



● Detection of Plasticizers and Flame Retardants in Polymers by Pyrolysis GC-APCI QTOF MS

The ability to confidently detect specific target compounds is critical in many analytical workflows related to human health and safety. In some cases, such screening is challenged by the physical form of the samples and by the chemical nature of the targets themselves. In this study, pyrolysis GC-APCI QTOF MS is used to detect potentially hazardous plasticizers and flame retardants in various fabric samples.

Introduction

Polymeric materials are made in a wide array of forms to serve an equally wide scope of uses within day to day life, from plastic bottles to toys and upholstery foams to

garment fabrics. In order to meet necessary requirements for utility (e.g., flexibility or durability) or safety (e.g., resistance to fire or tensile strength), plasticizers or flame-retardants are often added. In the case of clothing

fabrics, such compounds may be applied to natural fibers as well. Unfortunately, many of these compounds have been shown to be toxic to humans. Halogenated flame retardants, for example, widely found in indoor/outdoor

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environments and protective clothing, are shown to have adverse health effects [1,2]. Substantial concerns have been expressed over the safety of some plasticizers, including widely used ortho-phthalates, which have been classified as potential endocrine disruptors with developmental toxicity reported. Other newly developed additives may yet have unknown health risks. Because of these potential hazards, there are recent and pending regulation changes within many states in the US and the European Union.

Given that many of these treated fabrics may be in close and constant contact with the skin, it is advantageous to be able to quickly and accurately detect the presence of compounds with potential adverse effects on human health. Pyrolysis GC-MS provides a straightforward way to analyze many sample types not amenable to direct analysis by chromatographic mass spectrometry (Figure 1). Vaporized sample components and fragments generated by the pyrolysis are passed through the GC for separation, followed by mass analysis. Frequently, the major peaks in the resulting chromatogram (pyrogram) are easily identifiable and give direct structural information about the material being pyrolyzed (Figure 2). Using the Bruker compact QTOF MS system, all components eluting from the GC are detected with both mass accuracy (<2 ppm) and isotopic distribution (<2% error). Accurate isotope ratios can be critical in the confident determination of the elemental composition of unknown compounds [3]. With the combination of the structure of the polymer, the elemental formula, and MS/MS spectra, most compounds can readily be identified. As the generated pyrograms are often complex, powerful software tools are necessary for data mining for compounds of specific



Figure 1: Components of the Pyrolyzer GC APCI QTOF MS system used in this study: (left to right) CDS Analytical Model 6200 Pyroprobe, Bruker Daltonics 456 GC, Bruker Daltonics compact QTOF MS

Table 1: Pyrolysis GC-MS Conditions

Pyrolyzer	
Instrument	CDS 6200 Pyroprobe (CDS Analytical LLC)
Temperature program	40°C (2 seconds), 50°C/second, 750°C (20 seconds)
Interface	300°C
Transfer line	300°C
Valve oven	300°C
Gas Chromatography	
Instrument	Bruker 456 GC
Column	Restek RXI-5Sil MS 30m X 0.25mm ID. X 0.25 μm df
Temperature program	40°C (1 minute), 6°C/minute, 320°C (5 minutes)
Injector	split 50X at 280°C
Transfer line	300°C
Mass Spectrometry	
Instrument	Bruker compact UHR-QTOF MS/MS with GC-APCI interface
Ionization	Positive
Calibration	PFTBA
Corona needle	4000 mA
Nebulizer gas	2 bar
Dry gas	1 L/min
Dry temperature	150°C
m/z range	20-1000
MS spectra rate	3 Hz

