

Investigation of Extracted Analytes from Packaging Materials with GC-MS and High Resolution MS

Elizabeth M. Humston-Fulmer and Joseph E. Binkley | LECO Corporation, St. Joseph, MI

Introduction

Migration or leaching of analytes from packaging material is a concern for manufacturers and consumers because of the potential contamination of food and beverages. This leaching can impact the quality of the product, the integrity of the packaging material, and cause concern related to consumer health and product safety. To investigate analytes with the potential for leaching, an extraction of a variety of food packaging or storage products, including sealable plastic bags and plastic food containers, was performed. Solvent was placed inside each packaging product for an extended period of time and then concentrated through evaporation prior to analysis. General screening of this extract with non-targeted analytical techniques was used to understand what analytes were extracted and may have the potential to leach. GC was used for separating analytes from each other and TOFMS provided full mass range spectral data. Nominal mass TOFMS data were acquired and were searched against library databases for tentative identifications. High resolution TOFMS data were also acquired to add confidence to identifications with accurate mass information. Several analytes were characterized and are highlighted here.

Methods

Analytes were extracted from a variety of food storage products, including three different brands of sealable bags and one plastic reusable box. 100 mL of a 1:1 hexane/acetone solution was placed inside each food storage container for 20 hours at room temperature. The solvent was then evaporated to 1 mL under nitrogen prior to analysis. The concentrated solvent was then analyzed by GC-TOFMS with EI (Pegasus[®] BT, LECO, Saint Joseph, MI) and by GC-HR-TOFMS with EI and CI (Pegasus HRT, LECO, Saint Joseph, MI). GC and MS instrument conditions are listed in Tables 1 and 2, respectively.

Table 1. GC Conditions

| Gas Chromatograph | Agilent 7890 |
|---------------------|--|
| Injection | 0.5 µL (BT EI), 1µL (HRT EI); 2µL (HRT CI), splitless @ 250 °C |
| Carrier Gas | He @ 1.0 mL/min, Constant Flow |
| Column | Rxi-5ms, 30 m x 0.25 mm i.d. x 0.25 µm coating (Restek) |
| Temperature Program | 40 °C (4 min) ramped to 330 °C @ 20 °C/min (10 min) |
| Transfer Line | 250 °C (BT), 300 °C (HRT) |

Table 2. MS Conditions

| Mass Spectrometer | LECO Pegasus BT |
|------------------------|---|
| Ion Source Temperature | 250 °C |
| Mass Range | 33-900 m/z |
| Acquisition Rate | 10 spectra/s |
| Mass Spectrometer | LECO Pegasus HRT |
| Ion Source Temperature | 250 °C (EI); 200 °C (CI) |
| Acquisition Mode | High Resolution, R = 25,000 (FWHM) |
| Ionization Mode | EI and CI (Reagent Gases: CH ₄ and 5% NH ₃ in CH ₄) |
| Mass Range (m/z) | 33-900 (EI); 60-800 (CI) |
| Acquisition Rate | 10 spectra/s |

Identification Workflow

This multi-platform approach was used to determine analyte identifications and explore benefits of adding analytical capabilities. Nominal mass and accurate mass data were collected and analyzed. Identifications were determined with the combination of deconvolution, library searching, retention index calculations, and formulae determinations of data acquired across platforms.



