

The use of DART-HRMS for the rapid identification chemical substances in food contact materials

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Abstract

Background

In 2005, Cody et al. introduced a new ionization source: Direct analysis in real time (DART), which when coupled to a high-resolution mass spectrometer (HRMS), can be used as ambient mass spectrometric sample introduction technique. The main advantage of this technique is that can identify chemical substances in different types of matrices and obtain reliable results in minutes without any sample preparation.

Purpose

The Division of Analytical Chemistry (DAC) at the Center for Food Safety and Applied Nutrition (CFSAN) has been using DART-HRMS for the rapid identification of potential migrants in food contact materials (FCMs) for over 10 years¹⁻¹⁰. Monomers and additives used in the manufacture of FCMs as well contaminants, have been successfully identified in almost any type of analyzed matrix (e.g. plastics, food simulants, and foods). Thus, the purpose of this poster is to summarize the obtained identification results to date and the implications for future research in the food safety field.

Methodology

DART-HRMS is a DART ion source and a HRMS. The DART flows excited helium (~300-500 °C) to liberate and ionize chemicals from samples. The HRMS spectra (positive and negative mode) were typically collected from 85 to 1200 Da, although MS/MS was occasionally used as well. Samples (food packaging, food contact articles, food, and food simulating liquids) are placed in between the DART source and the HRMS for approx. 5 seconds using previously cleaned tweezers or glass capillary tips.

Results

Several potential migrants such as starting substances used in the FCM as well as non-intentionally added substances (e.g. brominated flame retardants, photo-initiators, polyester oligomers) have been rapidly identified in several matrices such as food contact polymers (e.g. nylon), food (e.g. milk) and food simulants (e.g. 50 % ethanol) obtaining satisfactory results in just a few minutes. Some polymers have been identified, and the presence of ink-setoff was detected as well.

Conclusions

DART-HRMS is a powerful analytical technique with potential application as rapid identification technique for regulatory screening purposes.

Introduction

Direct analysis in real time (DART) coupled to a high-resolution mass spectrometer (HRMS) is an analytical technique that be used for the rapid screening of chemical compounds in almost any type of matrix, including Food Contact Articles (FCAs). One of the main advantages is that it needs little to no sample preparation and results can be obtained in minutes. In our laboratory we have been using this technique in the field of food safety for over a decade obtaining very good results. Here we summarize the main findings obtained to date by using DART-HRMS.

Materials and Methods

DART-HRMS consisted of a DART ion source and a HRMS. The DART flows excited helium (between 300-500 °C) to liberate and ionize chemicals from samples. The HRMS spectra (positive and negative mode) were typically collected from 85 to 1200 Da, although MS/MS was occasionally used as well. Samples (food packaging, food contact articles, food, and food simulating liquids) are placed in between the DART source and the HRMS for ~5-15 seconds using previously cleaned tweezers or glass capillary tips. In some cases, the use of dopands such as solution of 20% NH₄ was used^{2,3}. Data processing is conducted by using appropriate software (e.g. QualBrowser, TOX ID, Excel) and settings (e.g. mass tolerance of 5 ppm).

Results and Discussion

Analysis of primary aromatic amines (PAA) analysis in kitchen utensils⁴.

During the first decade of the century, several publications related with the presence of PAA in cooking utensils were published. Since those initial studies, several alerts related with PAAs in food contact materials were reported in the Rapid Alert System for Food and Feed (RASFF) in the European Union (EU). The main disadvantage in the determination of PAA is that methods can be time consuming and therefore, the development of rapid screening methods for the rapid analysis of PAAs was required.

We developed a DART-HRMS method for the analysis of PAAs in kitchen utensils. For the sample introduction, small pieces of the samples (triplicate) were cut and analyzed directly by DART. To validate the study, we compared the DART results with results obtained using a more traditional analytical technique (UPLC- MS/MS). By using DART, we were able to identify PAAs directly in the materials in just few minutes (figure 1). By using threshold of zero during the data analysis, DART was able to identify 100% of non-compliant samples. However, the number of false positives was excessive. A way to correct this high positive rate, was by increasing the threshold. By using a threshold of 1 during the data analysis, DART identified 88 % of the samples considered violative samples in the EU and significantly decreased the false positive rate. However, by increasing the threshold, false negatives were also increased. This study showed that adjusting the response threshold or further evaluate DART methods is required to use DART-MS an effective tool in PAA determination.