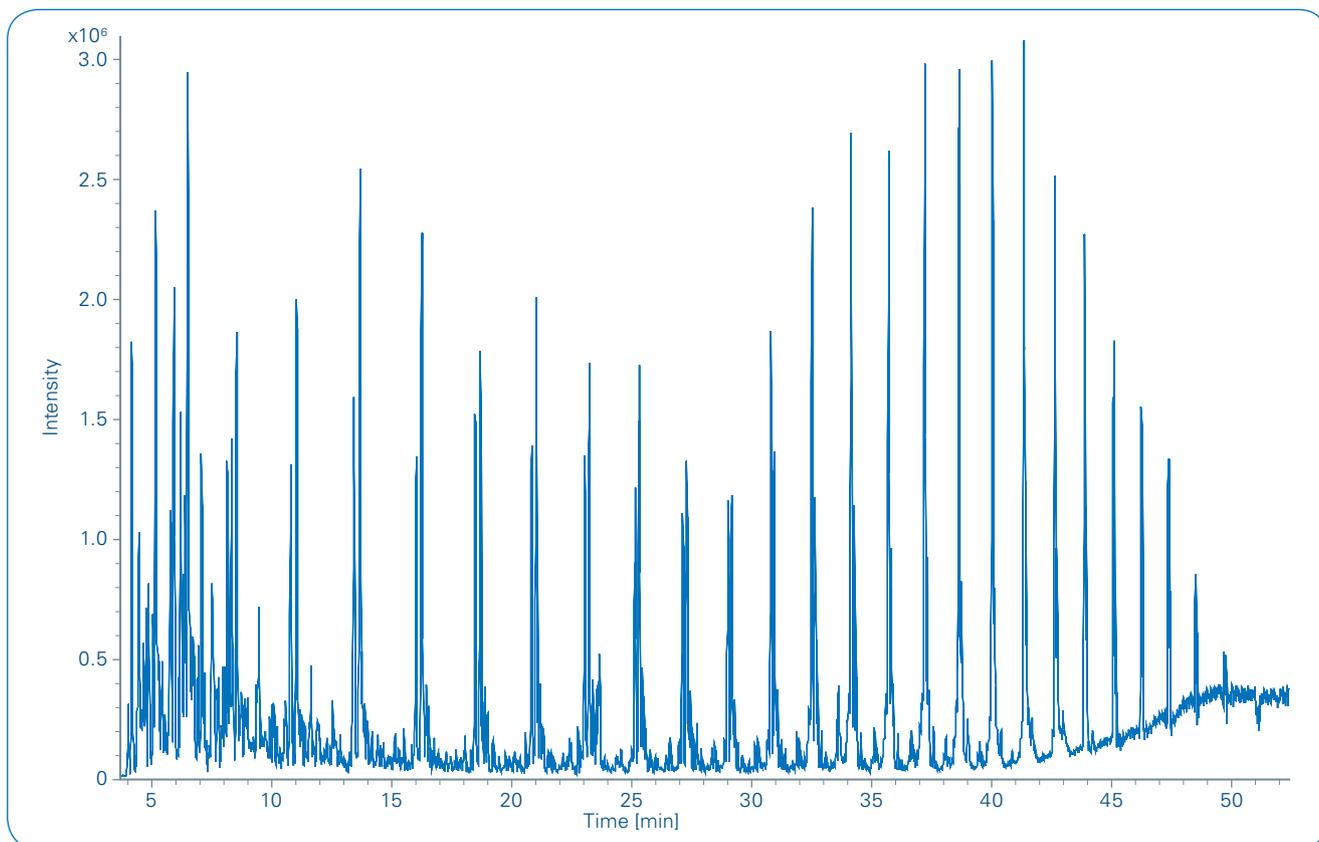


Figure 2: Example pyrogram of a solid polyethylene sample, illustrating a clear and even distribution of oligomer fragmentation products. Data was collected following the same instrumental parameters described for the fabric samples.

interest. Bruker's TASQ (Target Analysis for Screening and Quantitation) software is specifically designed to exploit high resolution accurate mass data generated by Bruker QTOF mass spectrometers. TASQ provides a turnkey solution when there is a requirement to screen, confirm, or quantify dozens or hundreds of compounds.

In this experiment, samples taken from five distinct types of fabric were analyzed by pyrolysis GC-APCI QTOF MS for 85 target plasticizers and flame retardants. Samples included a common cotton T-shirt, a common polyester T-shirt, protective gear moisture barrier fabric, protective gear thermal barrier material, and a protective gear outer lining. The fabrics of the protective gear were made with Kevlar®, Nomex®, and PBI® in various combinations and ratios.

Experimental

Names and formulas of 85 commonly used flame retardants and plasticizers were obtained from a web search. Within TASQ, a custom compound list was created to utilize the TASQ Suspect Finder workflow (Figure 3). As the retention times of these compounds within the GC method were unknown, this value was set to zero to direct TASQ to search for these compounds over the entire chromatogram.

A very small piece of the fabric (100-200 μg) was inserted in the quartz sample tubes of the pyrolyzer. After pyrolyzing at 750°C the products were directly transferred to the injector of the GC. As a slow GC temperature gradient was applied, the effluent was ionized by APCI and introduced into the compact QTOF mass spectrometer (Table 1).

