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Assessing direct analysis in real-time-mass spectrometry (DART-MS) for the rapid identification of additives in food packaging

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The ambient ionization technique direct analysis in real time (DART) was characterized and evaluated for the screening of food packaging for the presence of packaging additives using a benchtop mass spectrometer (MS). Approximate optimum conditions were determined for 13 common food-packaging additives, including plasticizers, anti-oxidants, colorants, grease-proofers, and ultraviolet light stabilizers. Method sensitivity and linearity were evaluated using solutions and characterized polymer samples. Additionally, the response of a model additive (di-ethyl-hexyl-phthalate) was examined across a range of sample positions, DART, and MS conditions (temperature, voltage and helium flow). Under optimal conditions, molecular ion ($M+H^+$) was the major ion for most additives. Additive responses were highly sensitive to sample and DART source orientation, as well as to DART flow rates, temperatures, and MS inlet voltages, respectively. DART-MS response was neither consistently linear nor quantitative in this setting, and sensitivity varied by additive. All additives studied were rapidly identified in multiple food-packaging materials by DART-MS/MS, suggesting this technique can be used to screen food packaging rapidly. However, method sensitivity and quantitation requires further study and improvement.

Keywords: in-house validation; screening assays; food-contact materials; packaging additives; paper; plastics

Introduction

Polymeric food-contact materials are important in protecting food during processing, shipping, and retail sale. Polymeric packages come in contact with approximately 80% of the average diet in the United States. Formulations of food-packaging materials and additives may vary dramatically across food and packaging type, and are subject to frequent change due to product and packaging facility changes, packaging redesigns, material and processing costs, recycling demands, and the introduction of new packaging materials. Additives are essential for many desirable packaging characteristics such as shatter-resistance, clarity, longevity, colour, grease-resistance, heat-stability, ink-fastness, and active characteristics such as microwave enhancement, and oxygen and photo-quenching. Additives can also function as processing aids, allowing quick, inexpensive, and sterile packaging of food.

Characterization of food packaging for additive presence and identity is important to support good manufacturing practices, compliance with food safety regulations, and to prevent off-colours, flavours, or odours. Chemicals in food packaging are subject to regulation as food additives due to migration of monomers, additives, or their products into foods.

Methods to analyse food-contact materials for additives and other potential migrants often involve exhaustive extractions, which tend to select certain chemical moieties, and can be problematic when some additives are chemically labile or photosensitive (Nielson 1993; Bart 2001a; Feigenbaum et al. 2002). Polymer extract sample preparation methods can be complicated, solvent intensive, and take considerable time in order to separate analytes from the polymer matrix (often precipitated), or else the resultant extracts contain large molecules and or high concentration co-extractants which hinder analysis or require frequent instrument maintenance (Zhou et al. 1999; Smith and Taylor 2002; Nerin et al. 2003b). Additionally, some multilayer packaging materials (layered recycled content, barrier layers) and concerns about surface contamination (blowing and slip agents, print offsets) can necessitate surface analysis instead of bulk sample analysis (Begley et al. 2002; Nerin et al. 2003a; Bradley et al. 2005). Single-sided extraction techniques may be cumbersome, not particularly useful, and constitute a separate, additional analysis when characterizing food packaging surfaces (Bradley et al. 2005). Non-extractive techniques such as headspace gas chromatography mass spectrometry (HS-GC-MS)

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and pyrolysis GC-MS avoid solvent solubility and polymer precipitation issues, but they tend to retain the chemical range (volatile, non-labile) of GC, or the non-specificity of pyrolysis (Cook and Lehrle 1993; Lattimer 1993; Bart 2001a, 2001b). They also do not provide surface analysis. Finally, to our knowledge there are few multiple-analyte methods which screen for a diverse array of food contact additives, and none that includes fluorinated grease-proofing agents.

A fast method to screen food packaging for the identity and presence of a wide variety of additives would be useful, especially if surface analysis could be easily incorporated. Previously, laser-desorption laser-photo-ionization MS (LDLPI or L²I-MS) has been used for polymeric surface analysis, but only for select additives with a suitable chromophore (Asamoto et al. 1990; Johlman et al. 1990; Schriemer and Li 1996).

