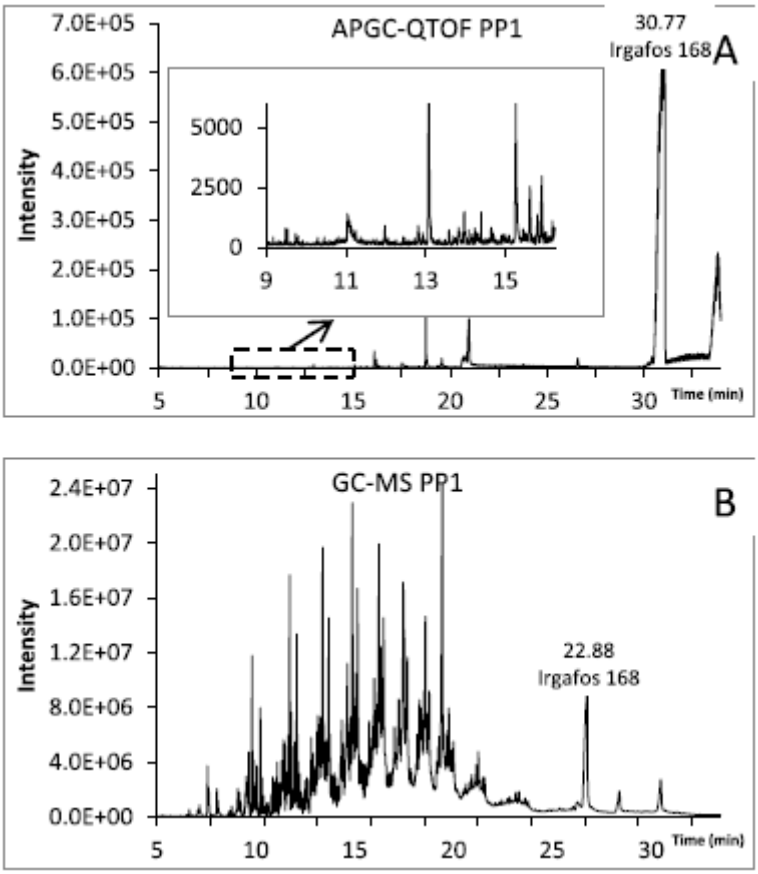

Fig. 2. Chromatograms of PP1 in APGC-QTOF-MS (A) and GC-MS (B).

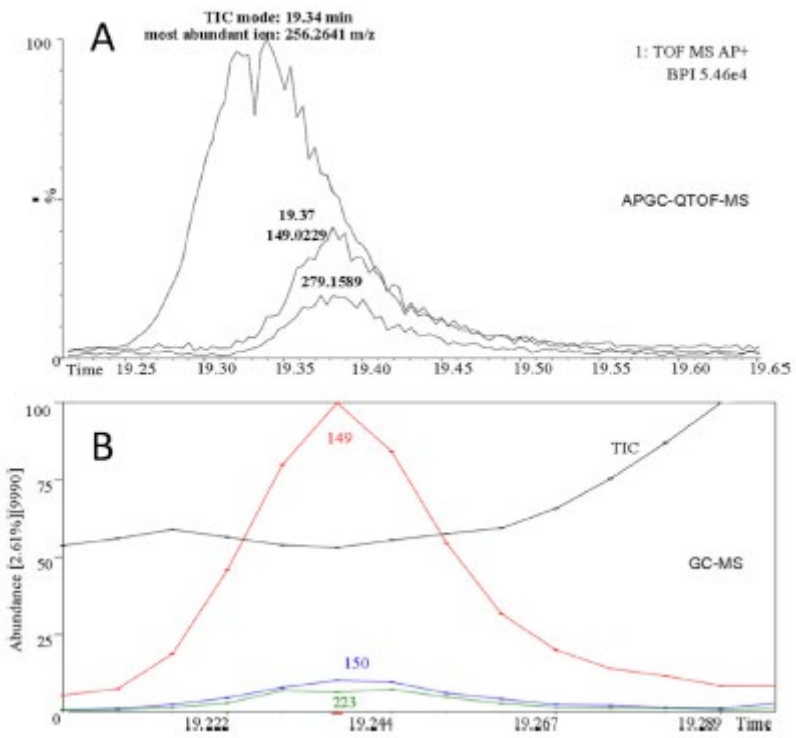

Fig. 3. Chromatograms (TIC and extracted ions) in APGC-QTOF-MS low energy (RT 19.37 min, A) and GC-MS (RT 19.24 min, B)