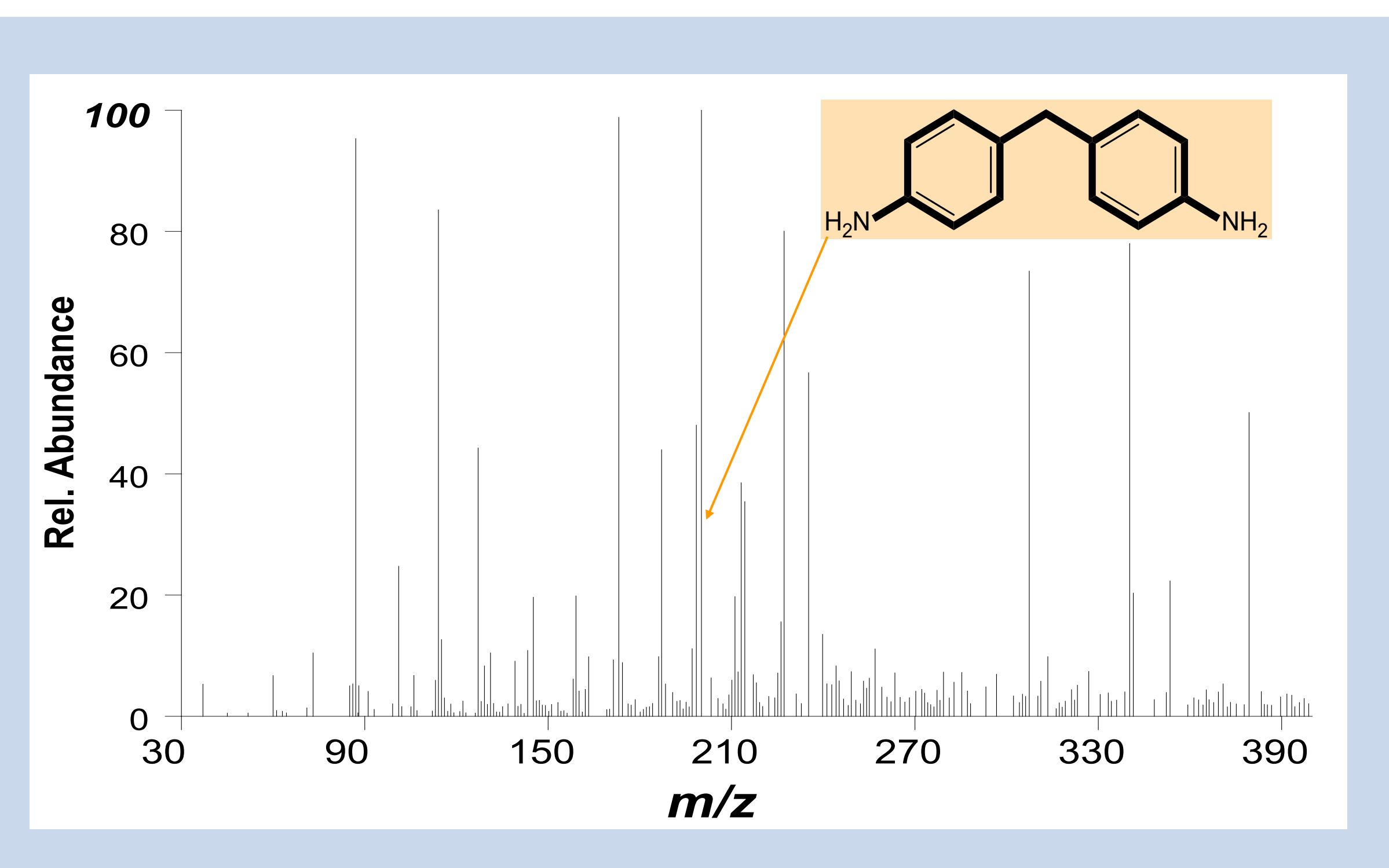


FIGURE 1 Example of DART-MS spectra of PAAs.

Determination of brominated flame retardants (BFRs) by using DART-HRMS^{5,6}.

Previous work has found BFRs in FCM. The use of BFRs in FCM and therefore as food additives is not allowed in the United States. We use DART-HRMS to rapidly identify BFRs in food contact polymers, food as well as food simulants. In the analyzed food contact articles⁶ we found that DART-HRMS 79% of the samples were in good agreement with the results obtained by GC-MS (used as reference) in the combined sample set. Estimated false positive incidences were 5% and false negative incidences of 4%. False-negative rates were 25% and false-positive rate of 6%. We also conducted migration studies in food and food simulants. By using DART-HRMS we were able to identify BFRs in in both including milk, chicken bouillon soup and 50 % ethanol food simulant.