Recently, multiple ambient surface-ionization MS techniques have been described (Van-Berkel et al. 2008). These new techniques appear to provide the potential for rapid, sample preparation-free MS analysis, as well as surface analysis. Of the multiple related ambient ionization techniques, direct analysis in real time (DART) and desorption electrospray ionization (DESI) are the most extensively described and widely available (Venter et al. 2008).

In DART, a high-voltage helium plasma is created inside a ceramic flow cell, and ions are subsequently quenched at a flow through grid-electrode, leaving a stream of neutral and excited, metastable helium atoms. The excited helium beam is heated and flows through an exit grid electrode (which repels sample ions, and neutralizes counter ions) towards a sample incident to the MS inlet. It appears that upon exiting the DART grid-electrode, the metastable helium reacts with atmospheric water to form protonated water clusters ($\text{H}_2\text{O}_n\text{H}^+$), in turn ionizing analytes liberated from the sample by the hot, energetic helium stream (Cody et al. 2005).

While not explicit, the available literature seems to suggest that DART is less selective, whereas DESI is more frequently suggested to be more quantitative (Harris et al. 2008; Van-Berkel et al. 2008; Venter et al. 2008). DART also has the added benefit of no exposed voltages or radioactive source materials. However, DART mechanisms, sensitivity, quantitation capabilities, and potential for matrix effects have not been fully characterized to date. DART has been used primarily with a particular time-of-flight (TOF) MS, and it has not been demonstrated how compatible it may be with more common benchtop quadrupole MS or MS/MS instruments.

The aim of this study was to assess the applicability of DART-MS/MS for rapid characterization of food-packaging additives. We characterized DART parameter effects on a model additive (DEHP), determined optimum conditions for analysis of a broad suite of

additives, and tested for quantitative response in solution and in packaging.

Materials and methods

Chemicals

Solvents (acetone, acetonitrile, dichloromethane, ethyl acetate, hexane, isooctane, isopropanol, and methanol) were purchased from Burdick & Jackson (Muskegon, MI, USA) and were all GC-pesticide grade. Liquid nitrogen was purchased from Roberts Oxygen (Rockville, MD, USA), and compressed helium (99.999%) from Airgas (Hyattsville, MD, USA). Analytical standards of additives were acquired at 98% purity or better: DEHA (*bis*(2-ethyl-hexyl)-adipate) was from ChemService (West Chester, PA, USA); Irganox 1076 (stearyl-3-(3',5'-di-*t*-butyl-4-hydroxy-phenyl)-propionate), Irganox1010 (*tetrakis*-[methylene-(3,5-di-*t*-butyl-4-hydroxy-hydro-cinnamate-)]-methane), Irgafos-168 (*tris*-(2,4-di-*tert*-butyl-phenyl)-phosphate), and Tinuvin 234 (2-(2H-benzo-triazol-2-yl)-4,6-*bis* (1-methyl-1-phenylethyl)-phenol) were from Ciba-Geigy (Hawthorne, NY, USA); BHT (2,6-di-*tert*-butyl-4-methylphenol), Chimassorb 81 ([2-hydroxy-4-(octyloxy)phenyl]-phenyl-methanone), and Uvitex-OB (2,2'-(2,5-thiophenediyl)*bis*[5-(1,1-di-methyl-ethyl)-benzoxazole]) were from Sigma-Aldrich (St. Louis, MO, USA); and DEHP (1,2-benzenedicarboxylic acid, *bis*(2-ethylhexyl) ester) was from Riedel de Haen (Seelze, Germany).

