Non-Targeted Investigation of Extracted and Leached Chemicals from Packaging Materials by GC-MS and HR GC-MS

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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.

METHOD

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), 1 µL (HRT EI): 2 µL (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 search

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.
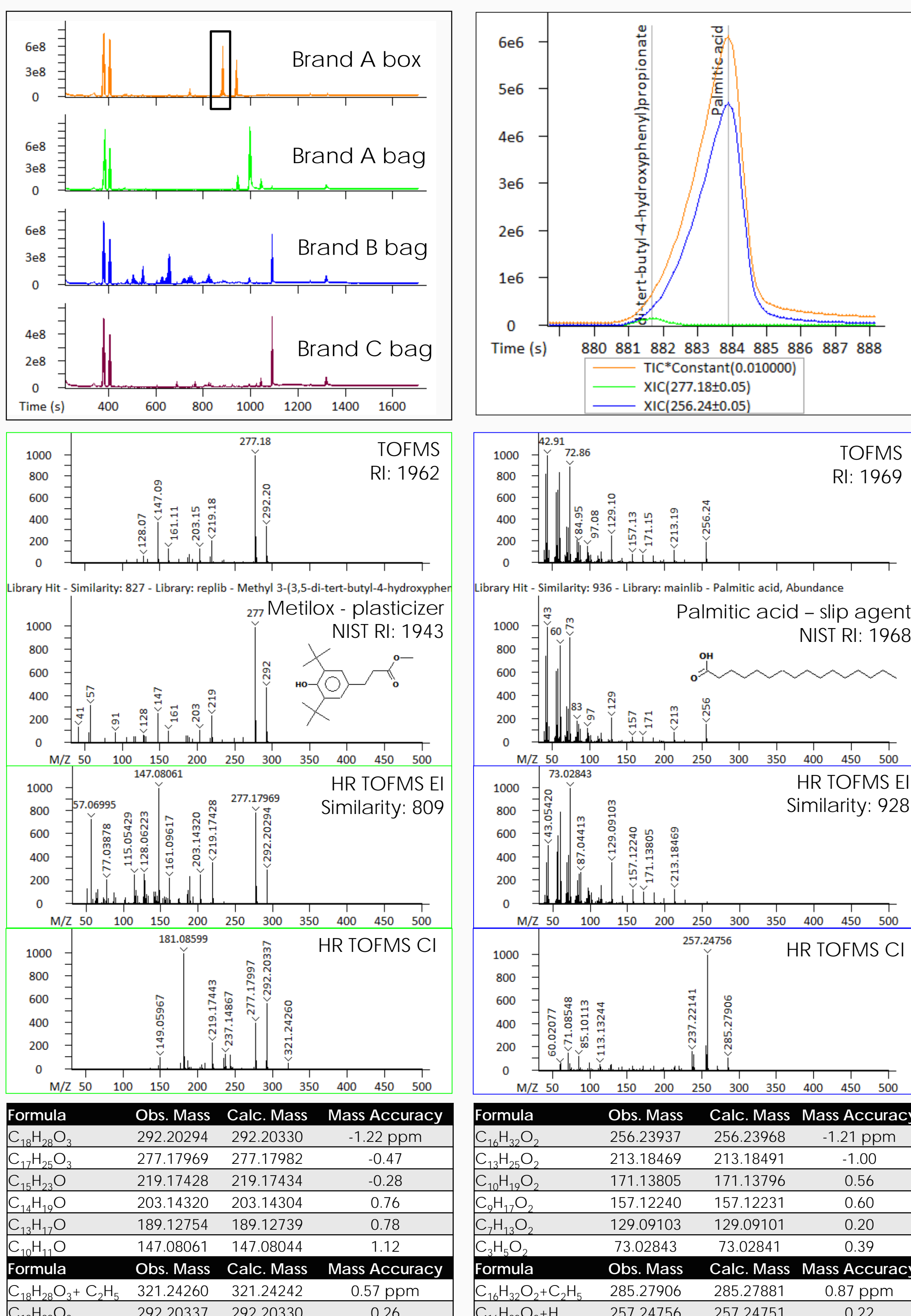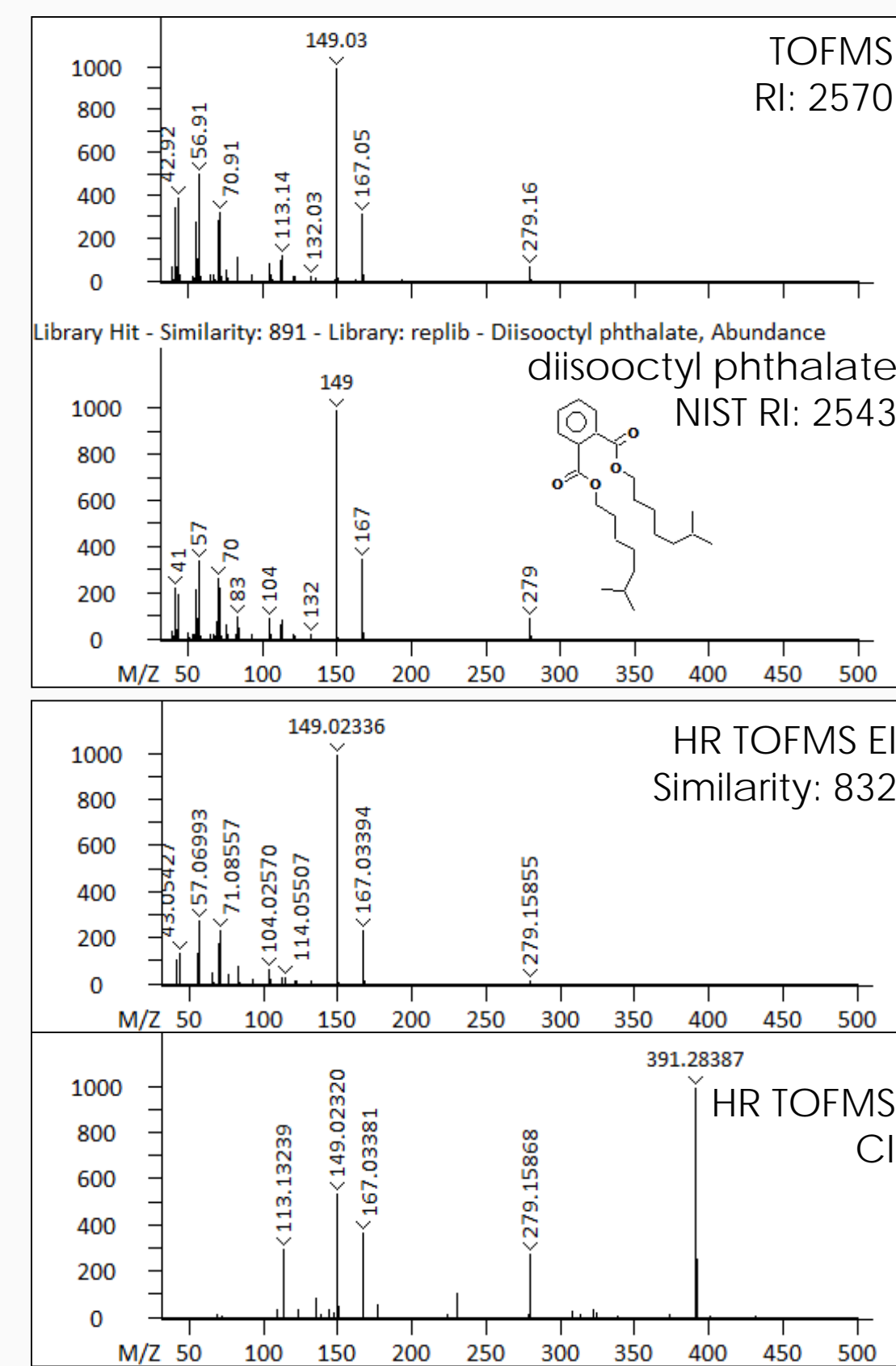

Figure 1. Representative TIC chromatograms are shown for each food storage product. Deconvolution separates Metilox and palmitic acid that chromatographically coelute. The identification workflow of these analytes combined deconvolution, library searching of nominal mass spectra, and retention index 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.