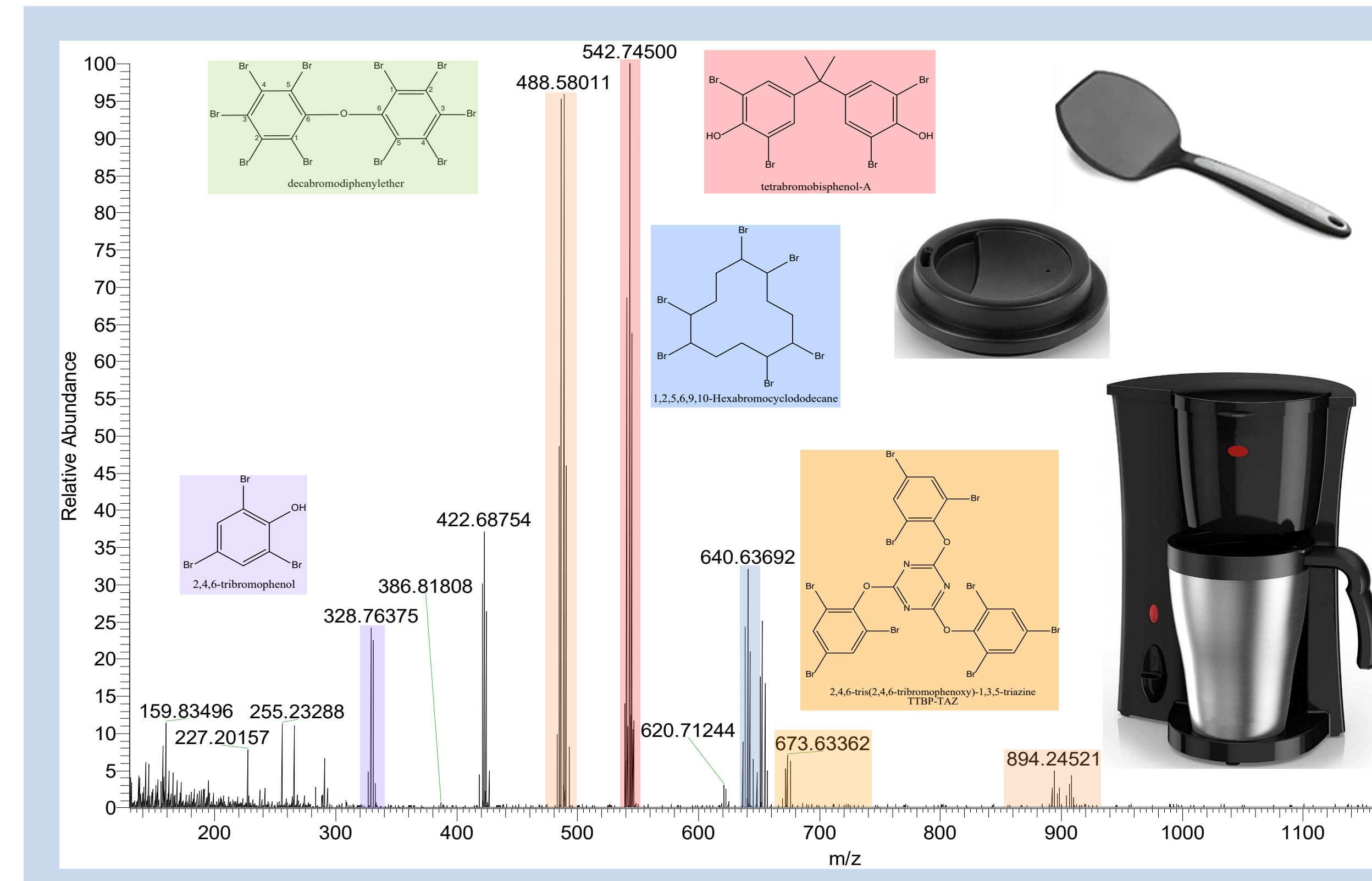


FIGURE 2 DART-MS spectra of Brominated Flame Retardants found in FCAs^{5,6}.

DART-HRMS detection and identification of printing ink set-off in food packaging.^{7,8,9}

Since the UV ink photoinitiator (PI) isopropylthioxanthone (ITX) was discovered in packaged milk, studies of packaging have included print contamination for consideration. Set-off is the unintentional transfer of substances used in printing from the external printed surface of food packaging to the inner, food-contact surface of adjacent packages (stacked or rolled) prior to filling. It is considered an issue of good manufacturing practice. This transfer is problematic because most printing materials typically have not been authorized for direct food contact. Also, set-off is not always visible to the human eye, and prints often contain numerous, variable, and reactive mixtures (ie UV photoinitiators etc). Rapid non-targeted methods were needed to detect and identify print set-off incidence in packaging.