Standards for some additives were not available as individual compounds and so were acquired in the form often used by manufacturers. These included two colorants from Ciba-Geigy: yellow 110, which was 85–90% (3E,3'E)-3,3'-(1,4-phenylene*bis*(azan-1-yl-1-ylidene-))-*bis*(4,5,6,7-tetrachloroisindolin-1-one) and 5–15% hydrogenated resin; and blue 15b, which was 90–99% (copper, (29H,31H-phthalocyaninato-(2-)-N29,-N30,-N31,N32)-, (SP-4-1)-) and 1–5% each of polymerized rosin and a copper phthalocyanine derivative. A fluorinated grease-proofing agent listed in the US Food and Drug Administration's (USFDA) Food Contact Notification #59 (USFDA 2009) was acquired from Ciba Specialty Chemical (Basel, Switzerland) and was primarily a mixture of one or two 6-, 8-, 10-, or 12-carbon perfluorinated chains bound as an ether to a *bis*(propene-diol)-amino-alkanoic acid. This fluorinated grease-proofer is here referred to as di-per-fluoro-alkoxy-amino acid (diPFAoAA). A second fluorinated grease-proofing agent was acquired from DuPont (Wilmington, DE, USA) and was primarily a mixture of two 6-, 8-, 10-, or 12-carbon perfluorinated chains bound by an alkyl group to a phosphate, and has been referred to as a di-perfluorinated alkyl phosphate surfactant or di-PAPS. The mixture, epoxidized soybean oil (ESBO, CAS#8013-07-8) was purchased from Fluka (Buchs, Switzerland).

Packaging materials

Reference materials consisting of high-density polyethylene (HDPE), low-density PE (LDPE), and polypropylene (PP) containing Chimassorb 81 and Uvitex-OB at 0.2–0.8 mg g⁻¹ were graciously provided by Dr R. Franz of the Fraunhofer Institut (Freising, Germany) as prepared for European Union Project No. G6RD-CT2000-00411. Additional samples of HDPE and LDPE containing Irganox 1010, Irganox 1076, and Irgafos 168 at various concentrations from 0.18 to 0.8 mg g⁻¹ were obtained as part of a laboratory round-robin study by ASTM International (West Conshohocken, PA, USA). Poly-vinyl chloride (PVC) and poly-vinylidene chloride (PVDC) food wrap (about 0.01 mm thick) were purchased from a local grocery store. Approximate concentrations of DEHA and DEHP in these PVC/PVDC stretch films were obtained from industry survey data. PVC foam gaskets previously characterized for ESBO were generously shared by Dr C. Simonaeu, EC-JRC Institute for Health & Consumer Protection (Ispra, Italy). Polystyrene (PS) samples were prepared previously with yellow 110 or blue 15b at 0.5% w/w (5.0 mg g⁻¹) with dual melt-screw extrusion techniques (Komolprasert 2006). Polyethylene terephthalate (PET) 500 ml bottles (about 0.35 mm wall) with known concentrations of Tinuvin 234 were provided by Captive Plastics (Hannover, MD, USA). Grease-proofed fast food sandwich-wrap paper was acquired from local restaurants and fluorinated grease-proofers were measured with traditional extraction techniques and LC-MS/MS, similar to methods described previously (Begley et al. 2008).

Equipment

All experiments were performed using a DART-100 (IonSense, Saugus, MA, USA) ion source bolted to the atmospheric pressure inlet source block of a Waters (Milford, MA, USA) Quattro Premier triple quadrupole MS. The DART source and a quartz ion-transfer tube were held in alignment with the MS inlet via bolts (16 cm) and an aluminium flange (Figure 1). The DART and a robotic autosampler, a CTC PAL (AutoDart-97, IonSense, Saugus, MA, USA) were also screwed to a steel foot plate (35 × 15 × 1 cm), which rested on a height-adjustable table (Anthro Corp, Tualatin, OR, USA). The autosampler was outfitted with conical metal tip, allowing sampling via a disposable pipette-tip/glass melting point tube (Ionsense), which fit over the metal tip of the robotic arm. This allowed the autosampler to dip the sealed end of the glass melting point tube into liquid samples, or pierce or abrade solid samples, before passing the sample coated glass tube through the DART's heated helium beam. Solid samples were manually attached to

alligator clips glued to the disposable plastic pipette tips, allowing the autosampler to more reproducibly introduce these samples to the DART's helium beam. Due to the configuration of the MS source block and the motion of the robotic autosampler arm, the DART ion source could not be located either in-line with the source inlet, nor any closer than about 13 cm from the inlet. As suggested by the DART manufacturer, a helium/ion 'transfer' tube (quartz, 6.35 mm o.d., 5 mm i.d., 14 cm length) was used to channel helium and analyte flow from the sample/DART to the inlet of the MS (Figure 1).