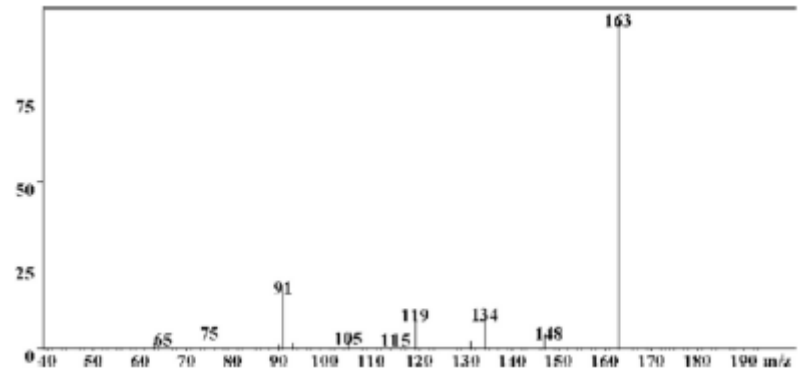

Fig. 4. GC-MS spectrum of the peak in 13.96 min.

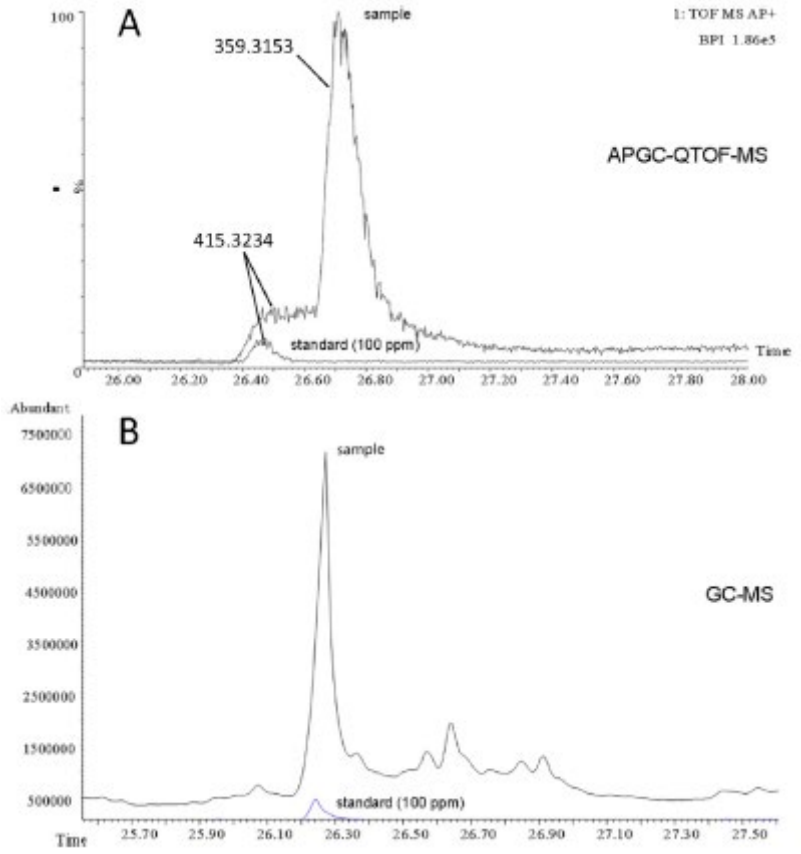

Fig. 5. Sample and standard chromatograms in APGC-QTOF-MS (A) and GC-MS (B).