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.

Figure 3. The workflow for identification is demonstrated for an analyte that could not be discerned without accurate mass data. The nominal mass molecular weight and fragments were the same, and the retention index information was very similar between the first two library hits. The accurate mass measurements strongly support hit #2 as the correct assignment.

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. 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	Formula	Mass Accuracy (ppm)	Brand A Box	Brand A bag	Brand B bag	Brand C Bag	NOTES
Isopropylbenzene	911	98-82-8	449	930:921	C_9H_{12}	0.29	x	x	x	x	aromatic
propylbenzene	914	103-65-1	470	960:953	C_9H_{12}	0.59	x	x	x	x	aromatic
phenol	758	108-95-2	486	983:908	C_6H_6O	0.98	x	x	x	x	phenol
4-n propyl- toluene	863	1074-55-1	531	1059:1040	$C_{10}H_{14}$	0.35	x	x	x	x	aromatic
methyl salicylate	859	119-36-8	607	1210:1192	$C_8H_8O_3$	0.50	x	x	x	x	
4-propyl benzaldehyde	916	28785-06-0	644	1305:1294	$C_{10}H_{12}O$	-0.30	x	x	x	x	benzaldehyde
anethole	932	104-46-1	648	1313:1286	$C_{10}H_{12}O$	0.04		x	x	x	aromatic
Surfynol 104	841	126-86-3	697	1418:1407	$C_{14}H_{26}O_2$		x	x	x	x	surfactant
2,4-di-tert-butylphenol	925	96-76-4	736	1519:1519	$C_{14}H_{22}O$	-0.35	x	x	x	x	antioxidant
BHT	802	128-37-0	739	1529:1513	$C_{15}H_{24}O$	-0.23	x	x	x	x	antioxidant
ethyl 4-ethoxybenzoate	893	23676-09-7	742	1538:1529	$C_{11}H_{14}O_3$	-0.26	x	x	x	x	aromatic
naphtho [2,1-b]furan	864	232-95-1	748	1552:1569	$C_{12}H_8O$	-0.33	x	x	x	x	
diethyl phthalate	908	84-66-2	768	1609:1594	$C_{12}H_{14}O_4$+H	0.63	x	x	x	x	plasticizer
Kodaflex txib	837	6846-50-0	768	1610:1588	$C_{16}H_{30}O_4$+H	-0.16	x	x	x	x	plasticizer
1-methylnonyl-benzene	886	4537-13-7	770	1615:1607	$C_{16}H_{26}$	0.21	x	x	x	x	
benzophenone	932	119-61-9	786	1660:1635	$C_{13}H_{10}O$	0.16	x	x	x	x	UV stabilizer
isopropyl myristate	897	110-27-0	840	1827:1827	$C_{17}H_{34}O_2$+H	0.06	x	x	x	x	
Sunarome O	870	118-60-5	841	1830:1811	$C_{15}H_{22}O_3$	-0.42	x	x	x	x	UV stabilizer
diisobutyl phthalate	902	84-69-5	858	1886:1870	$C_{16}H_{22}O_4$+H	0.14	x	x	x	x	plasticizer
homosalate	864	118-56-9	869	1922:1904	$C_{16}H_{22}O_3$	-1.85	x	x	x	x	UV filter
7,9-di-tert-butyl-1-aspiro(4,5) deca-6,9-diene-2,8-dione	918	82304-66-3	876	1947:1923	$C_{17}H_{24}O_3$	-0.30	x	x	x	x	
Metilox	827	6386-38-5	882	1962:1943	$C_{18}H_{28}O_3$	-1.22	x	x	x	x	plasticizer
palmitic acid	936	57-10-3	883	1969:1968	$C_{16}H_{32}O_2$	-1.21	x	x	x	x	slip agent
dibutyl phthalate	895	84-74-2	887	1980:1965	$C_{16}H_{22}O_4$	0.15	x	x	x	x	plasticizer
stearic acid	923	57-11-4	940	2170:2172	$C_{18}H_{36}O_2$	-1.51	x	x	x	x	slip agent
hexadecanamide	888	629-54-9	945	2192:2143	$C_{16}H_{33}NO$	-0.73	x	x	x	x	
oleamide	899	301-02-0	994	2381:2334	$C_{18}H_{35}NO$	-0.71	x	x	x	x	slip agent
diisooctyl phthalate	891	131-20-4	1039	2570:2543	$C_{24}H_{38}O_4$+H	-0.58	x	x	x	x	phthalate
erucamide	862	112-84-5	1090	2773:2625	$C_{22}H_{43}NO$	-1.59	x	x	x	x	slip agent
Irgafos 168	863	31570-04-4	1251	3468:3397	$C_{42}H_{63}O_3P$	0.25	x	x	x	x	processing stabilizer
Irganox 1076	861	2082-79-3	1319	3699:NA	$C_{35}H_{62}O_3$	-1.52	x	x	x	x	antioxidant
tris(2,4-di-tert-butylphenyl) phosphate	820	95906-11-9	1324	3720:3582	$C_{42}H_{63}O_4P$	1.32	x	x		x	transformation product Irgafos 168
Uvitex OB	830	7128-64-5	1492	4297: NA	$C_{26}H_{26}N_2O_2S$	0.29				x	thermal/chemical stabilizer