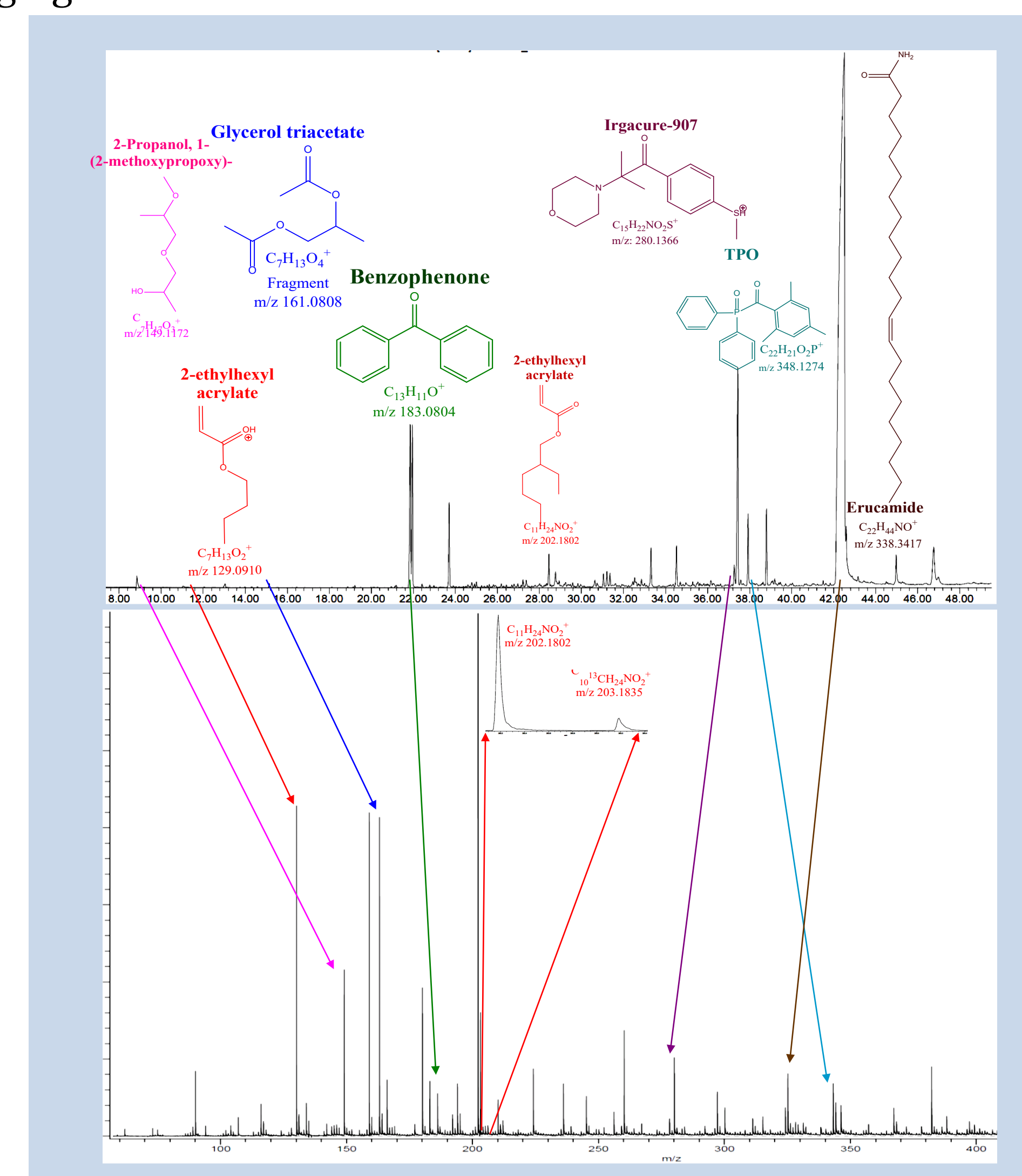


FIGURE 3 GC-MS vs DART-MS ID of print compounds on food contact surfaces

The use of DART-HRMS for the rapid identification of polyamides (nylon) polymers¹⁰.

Dozens of different polymers of different chemistries are authorized for use under certain conditions. As a result regulations authorizing the use of a particular polymer, (eg nylon 6) may require limited migration of additives and monomers (ie caprolactam, CPL). In the case of nylons, many different nylons are used commercially but only nylon-6 uses CPL as a monomer. However nylons are virtually indistinguishable by conventional polymer id (FTIR). In this work we used DART-HRMS(/MS) to directly and rapidly identify the different polyamides (nylons) using first principles according to their monomer structures, without lengthy digestion or migration tests.