Results and Discussion

Targeted compounds were detected in two of the five fabrics tested. Pyrograms for the cotton T-shirt and protective gear moisture barrier fabric are shown in Figures 4 and 5, respectively. Of the 85 target compounds, only the flame-retardant melamine was detected in the cotton T-shirt. In the protective gear fabric, many of the most prominent peaks within the pyrogram were breakdown products of Kevlar® and Nomex®. The plasticizer ethyl terephthalate could be clearly detected (labeled peak 11, Figure 5). A total of five (5) targets could be detected using TASQ's Suspect Finder workflow, including many with peak intensities too low to be visualized within the (full) pyrogram.

Based on the molecular formula provided during the creation of the suspect (target) list, TASQ software calculated the exact mass of the protonated species of each compound. Extracted ion chromatograms (EIC) of ± 3 millimass units (mDa) were then created around the exact mass. The target peaks were automatically sought within the experimental EICs. The target peaks were automatically sought within the experimental EICs. The isotopic patterns of all "hits" in the measured spectra were compared with the theoretical isotope patterns and given a milliSigma (mSigma) score between 0 and 1000, where lower values signify a better match.

Target or suspect analytes found in the protective gear moisture barrier fabric are shown in Figure 6 (TASQ Screener Results). The MRSQ icon (Mass, Retention time, mSigma, Qualifier ions) indicates how well the detected compounds compare with the expected values. Traffic light color-coding within the TASQ software facilitates rapid data review, including the absence or presence of (potentially) interfering compounds of the exact same mass as the specific targets sought.

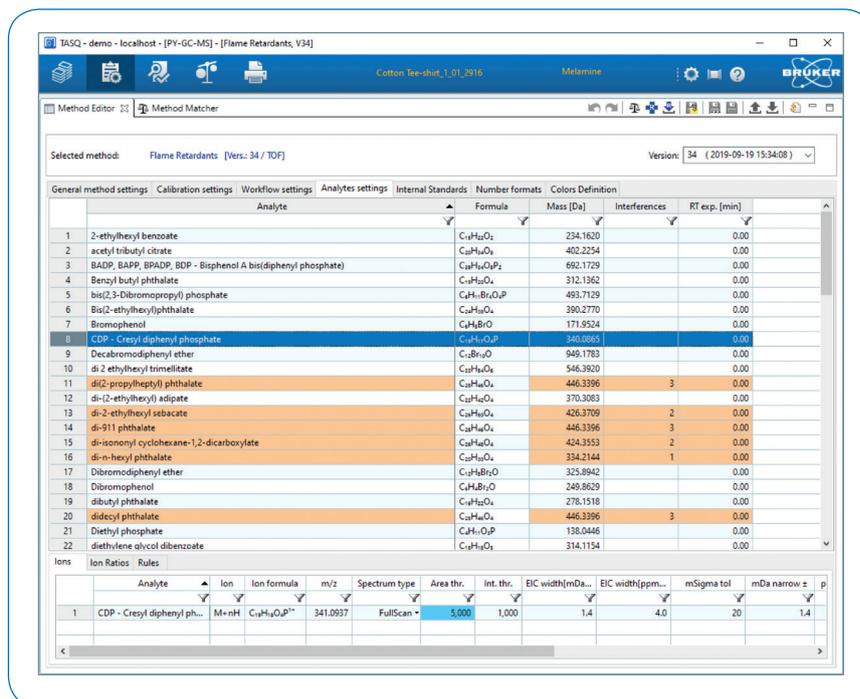


Figure 3: TASQ Method Editor View, where the list of target compounds is created. Analyte name, molecular formula, calculated molecular weight, and retention times may be added directly, imported from a .csv list, or copied from an existing method. In this study, the retention time is set to 0.00 min in order to search for target compounds across the entire pyrogram. The orange color coding within this Method Editor table indicates interfering compounds (with the same mass and overlapping retention time windows) are expected. The number of expected interferences is also shown. Within the Ions table (below the compound list), the main thresholds, including minimum area and intensity, extracted ion chromatogram (EIC) width, and maximum mSigma, are defined.