Pegasus BT - Nominal Mass System

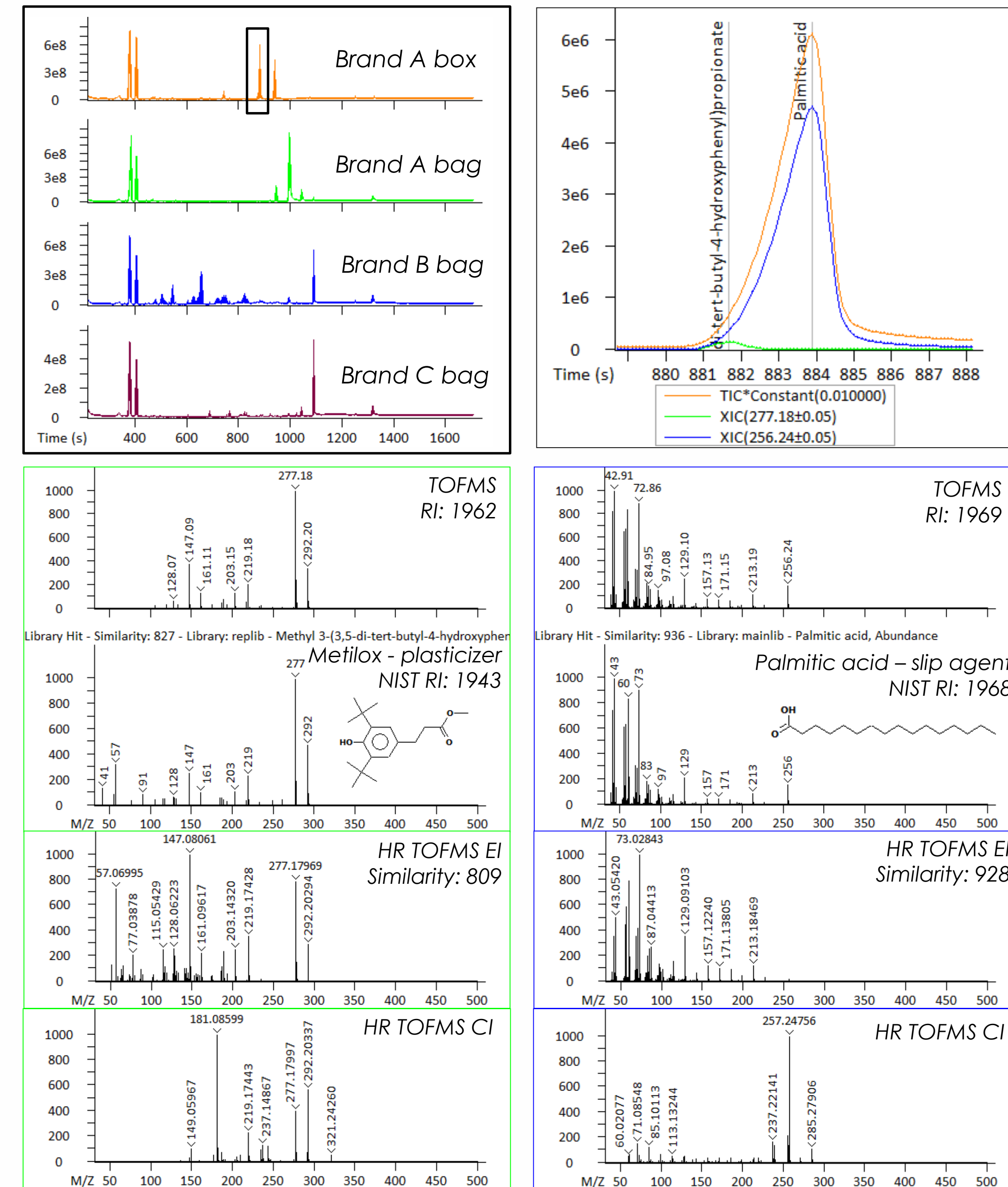
- Nominal mass library search (NIST)
- Retention index comparison

Pegasus HRT - High Resolution System

- EI library search (NIST)
- CI molecular ion verification
- Formulae determinations for molecular ion and fragments

GC-MS

A variety of food storage products were analyzed and representative nominal mass chromatograms for each sample are shown in Figure 1. Hundreds of analytes were separated from each other with both chromatographic separation and mathematical separation via deconvolution. A plasticizer and a slip agent chromatographically coelute, but were deconvoluted and identified with the workflow demonstrated in Figure 1.