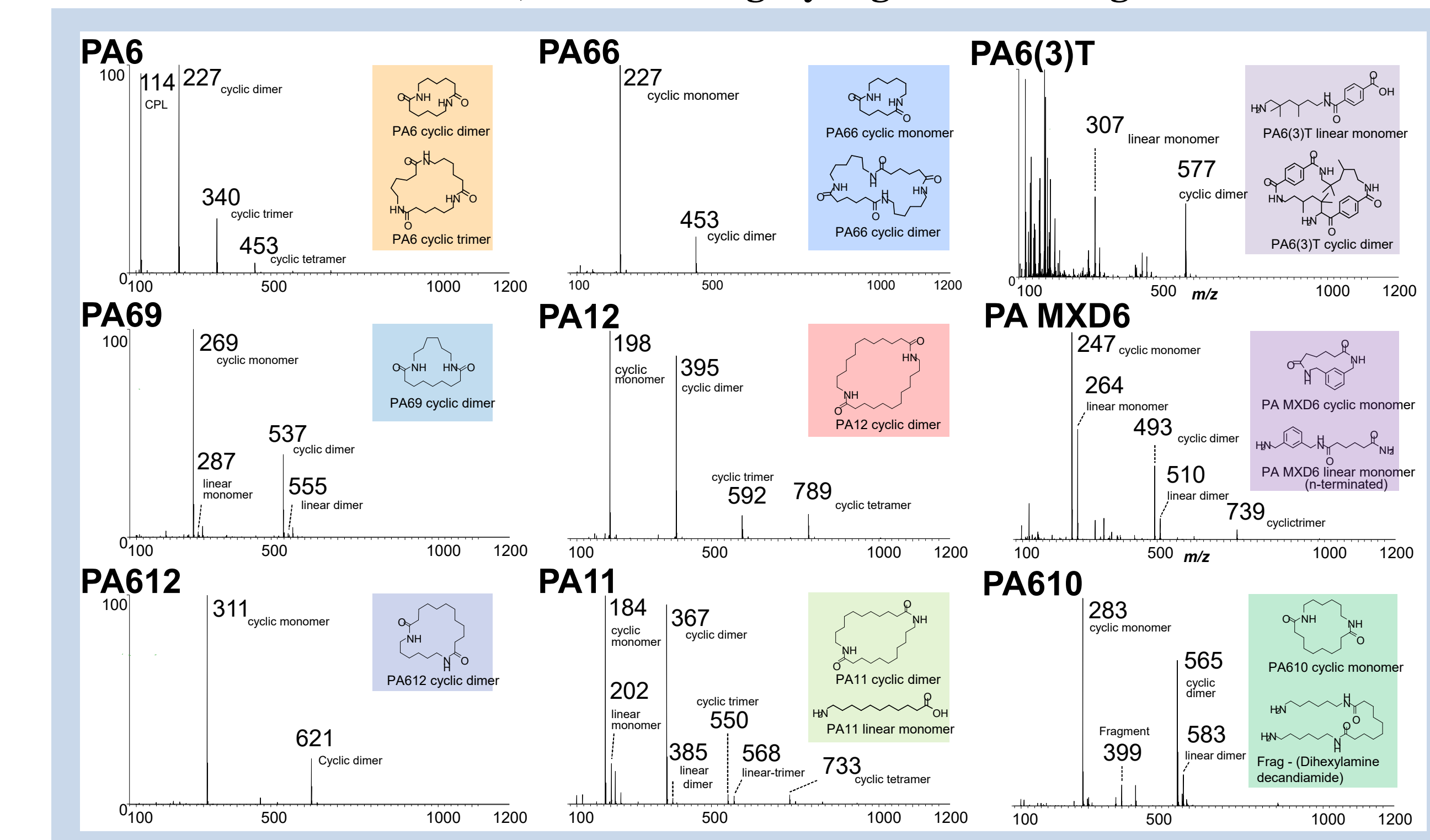


FIGURE 4 DART-MS identifications of 10 polyamides (nylons)¹⁰

Conclusion

Since 2011, ORS-DAC has developed DART-HRMS methods to:

- Identify >150 Additives & Contaminants in FCAs.
- Identify numerous migrants in FCAs, simulants, and foods.
- Identify polymer types.
- Identify the location of Additives or Contaminants in FCAs.
- Assess the incidence of Additive or Contaminant occurrence.

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