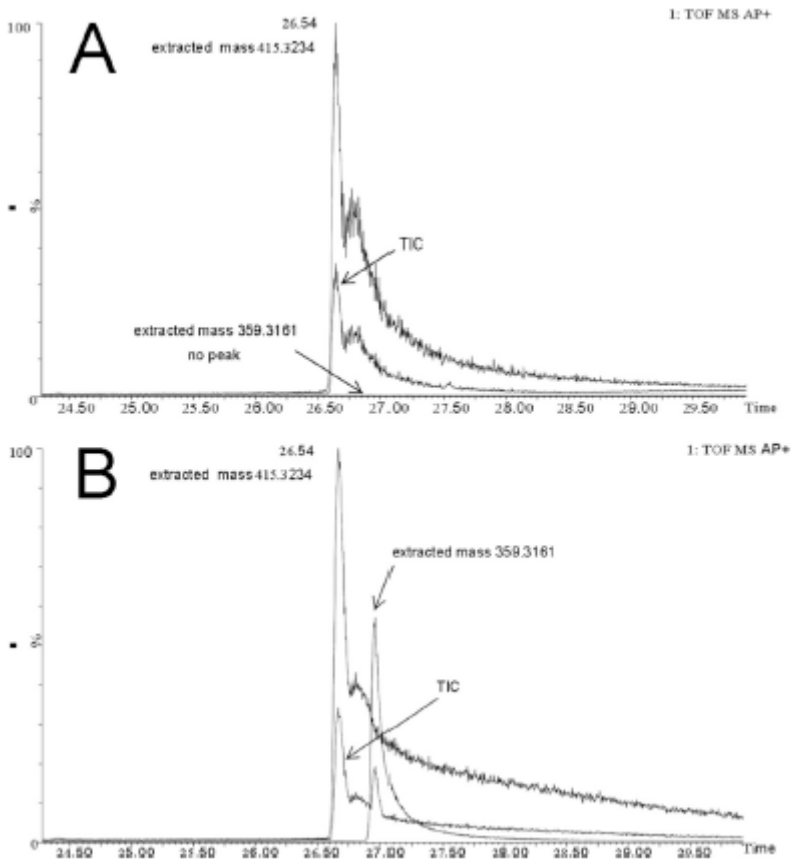

Fig. 6. TIC and extracted masses of 2-monostearoylglycerol standard in APGC-QTOF-MS at 100 µg/g (A) and 200 µg/g (B).

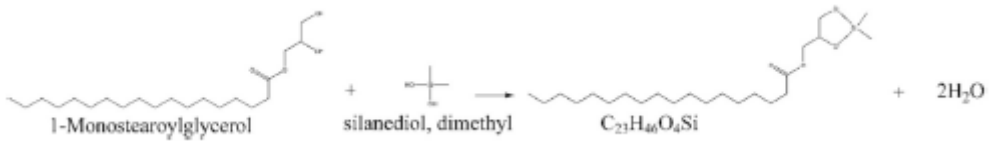

Fig. 7. Possible reaction between 1-monostearoylglycerol and silanediol, dimethyls.

Table 1 Compounds detected in PP samples by combination of APGC-QTOF-MS and GC-MS.