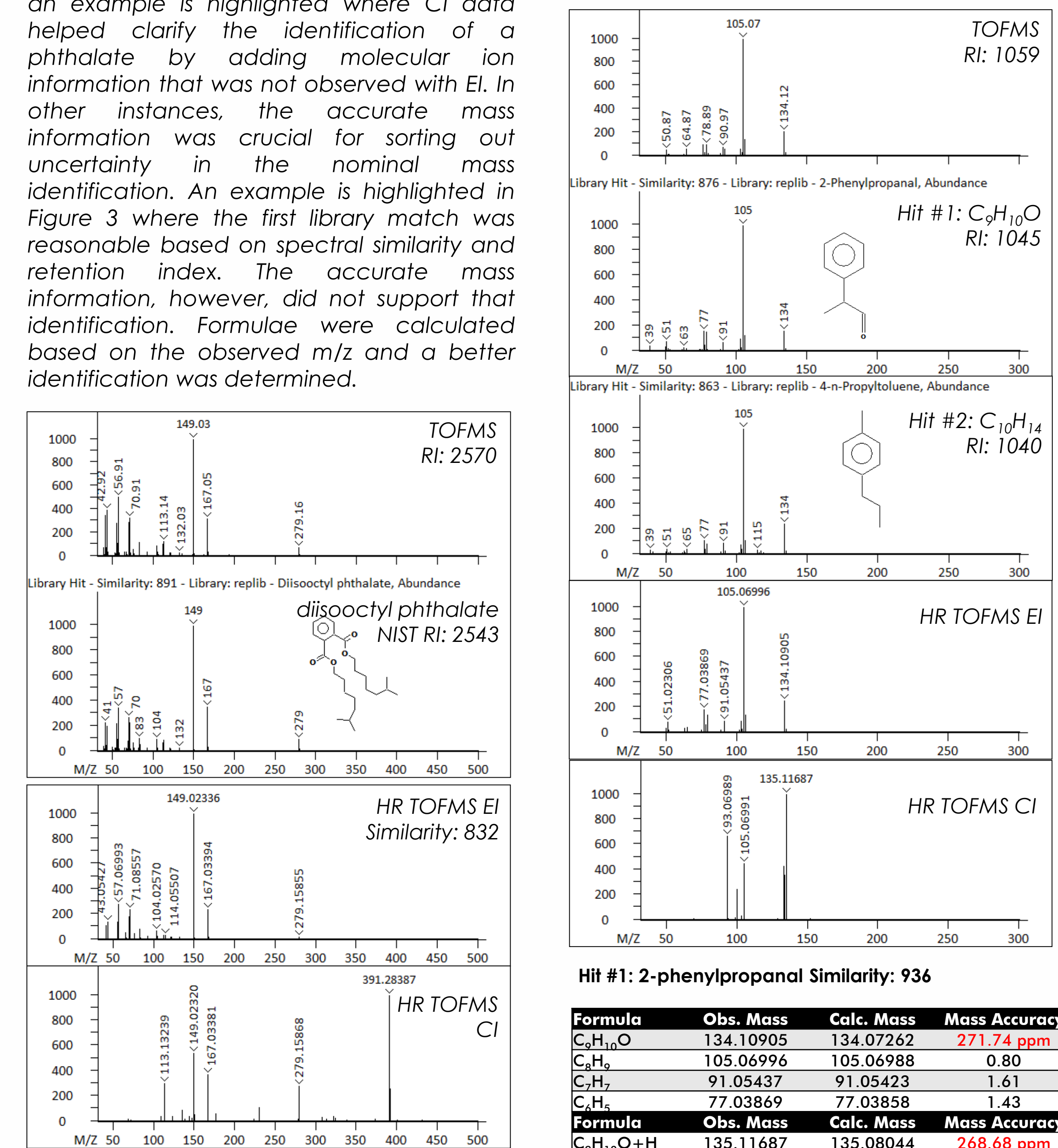


| Formula | Obs. Mass | Calc. Mass | Mass Accuracy |
|--|-----------|------------|---------------|
| C ₁₈ H ₃₄ O ₂ | 292.20294 | 292.20330 | -1.22 ppm |
| C ₁₈ H ₃₂ O ₂ | 277.17949 | 277.17992 | -0.47 |
| C ₁₈ H ₃₀ O ₂ | 219.17428 | 219.17434 | -0.28 |
| C ₁₈ H ₂₈ O ₂ | 203.14320 | 203.14304 | 0.76 |
| C ₁₈ H ₂₆ O ₂ | 189.12754 | 189.12739 | 0.78 |
| C ₁₈ H ₂₄ O ₂ | 147.08061 | 147.08044 | 1.12 |
| Formula | Obs. Mass | Calc. Mass | Mass Accuracy |
| C ₁₈ H ₃₄ O ₂ + C ₂ H ₆ | 321.24260 | 321.24242 | 0.57 ppm |
| C ₁₈ H ₃₂ O ₂ | 292.20337 | 292.20330 | 0.26 |

Figure 1. Representative TIC chromatograms are shown for each food storage product. Deconvolution separates Meliox and palmitic acid that chromatographically coelute. The identification workflow of these analytes combined deconvolution, library searching of nominal mass spectra, and retention index verification from TOFMS data. Accurate mass data and formulae determinations from both EI and CI HR TOFMS data added confidence to the identifications.