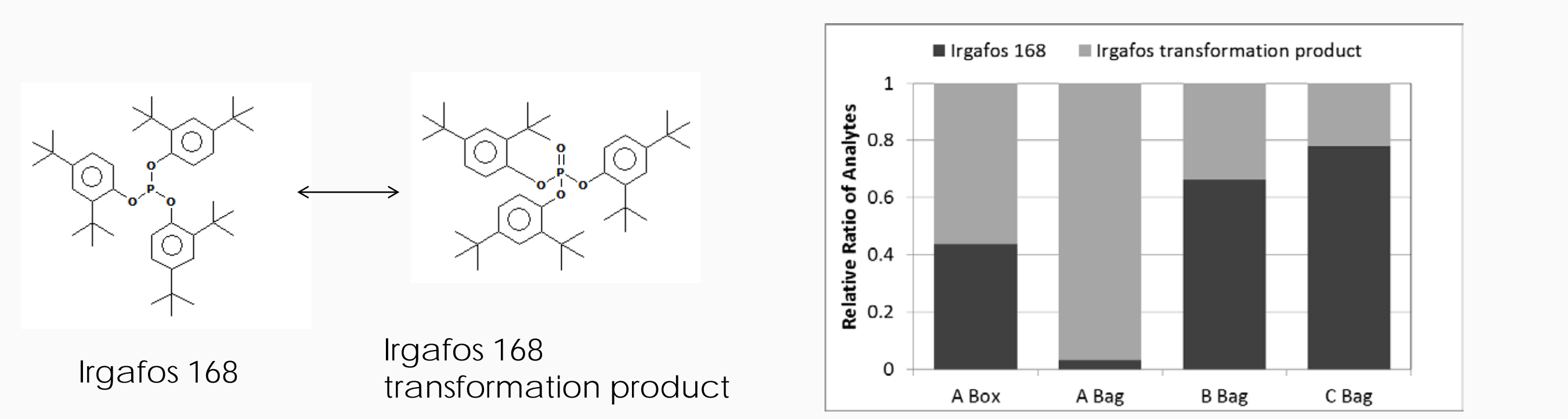Irgafos 168

Irgafos 168 transformation product

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 these 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 from 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.