DART experiments

Optimization of DART-MS response was characterized across various DART-MS configurations for a model additive, DEHP. Response (measured by select ion peak height, signal-to-noise (*S/N*), and peak area) was studied across the parameters listed in Table 1 as well as the angle between MS inlet and the DART transfer tube and the solvent in which DEHP was dissolved. Distances and speeds were measured with calipers and/or the *x*, *y*, *z* positions reported by the robotic autosampler. Voltages and flow rates were recorded from readbacks on the instrument software. Full-scan data of DEHP were collected at duty cycles of 2–9 Hz over a 50–790 Da range. This mass range allowed for the observation of fragments, adducts, or dimers that might form during the ionization process. Product ion spectra of the molecular ion were compared to those generated from electro-spray ionization (ESI) MS/MS. Responses of the molecular ion in full-scan mode were quantitated using Mass Lynx software (Waters, Waterbury, MA, USA).

Additive analysis

Full-scan and product ion DART-MS spectra were collected from single-component standards for all 13

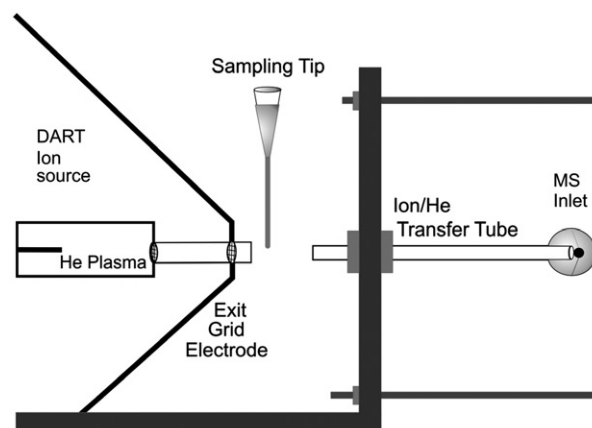


Figure 1. Schematic of DART ion source.

additives listed in Table 2. These spectra were obtained from about 100 mg l⁻¹ solutions of the additives (in ethyl acetate, trifluoroethanol or ethanol–water) and observed under the corresponding conditions listed in Table 2. For each compound listed in Table 2, the DART parameters of helium flow rate, temperature, sample introduction rate, MS scan rate, and collision voltage were investigated extensively until a mass spectrum with the highest intensities of high mass molecular or pseudo-molecular ions were obtained. Collision gas flow and collision energy were adjusted to achieve maximum abundance of two or three higher mass product ions with minimal adjustment of collision gas flow. While both positive and negative ion modes were investigated, much more time was spent on positive ion experiments. The MS scan rates varied with the width of the mass range studied for each compound, and initial mass ranges studied always allowed for observation of potential dimers. The conditions listed in Table 2 are approximate optimums. The parameters listed above were adjusted for each

compound while DART and MS inlet voltages were held constant due to their minor effects on DEHP sensitivity, and for simplicity.

Once characteristic ions and conditions were established for each compound, food-contact materials were studied in full-scan and product ion scan modes. Again, extensive investigations were performed on sample introduction speeds, orientations, spacing, DART temperatures, He flow rates, and MS scan speeds to optimize food-contact material analysis by DART-MS. To test quantitative response, DEHP solutions were prepared at concentrations between 100 mg and <0.1 mg l⁻¹. Response at *m/z* 391.3 was measured as changes in select ion current *S/N*, peak height, and peak area.

Results

DART characterization and optimization

Full-scan DART-MS spectra of DEHP yielded primarily molecular ion (Table 2) while its product ion spectra matched closely with the electro-spray product ion spectra (not shown). DART-MS response of DEHP was found to be most dependent upon DART-sample-transfer tube alignment with the MS inlet. Centering the transfer tube on the about 5 mm-wide helium beam of the DART, and centering the outflow of the transfer tube on the MS inlet were essential to observing response. Adjustments of 1 mm yielded drops of signal by several orders of magnitude.