High Resolution MS Benefits

When adding analytical capabilities, like high resolution TOFMS with EI and CI, there is the potential to improve the identifications and the confidence in the identifications. In Figure 2, an example is highlighted where CI data helped clarify the identification of a phthalate by adding molecular ion information that was not observed with EI. In other instances, the accurate mass information was crucial for sorting out uncertainty in the nominal mass identification. An example is highlighted in Figure 3 where the first library match was reasonable based on spectral similarity and retention index. The accurate mass information, however, did not support that identification. Formulae were calculated based on the observed m/z and a better identification was determined.



| Formula | Obs. Mass | Calc. Mass | Mass Accuracy |
|---|-----------|------------|---------------|
| C ₁₈ H ₃₀ O ₄ | 279.15855 | 279.15909 | -1.94 ppm |
| C ₁₈ H ₂₈ O ₄ | 167.03394 | 167.03389 | 0.33 |
| C ₁₈ H ₂₆ O ₄ | 149.02336 | 149.02332 | 0.25 |
| C ₁₈ H ₂₄ O ₄ | 104.02570 | 104.02567 | 0.30 |
| C ₁₈ H ₂₂ O ₄ | 83.08560 | 83.08553 | 0.85 |
| C ₁₈ H ₂₀ O ₄ | 71.08557 | 71.08553 | 0.64 |
| C ₁₈ H ₁₈ O ₄ | 57.04927 | 57.04928 | 0.87 |
| Formula | Obs. Mass | Calc. Mass | Mass Accuracy |
| C ₁₈ H ₃₀ O ₄ +H | 391.28387 | 391.28429 | -1.06 ppm |
| C ₁₈ H ₂₈ O ₄ | 279.15868 | 279.15909 | -1.46 |
| C ₁₈ H ₂₆ O ₄ | 167.03388 | 167.03389 | -0.47 |
| C ₁₈ H ₂₄ O ₄ | 149.02320 | 149.02332 | -0.79 |

Figure 2. The identification workflow is demonstrated for diisooctyl phthalate. Library searching, retention index verification, and formulae determinations assisted in the identification. CI added information on the molecular ion that was not observed with EI.

Representative Examples

This workflow was used to compile Table 3 that contains representative analytes observed in these samples. This table compiles data across the instrument platforms and includes NIST database information. For each analyte, similarity scores compared to NIST library spectra are presented. The observed retention index values were calculated based on alkane elution and compared to the semi-standard non polar NIST database values with the percent deviation between the two reported. Molecular ion formulae and mass accuracy are also presented from the high resolution EI data. In the absence of an EI molecular ion, the CI molecular ions are presented as indicated by the formula. The presence or absence of an analyte in each sample is indicated with "x" and the purpose of the analyte as an additive is indicated, when known. Several additives and other analytes of potential interest were extracted and observed in these data. An analyte pair of particular interest is highlighted in Figure 4.