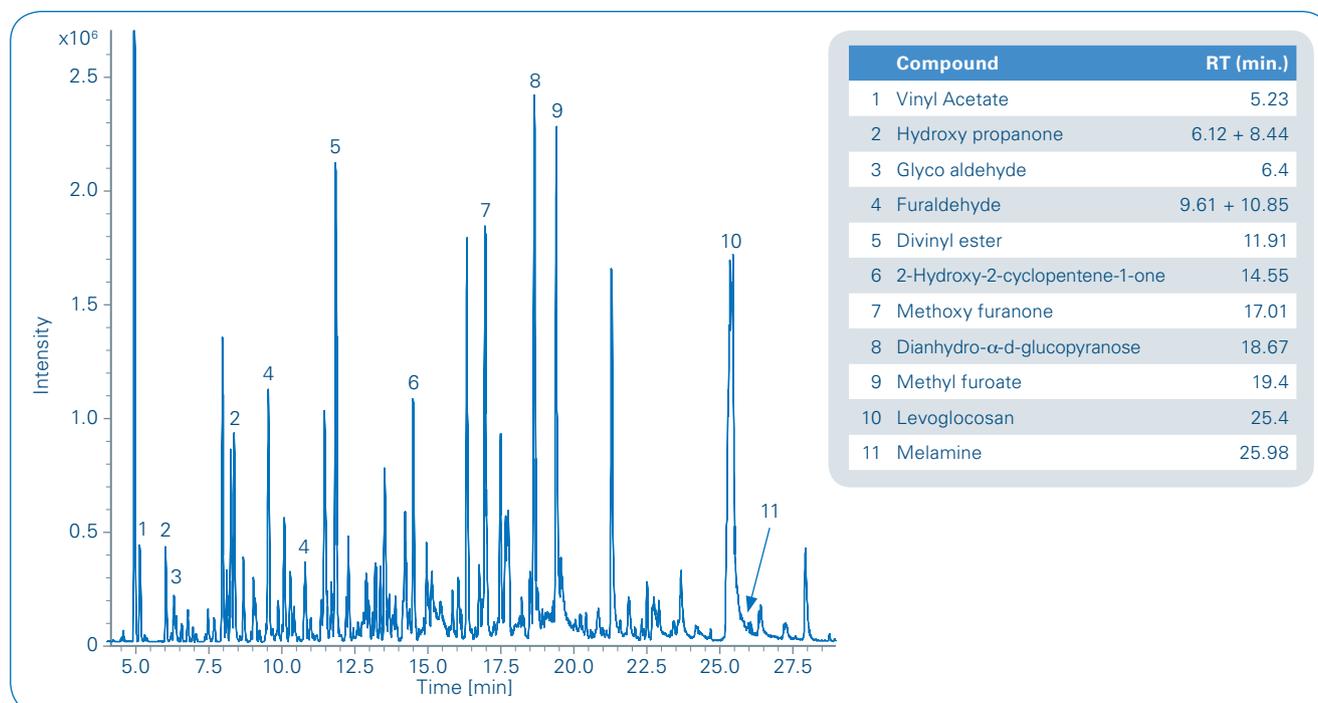


Figure 4: High resolution pyrogram of the cotton T-shirt sample. Peaks 1 through 10 were determined to be breakdown products of the cotton fibers. Elemental compositions are determined via the accurate mass and isotope distribution of each peak. Peak 11 is a small amount of the flame-retardant melamine ($C_3H_6N_6$).