Similarly, 1 mm changes in DART-to-sample distance, and 0.1 mm changes in the sample penetration depth (into the helium beam) changed DEHP response by nearly an order of magnitude. Therefore, even though reproducibility of raw response was poor (RSD about 20%), sample positioning was important enough that responses at most positions were still significantly different from adjacent locations. Interestingly, tip

Table 1. Range of DART-MS parameters.

Parameter	Range	Unit	Selected optimal
DART temperature	50–450	°C	n.a.
Helium (He) flow rate	1.0–6.0	l min ⁻¹	2.0–4.0
Sample depth in the He beam	–0.2 to 5.5	mm	0.5
DART sample distance	0–6.0	mm	0.5
Sample transfer tube distance	2.0–8.0	mm	5.0
Sample speed in the He beam	250–2000	mm s ⁻¹	500–1200
DART exit grid voltage	0–450	V	200
MS cone voltage	0–80	V	40
MS extractor voltage	0–8	V	1
MS RF lens voltage	0–0.8	V	0.1

Table 2. Additive specific analysis conditions.

Additive	Use of additive	DART temperature (°C)	Precursor ion		Product ions		Collision voltage (V)
			<i>m/z</i>	i.d.	<i>m/z</i>	<i>m/z</i>	
Chimassorb81	UV stabilizer	200	327.2	M + H ⁺	137	215	20
DEHA	Plasticizer	200	371.3	M + H ⁺	129	147	12
DEHP	Plasticizer	200	391.3	M + H ⁺	149	113	10
Uvitex OB	Colorant	200	431.2	M + H ⁺	415	399	50
Tinuvin 234	UV stabilizer	250	448.2	M + H ⁺	370	119	30
diPFAoAA	Grease proofer	300	489.0	M ⁻	419	219	30
Irganox 1076	Antioxidant	300	531.5	M + H ⁺	147	515	29
Blue 15b	Colorant	450	576.1	M + H ⁺	574	191	70
Yellow 110	Colorant	450	642.8	M + H ⁺	240	268	60
Irgafos 168	Antioxidant	350	647.5	M + H ⁺	147	347	40
diPAPS	Grease proofer	300	889.0	M ⁻	443	543	30
ESBO	Plasticizer	350	992.8	M + H ₃ O ⁺	295	277	45
Irganox 1010	Antioxidant	450	1196	M + H ₃ O ⁺	731	785	35

pickup by the autosampler occasionally resulted in a slight off-vertical orientation of the glass sampling tubes, yielding a about 0.5 mm variation in the DART-to-sample distance, increasing signal variability (about 5–10% RSD). Therefore, when possible, a single tip was used to minimize this effect.

Helium flow rates had the next most significant effect on DEHP peak heights and areas. Helium flow rates increased DEHP response about two–five-fold every 1 min⁻¹ increase (from 1 to 6 L min⁻¹), but the effect on *S/N* was slightly lower (1.5-fold). DART temperatures were not as effective as MS cone voltages in changing DEHP response, although for larger molecular weight compounds the temperature effects were considerably larger. MS inlet voltages (extractor and RF) and DART voltages had small but measurable effects on DEHP response.

Additive mass spectra

As was observed previously by other researchers, the dominant ions produced by DART-MS in positive mode were primarily *M* + *H*⁺ molecular ions (Table 2) (Cody et al. 2005; Haefliger and Jeckelmann 2007; Petucci et al. 2007). Rarely were spectra observable in the negative ion mode, except for the fluoro-chemicals. Protonated/de-protonated molecular ions were the base peaks for most compounds, although water adducts were present and dominant in some cases (Table 2 and Figure 2b).

In the negative mode, the molecular ions also dominated the spectra of the fluoro-chemical grease-proofers. In the case of diPFPPoAA, the mixture's

intended product did not dominate the spectra. A highly unique co-product in the formulation, a perfluoroalkenic acid (PFAeA), was the base peak in its spectra (with a C₆F₁₃ tail, *m/z* 489), and was used as a precursor ion for MS/MS (Table 2). An ion series, differing by 100 Da, (489-C₆, 589-C₈, ...) was observed in both fluorinated additive spectra, and corresponds to the perfluoro analogues with different C₂F₄ chain lengths. This 100 Da series was also characteristic of the diPFPPoAA molecular ions (1138, 1238, ...) and the mono-PFPPoAA ions (680, 780, ...) in the ESI spectra of the formulation and extracts from coated papers (Begley et al. 2008). A similar series (889, 989, ...) of molecular ions was observed for the diPAPs fluoro-chemical grease-proofer (Table 2).