Table 3. Representative Analytes and Analyte Identification Information

| Similarity | CAS | IR | RI | Obs/NIST | % Deviation | Formula | Mass Accuracy (ppm) | Brand A Box | Brand A Bag | Brand B Bag | Brand C Bag | NOTES |
|------------|------------|------|-----------|----------|-------------|---|---------------------|-------------|-------------|-------------|-------------|-----------------------------|
| 911 | 98-82-8 | 449 | 930:921 | 0.98 | | C ₉ H ₁₀ | 0.29 | x | x | x | x | aromatic |
| 914 | 103-65-1 | 470 | 960:953 | 0.73 | | C ₉ H ₁₀ | 0.59 | x | x | x | x | aromatic |
| 758 | 108-95-2 | 486 | 983:908 | 0.31 | | C ₆ H ₆ O | 0.98 | x | x | x | x | phenol |
| 863 | 1074-55-1 | 531 | 1059:1040 | 1.83 | | C ₁₀ H ₁₄ | 0.35 | x | x | x | x | aromatic |
| 859 | 119-36-8 | 607 | 1210:1192 | 1.51 | | C ₁₀ H ₁₄ O | 0.50 | x | x | x | x | |
| 916 | 28785-06-0 | 644 | 1305:1294 | 0.85 | | C ₁₀ H ₁₀ O | -0.30 | x | x | x | x | benzaldehyde |
| 932 | 104-46-1 | 648 | 1313:1286 | 2.10 | | C ₁₀ H ₁₀ O | 0.04 | x | x | x | x | aromatic |
| 841 | 126-86-3 | 697 | 1418:1407 | 0.78 | | C ₁₁ H ₁₆ O ₂ | | x | x | x | x | surfactant |
| 925 | 96-76-4 | 736 | 1519:1519 | 0.00 | | C ₁₁ H ₁₆ O | -0.35 | x | x | x | x | antioxidant |
| 802 | 128-37-0 | 739 | 1529:1513 | 1.06 | | C ₁₁ H ₁₆ O | -0.23 | x | x | x | x | antioxidant |
| 893 | 23676-09-7 | 742 | 1538:1529 | 0.59 | | C ₁₁ H ₁₆ O | -0.26 | x | x | x | x | aromatic |
| 864 | 232-95-1 | 748 | 1552:1569 | 1.08 | | C ₁₁ H ₁₆ O | -0.33 | x | x | x | x | |
| 916 | 28785-06-0 | 644 | 1305:1294 | 0.85 | | C ₁₀ H ₁₀ O | -0.30 | x | x | x | x | benzaldehyde |
| 932 | 104-46-1 | 648 | 1313:1286 | 2.10 | | C ₁₀ H ₁₀ O | 0.04 | x | x | x | x | aromatic |
| 841 | 126-86-3 | 697 | 1418:1407 | 0.78 | | C ₁₁ H ₁₆ O ₂ | | x | x | x | x | surfactant |
| 925 | 96-76-4 | 736 | 1519:1519 | 0.00 | | C ₁₁ H ₁₆ O | -0.35 | x | x | x | x | antioxidant |
| 802 | 128-37-0 | 739 | 1529:1513 | 1.06 | | C ₁₁ H ₁₆ O | -0.23 | x | x | x | x | antioxidant |
| 893 | 23676-09-7 | 742 | 1538:1529 | 0.59 | | C ₁₁ H ₁₆ O | -0.26 | x | x | x | x | aromatic |
| 864 | 232-95-1 | 748 | 1552:1569 | 1.08 | | C ₁₁ H ₁₆ O | -0.33 | x | x | x | x | |
| 908 | 84-66-2 | 768 | 1609:1594 | 0.94 | | C ₁₁ H ₁₆ O ₂ +H | 0.63 | x | x | x | x | plasticizer |
| 837 | 6846-50-0 | 768 | 1610:1588 | 1.39 | | C ₁₁ H ₁₆ O ₂ +H | -0.16 | x | x | x | x | plasticizer |
| 886 | 4537-13-7 | 770 | 1615:1607 | 0.50 | | C ₁₁ H ₁₆ | 0.21 | x | x | x | x | |
| 932 | 119-61-9 | 786 | 1660:1635 | 1.53 | | C ₁₁ H ₁₆ O | 0.16 | x | x | x | x | UV stabilizer |
| 897 | 110-27-0 | 840 | 1827:1827 | 0.00 | | C ₁₁ H ₁₆ O ₂ +H | 0.06 | x | x | x | x | |
| 870 | 118-60-5 | 841 | 1830:1811 | 1.05 | | C ₁₁ H ₁₆ O ₂ | -0.42 | x | x | x | x | UV stabilizer |
| 902 | 84-69-5 | 858 | 1886:1870 | 0.86 | | C ₁₁ H ₁₆ O ₂ +H | 0.14 | x | x | x | x | plasticizer |
| 864 | 118-56-9 | 869 | 1922:1904 | 0.95 | | C ₁₁ H ₁₆ O | -1.85 | x | x | x | x | UV filter |
| 918 | 82304-66-3 | 876 | 1947:1923 | 1.25 | | C ₁₁ H ₁₆ O ₃ | -0.30 | x | x | x | x | |
| 827 | 6386-38-5 | 882 | 1962:1943 | 0.98 | | C ₁₁ H ₁₆ O | -1.22 | x | x | x | x | plasticizer |
| 936 | 57-10-5 | 883 | 1969:1968 | 0.05 | | C ₁₁ H ₁₆ O ₂ | -1.21 | x | x | x | x | slip agent |
| 895 | 84-74-2 | 887 | 1980:1965 | 0.76 | | C ₁₁ H ₁₆ O ₂ | -0.15 | x | x | x | x | plasticizer |
| 923 | 57-11-4 | 940 | 2170:2172 | 0.09 | | C ₁₁ H ₁₆ O ₂ | -1.51 | x | x | x | x | slip agent |
| 888 | 629-54-9 | 945 | 2192:2143 | 2.29 | | C ₁₁ H ₁₆ NO | -0.73 | x | x | x | x | |
| 899 | 301-02-0 | 994 | 2381:2334 | 2.01 | | C ₁₁ H ₁₆ NO | -0.71 | x | x | x | x | slip agent |
| 891 | 131-20-4 | 1039 | 2570:2543 | 1.06 | | C ₁₁ H ₁₆ O ₂ +H | -0.58 | x | x | x | x | phthalate |
| 862 | 112-84-5 | 1090 | 2773:2625 | 5.64 | | C ₁₂ H ₁₈ NO | -1.59 | x | x | x | x | slip agent |
| 863 | 31570-04-4 | 1251 | 3468:3397 | 2.09 | | C ₁₂ H ₁₈ O ₂ P | -0.61 | x | x | x | x | processing stabilizer |
| 861 | 2082-79-3 | 1319 | 3699:NA | | | C ₁₂ H ₁₈ O ₂ | -1.52 | x | x | x | x | antioxidant |
| 820 | 95906-11-9 | 1324 | 3720:3582 | 3.85 | | C ₁₂ H ₁₈ O ₂ P | 1.32 | x | x | x | x | transformation product |
| 830 | 7128-64-5 | 1492 | 4297:NA | | | C ₁₈ H ₂₆ N ₂ O ₃ S | 0.29 | x | | | | thermal/chemical stabilizer |