APGC-QTOF-MS			Peak Nº	GC-MS					Formula	MW (Monoiso)	Status	Fixation	Note
Fragment Ions	Precursor Ion	RT		RT	Ions	Candidate Number > 700	Candidates (mass error < 5 ppm and Kovats Index < 30 if it exists)	CAS/NIST					
75.0266 157.1052 105.0371	**189.1314**	10.56	**1**	10.62	105, 75, **188**	3	Silane, cyclohexyldimethoxymethyl-	17865-32-6	C9H20O2Si	188.1233	**Confirmed**	$[M+H]^+$	Catalyst in propylene polymerization
73.0470 155.1252 143.0887 89.0422	**173.1355**	11.32	**2**	11.34	89, 61, 143, **172**	0	–	–	C9H20OSi	172.1283	Clear MF	$[M+H]^+$	Small peak
91.0548 119.0864	**149.0966**	12.44	**3**	12.35	91, 119, **148**	9	Benzaldehyde, 4-propyl-	28785-06-0	C10H12O	148.0888	Confirmed	$[M+H]^+$	Degradation product of clarified agent NX8000
134.0729 119.0495 91.0545	**163.1123**	14.02	**4**	13.96	**163**, 134, 119, 91	26	–	–	C7H18NOP	163.1126	Clear MF	$M^{+\cdot}$	Small peak
							1-propanamine, 3-[(2-methylpropyl) phosphinyl]-	55359-13-2	C7H18NOP	163.1126	Tentative	$M^{+\cdot}$	Starting material of azaphospholanes (lubricating oil antioxidants or flame retardants in plastic)
165.0900 193.1580	**221.1535**	14.87	**5**	–	–	–	–	–	C14H20O2	220.1463	Clear MF	–	Small peak
							2,6-di-tert-butylbenzoquinone	719-22-2	C14H20O2	220.1463	**Confirmed**	$[M+H]^+$	Transformation product of BHT; $[M+NO]^+$ was also observed
191.1424 163.1114	**206.1665**	15.25	**6**	15.27	191, **206**, 163	34	2,4-di-tert-butylphenol	96-76-4	C14H22O	206.1671	**Confirmed**	$M^{+\cdot}$	
							2,5-di-tert-butylphenol	5875-45-6	C14H22O	206.1671	Non-confirmed	–	
							3,5-di-tert-butylphenol	1138-52-9	C14H22O	206.1671	Non-confirmed	–	
219.1379 191.1067	**235.1698**	18.27	**7**	18.21	219, **234**, 191	9	3,5-di-tert-butyl-4-hydroxybenzaldehyde	1620-98-0	C15H22O2	234.1620	**Confirmed**	$[M+H]^+$	
							2,6-ditert-butyl-4-(hydroxymethylene)-2,5-cyclohexadien-1-one	101100-38-3	C15H22O2	234.1620	Non-confirmed	–	
							3,5-di-tert-butylbenzoic acid	16225-26-6	C15H22O2	234.1620	Non-confirmed	–	
193.1230 233.1542 205.1231	**249.1850**	18.90	**8**	18.77	233, **248**, 205	27	3,5-di-tert-butyl-4-hydroxyacetophenone	14035-33-7	C16H24O2	248.1776	Tentative	–	
							2-methyl-2-[2-(2,6,6-trimethyl-3-methylene-cyclohex-1-enyl)-vinyl]-[1,3]dioxolane	194769[a]	C16H24O2	248.1776	Tentative	–	
							2,4,6-triisopropylbenzoic acid	49623-71-4	C16H24O2	248.1776	Tentative	–	
88.0763 74.0602	**256.2641**	19.09	**9**	–	–	–	–	–	C16H33NO	255.2562	Clear MF	$[M+H]^+$	Small peak
							Palmitamide	629-54-9	C16H33NO	255.2562	Not	–	Rejected by standard
							Dodecanamide, N,N-diethyl-	3352-87-2	C16H33NO	255.2562	Tentative	–	Found in literature, MassFragment match
88.0762 74.0604	**256.2641**	19.34	**10**	–	–	–	–	–	C16H33NO	255.2562	Clear MF	$[M+H]^+$	Relatively big peak, < !–Soft-enter Run-on– > Isomer of RT 19.09 min
149.0229	**279.1589**	19.37	**11**	19.24	149	> 30 Match > 850	Diisobutyl phthalate	84-69-5	C16H22O4	278.1518	**Confirmed**	$[M+H]^+$	
							1-butyl 2-isobutyl phthalate	17851-53-5	C16H22O4	278.1518	Non-confirmed	–	Catalyst
							Di-sec-butyl phthalate	4489-61-6	C16H22O4	278.1518	Non-confirmed	–	