Interestingly, two of the largest molecular weight additives (ESBO, Irganox 1010) produced water adducts as their base peaks under the conditions described here (Table 2). The plasticizer, ESBO, is a mixture of epoxidized triglycerides, diglycerides and fatty acids. In DART-MS the water adduct (*M* + H₃O⁺) of the epoxidized triglyceride of linoleic acid (LLL) was the base peak and molecular ions were also present at very low levels. For Irganox 1010, the water adduct of the molecular ion was the base peak, although molecular ion was present in small quantities (Figure 2b).

The product ion spectra of the 13 additive standards varied slightly in complexity and mass range. However, collision energies required to produce unique spectra (near equivalent amounts of unique product ions) for each additive ranged from 10 to 70 eV when about 10⁻³ Torr of Argon was present in the collision cell (Table 2). Additional sensitivity might be gained

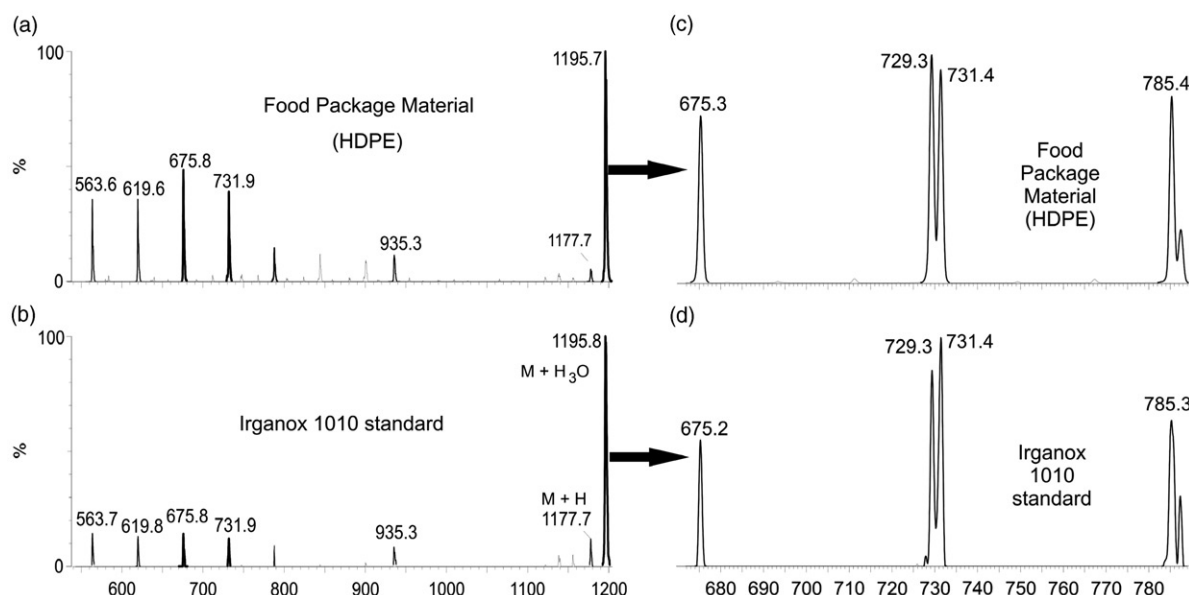


Figure 2. DART-MS spectra of Irganox 1010 in food-packaging material (a), Irganox 1010 standard solution (b), and their MS/MS product ion spectra (c, d).

from optimizing the collision conditions for each of the two or three most intense product ions and only monitoring these reactions. However, additional spectral information was gleaned from the product ion scans of these additives under significant collision energies, which proved useful in comparisons with food packaging (Figure 2).