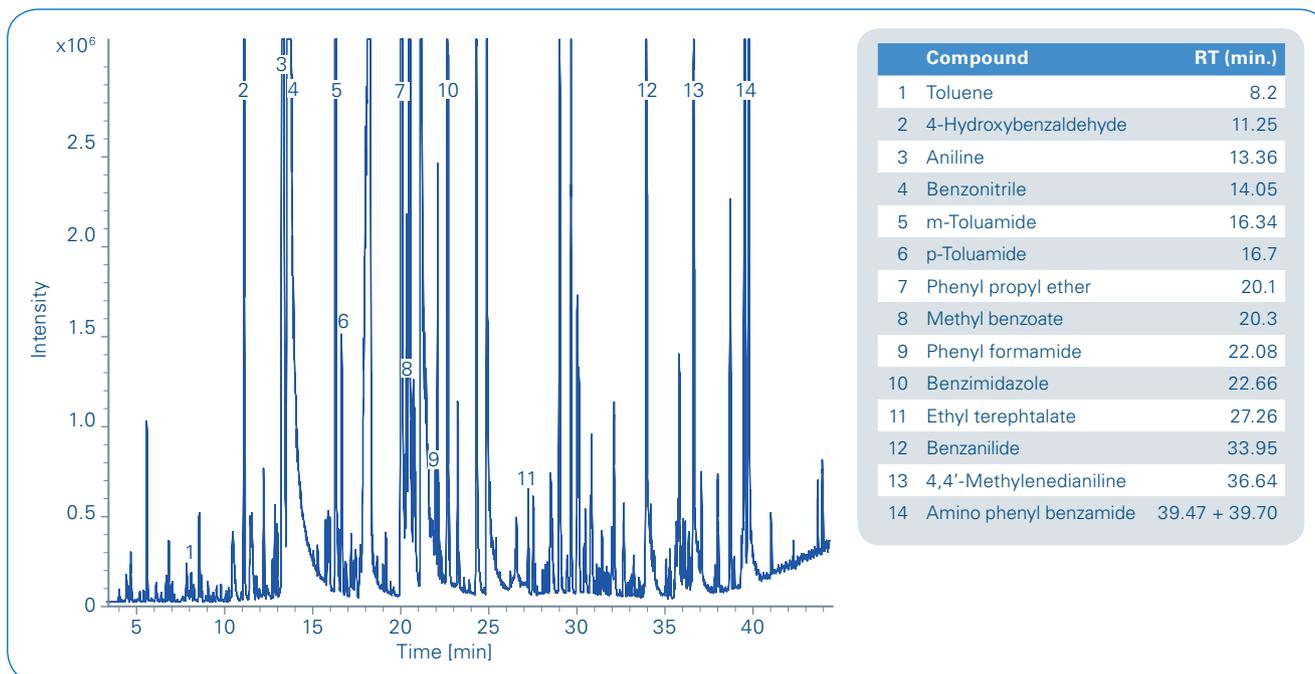


Figure 5: High resolution pyrogram of a sample of protective gear fabric made with Kevlar® and Nomex® (DuPont). Most peaks were determined to be breakdown products of these polymers. Peak 11 was determined to be ethyl terephthalate, one of the targeted plasticizers. Using TASQ software (see Figures 3 and 6), several flame retardants not visible in the pyrogram (due to their low relative abundance) were detected and identified.

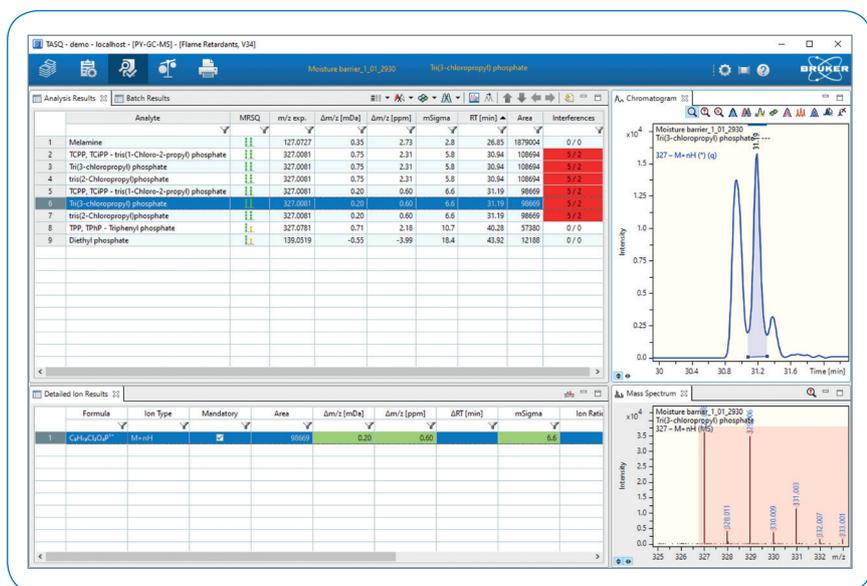


Figure 6: TASQ Screener Analysis Results View showing examples of target compounds detected in the protective gear moisture barrier fabric sample. Within the main panel, the MRSQ icon (Mass, Retention time, mSigma, Qualifier ions) indicates how well the detected compounds compare with the expected values, with green indicating good, yellow indicating a further check is recommended, and red indicating no match. The expected mass and mass error, mSigma, retention time, peak area, and number of interferences (expected and detected) are also shown. In the side panels, EIC (top) and mass spectrum (bottom) of one target compound is shown. As shown within the main table, the peaks at 30.94 and 31.19 minutes are each identified three times. The identified compounds are positional isomers. As such, their mass and isotopic distributions are the same and differentiation between them is not possible using this workflow.

Conclusion

- High resolution, accurate mass pyrograms can be generated to characterize and identify various polymeric compounds using the CDS Analytical 6000 series Pyroprobe pyrolyzer combined with Bruker's 456 GC and compact OTOF mass spectrometer with a GC-APCI interface. This analytical solution is amenable to diverse material structures and states and requires no sample preparation.
- Using Bruker's TASQ software, a customized list of known and potentially hazardous flame retardants and plasticizers was created, and these "suspects" could be rapidly sought in natural and artificial polymeric fibers.
- Together with appropriate chromatographic separation, the combination of Bruker's high-resolution OTOF mass spectrometry systems and powerful TASQ data analysis software is well suited to screen for suspect compounds in many complex sample matrices.



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