APGC-QTOF-MS			Peak Nº	GC-MS					Formula	MW (Monoiso)	Status	Fixation	Note
Fragment Ions	Precursor Ion	RT		RT	Ions	Candidate Number > 700	Candidates (mass error < 5 ppm and Kovats Index < 30 if it exists)	CAS/NIST					
221.1172 203.1067 161.0965	**277.1802**	19.41	**12**	–	–	–	–	–	C11H14NP	276.1725	Clear MF	$[M+H]^+$	Small peak; Could be isomer of peak 19.90
							1-oxaspiro[4.5]deca-7, 9-diene-2, 6-dione, 7,9-bis(1, 1-dimethylethyl)-	1783860-53-6	C17H24O3	276.1725	Tentative	–	Has similar structure to the compound (RT 19.90)
							1-oxaspiro[4.5]deca-7, 9-diene-2, 6-dione, 7,9-bis(1, 1-dimethylethyl)-, (5S)-	1399009-49-4	C17H24O3	276.1725	Tentative	–	Stereo structure with the former one
161.0965 221.1177 203.1071	**277.1801**	19.90	**13**	19.76	205, 217, 175, 189, 220, **276**	1	7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	82304-66-3	C17H24O3	276.1725	Probable	$[M+H]^+$	Impurity of Irganox; Although most abundant fragments are not the same, mass match
178.0782 165.0703 152.0624	**191.0862**	19.97	**14**	–	–	–	–	–	C15H10	190.0783	Clear MF	$M^{+\cdot}$	Big peak; $[M + H2O]^+$ was also observed, but very small
107.0491 277.1807 147.0803	**292.2036**	20.12	**15**	19.95	277, **292**, 147	22	Metilox or Irganox 1300	6386-38-5	C18H28O3	292.2038	**Confirmed**	$M^{+\cdot}$	Antioxidant
87.0445 239.2378 129.0914 213.1850	**257.2474**	20.27	**16**	20.08	73, 60, 129, 213, **256**	3	Palmitic acid	57-10-3	C16H32O2	256.2402	**Confirmed**	$[M+H]^+$	Lubricant; $[2M + H]^+$ (513.4880) was also observed
88.0764 74.0604	**284.2956**	21.36	**17**	–	–	–	–	–	C18H37NO	283.2875	Clear MF	$[M+H]^+$	Small peak
							Stearamide	124-26-5	C18H37NO	283.2875	Not	–	Slip agent, but Rejected by Standard
							Tetracosanamide, N,N-diethyl-	57303-20-5	C18H37NO	283.2875	Not	–	Found in literature, MassFragment match
87.0446 267.2684 129.0915 185.1540	**285.2793**	22.10	**18**	21.98	73, 60, 129, **284**, 241, 185	2	Stearic acid	57-11-4	C18H36O2	284.2715	**Confirmed**	$[M+H]^+$	Lubricant; $[2M + H]^+$ (569.5507) was also observed
129.0187 185.0812 259.1545	**403.2327**	22.99	**19**	22.83	185, 129, 259	2	Tributyl acetylcitrate	77-90-7	C20H34O8	402.2253	**Confirmed**	$[M+H]^+$	Plasticizer
131.0525 75.0260	**387.2929**	24.87	**20**	–	–	–	–	–	C21H42O4Si	386.2852		$[M+H]^+$	reaction product during analysis
313.2734 239.2370 257.2479	**331.2848**	25.03	**21**	24.83	98, 239, 134	3	1-monohexadecanoylglycerol	542-44-9	C19H38O4	330.2770	Tentative	$[M+H]^+$	
							2-monohexadecanoylglycerol	23470-00-0	C19H38O4	330.2770	Tentative	$[M+H]^+$	
131.0525 75.0258 399.2932	**415.3234**	26.54	**22**	–	–	–	–	–	C23H46O4Si	414.3165		$[M+H]^+$	reaction product during analysis
341.3056 267.2686 95.0855	**359.3161**	26.71	**23**	26.42	98, 134, 267, 285, 327	4	1-monostearoylglycerol	123-94-4	C21H42O4	358.3083	Tentative	$[M+H]^+$	They have same RT and spectra, thus cannot be differentiated
							2-monostearoylglycerol	621-61-4	C21H42O4	358.3083	Tentative	$[M+H]^+$	
441.2983	**647.4598**	32.86	**24**	32.56	441, **646**	1	Antioxidant Irgafos 168	31570-04-4	C42H63O3P	646.4515	**Confirmed**	$[M+H]^+$	Antioxidant
133.1018 117.0371	**541.2986**	34.12	**25**	–	–	–	–	–	C31H44O6Si	540.2907		$[M+H]^+$	reaction product during analysis

APGC-QTOF-MS			Peak Nº	GC-MS					Formula	MW (Monoiso)	Status	Fixation	Note
Fragment Ions	Precursor Ion	RT		RT	Ions	Candidate Number > 700	Candidates (mass error < 5 ppm and Kovats Index < 30 if it exists)	CAS/NIST					
133.1013 147.0805 91.0543	**485.2911**	34.53	**26**	34.20	147, 91, 483	0	NX 8000	882073-43-0	C29H40O6	484.2825	**Confirmed**	$[M+H]^+$	Clarified agent, confirmed by standard
495.2682 647.4250	**663.4557**	35.93	**27**	35.45	316, 647, **662**	1	Oxidized Irgafos 168	95906-11-9	C42H63O4P	662.4464	**Confirmed**	$[M+H]^+$	Oxidized Irgafos 168

Note: "-" means not available; * means NIST number.