Spectra of additives in packaging

Primary MS spectra of the 20 food-packaging materials contained the same three most abundant ions as the corresponding additive standard (Table 3). The food-packaging materials' product ion spectra also matched the standards' three most abundant product ions (Table 3). An example can be seen in the comparison of Irganox 1010's standard spectra and the corresponding reference HDPE sample with Irganox 1010 present at 0.172 mg g^{-1} (Figure 2). For example, the three most intense ions of the Irganox 1010 standard (1195.8, 675.8, and 731.9) were present and dominant in the corresponding food packaging's DART-MS spectra (Figure 2a, b, and Table 3). Additionally, the three most intense ions of the Irganox 1010 standard's product ion spectra (729.3, 731.4, and 785.3) were present and dominant in the corresponding food packaging DART-MS/MS product spectra (Figure 2c, d, and Table 3). The product ion spectra of food packaging appeared to only include the same ions as those generated by the standards (Figure 2c, d).

For some food-packaging materials, the relative abundances of the major ions in the primary spectra deviated substantially from the standard (Table 3). These deviations were observed most prominently when the additive was a mixture. These differences in relative ion abundance between standards and food packaging could have been caused by multiple factors. There may have been different compositions of the additive mixtures applied to the packaging and the standards we acquired. There also may have been in-packaging degradation/transformation of the additives. Different relative ion abundances may also have been due to fluctuations in ionization and transfer efficiency of the different chemical species in these mixtures. Finally, matrix effects of the packaging material may have skewed these DART-MS spectra. For the mixtures analysed, the cause is unclear.

For most additives, the relative ion abundances in food packaging deviated from DART-MS of their standards by less than 12%. In most cases, this was an increase in fragment ion abundance, suggesting in packaging or in-source fragmentation of the target additive. In all cases, following packaging material introduction, the primary MS spectra additive ions peaked within 1 s or 1 scan of each other. These ions usually peaked within 1 s of sample introduction, and always at a S/N ratio greater than 3:1.

The DART-MS/MS product ion spectra from food packaging samples exhibited a stronger correlation with standard's MS/MS spectra than their primary spectra.

Table 3. DART-MS confirmation of additives in packaging.

Additive	Packaging		MS confirmation		MS/MS confirmation	
	Material	Concentration (mg g^{-1})	Top three ions?	Relative ion abundance (% deviation)	Top three ions?	Relative ion abundance (% deviation)
Chimassorb81	HDPE	0.90	Y	<8%	Y	<6%
DEHA	PVC	0.50	Y	<37%	Y	<7%
DEHA	PVC	About 110	Y	<12%	Y	<2%
DEHP	PVC	0.20	Y	<40%	Y	<5%
Uvitex OB	HDPE	0.46	Y	<4%	Y	<3%
Tinuvin 234	PET	2.4	Y	<7%	Y	<4%
diPFAoAA	Paper	0.13	Y	<25%	Y	<10%
Irganox 1076	HDPE	0.21	Y	<26%	Y	<4%
Irganox 1076	HDPE	0.78	Y	<18%	Y	<4%
Irganox 1076	LDPE	0.60	Y	<5%	Y	<4%
Irganox 1076	PP	1.4	Y	<4%	Y	<2%
Blue 15b	PS	5.0	Y	<10%	Y	<5%
Yellow 110	PS	5.0	Y	<80%	Y	<5%
Irgafos 168	HDPE	1.0	Y	<38%	Y	<3%
Irgafos 168	LDPE	0.54	Y	<8%	Y	<4%
Irgafos 168	PP	1.5	Y	<3%	Y	<2%
diPAPs	Paper	2.3	Y	<80%	Y	<10%
ESBO	PVC	About 100	Y	<69%	Y	<6%
Irganox 1010	HDPE	0.17	Y	<26%	Y	<8%
Irganox 1010	HDPE	0.72	Y	<4%	Y	<3%

Note: Y, yes.

On average, packaging samples' relative ion abundances matched additive standards to within 5% (Table 3). These MS/MS spectra deviated from standards by no more than 10% for all 13 compounds in all 20 samples (Table 3). As with the primary DART-MS spectra from food-packaging materials, upon sample introduction, the product ions peaked within 1 s or 1 scan of each other, usually within 1 s of sample introduction, and at a S/N greater than 3:1. Finally, triplicate DART-MS analysis of a food-packaging material (including positive and negative controls) took less than 2 min.