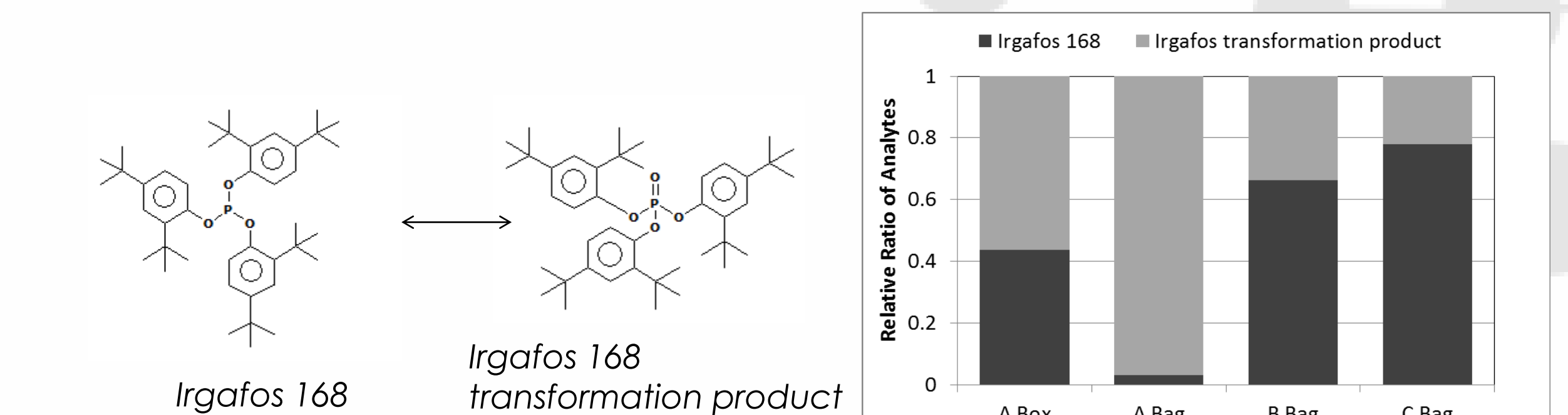


Figure 4. The relative ratios of Irgafos 168 and its transformation product, tris(2,4-di-tert-butylphenyl) phosphate, are shown. As these are processing stabilizers, the transformation between the two additives and their relative ratios may be of interest to engineers monitoring process controls.

Conclusions

This study investigated extracts of food storage materials to gain insight to potential leachable analytes. General extract screening was done with non-targeted analytical methods in order to understand what analytes could potentially leach into food or beverage products. GC and MS deconvolution effectively separated analytes within the complex mixture and TOFMS provided full mass range spectral data for identification. Nominal mass TOFMS data were searched against library databases for preliminary identifications, which were then confirmed or updated based on retention index. High resolution TOFMS data were then used to further confirm or update identifications with accurate mass information and formulae determinations. Several analytes were determined and were highlighted. The study demonstrated a workflow which was effectively employed to confidently characterize components present as extractables from food packaging materials.