Quantitative analysis

Attempts to create calibration curves with standard solutions of DEHP (<0.1 – 100 mg l^{-1}) yielded small variation in DART-MS signal response as measured by peak heights, peak areas, or S/N , and no response was observed below 0.1 mg l^{-1} . The most concentrated solutions generally yielded larger responses and were frequently significantly different from the lowest concentration solutions. The corresponding least squares linear regression estimates ($r^2 < 0.45$) often failed lack-of-fit F -tests ($p > 0.10$), suggesting that a linear relationship was not observed. Although variability in DART-MS response under these conditions was significant (RSD about 10–25%), the small change in DART-MS response across this large concentration range likely played a large role in the absence of a linear external response curve. Since DART-MS/MS product ion spectra for DEHP were found to consist solely of molecular ion fragments, it was assumed that multiple reaction monitoring MS/MS would yield similar non-linear results.

The analysis of food-packaging materials for additives at multiple concentrations also indicated that DART-MS was not responding linearly to different concentrations of these additives. Although food packaging samples with the highest concentrations of DEHA, Irganox 1076, Irgafos 168, and Irganox 1010 yielded higher responses than the lowest concentrations, the concentration effects were not always significant. Additionally, concentration responses were not consistent over the course of weeks, across replacement of the quartz transfer tubes, or sample tips. This is similar to what has been observed previously for DART-MS analysis of surfaces. Although some of this inconsistency may be due to alignment differences, great efforts were taken to ensure consistent DART sample-MS alignment. Perhaps just as likely is significant variation in surface concentrations of additives across a packaging article (Begley et al. 2008). There are some indications that more quantitative responses are possible with better DART-sample positioning and the use of isotope

labelled internal standards (Morlock and Ueda 2007; Petucci et al. 2007; Grange and Sovocool 2008). It is unclear whether the apparent insensitivity observed was due to the experimental set-up employed here or other more fundamental aspects of DART sample introduction and ion transfer. More study is needed to better understand and address DART-MS quantitation.

In comparison with other direct or surface analysis techniques employed for food packaging analysis, DART-MS required none of the sample preparation employed for matrix assisted laser desorption MS (MALDI-MS), HS-GC-MS, pyrolysis GC-MS, desorption chemical ionization MS (DCI-MS), or fast atom bombardment MS (FAB-MS) (Juo et al. 1995; Bart 2001a, 2001b; Hsiao et al. 2001; Feigenbaum et al. 2002; Herrera et al. 2003; Nerin et al. 2003a). As suggested earlier, DART-MS did not require sample pulverization, and did not appear to suffer pyrolytic analyte decomposition as observed with pyrolysis-MS. Additionally, DART-MS can be automated and could perform surface analysis not available to pyrolysis-MS techniques (Lattimer 1993; Herrera et al. 2003). In comparison to LDLPI-MS, DART-MS of additives appeared to be more universal and provide no accessible hazards such as high energy lasers (Wright et al. 1996).

Conclusions

DART-MS, upon characterization and optimization, was successfully applied to the rapid screening of 20 food-packaging samples for the presence of 13 common additives using a benchtop MS. It was determined that DART sample-MS positioning and alignment had the largest impact on sensitivity, while DART temperature and helium flow also played a significant role. These parameters, along with MS scan rates, needed to be matched or optimized for each additive separately, although there was some overlap in optimal conditions between additives. DART-MS spectra for packaging additives appear to be quite unique, producing predominately molecular ion. DART-MS was found to identify a wide range of packaging additives reliably, including plasticizers, anti-oxidants, colorants, grease-proofers, and UV-stabilizers in their respective food-packaging materials. Primary DART-MS spectra of characterized food-packaging materials matched well with spectra from standards of their additives. Product ion spectra matched even more closely. In all cases, S/N ratios and ion timing indicated additives' unambiguous presence in packaging materials. However, method sensitivity and linearity were difficult to establish and will require future study.

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