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

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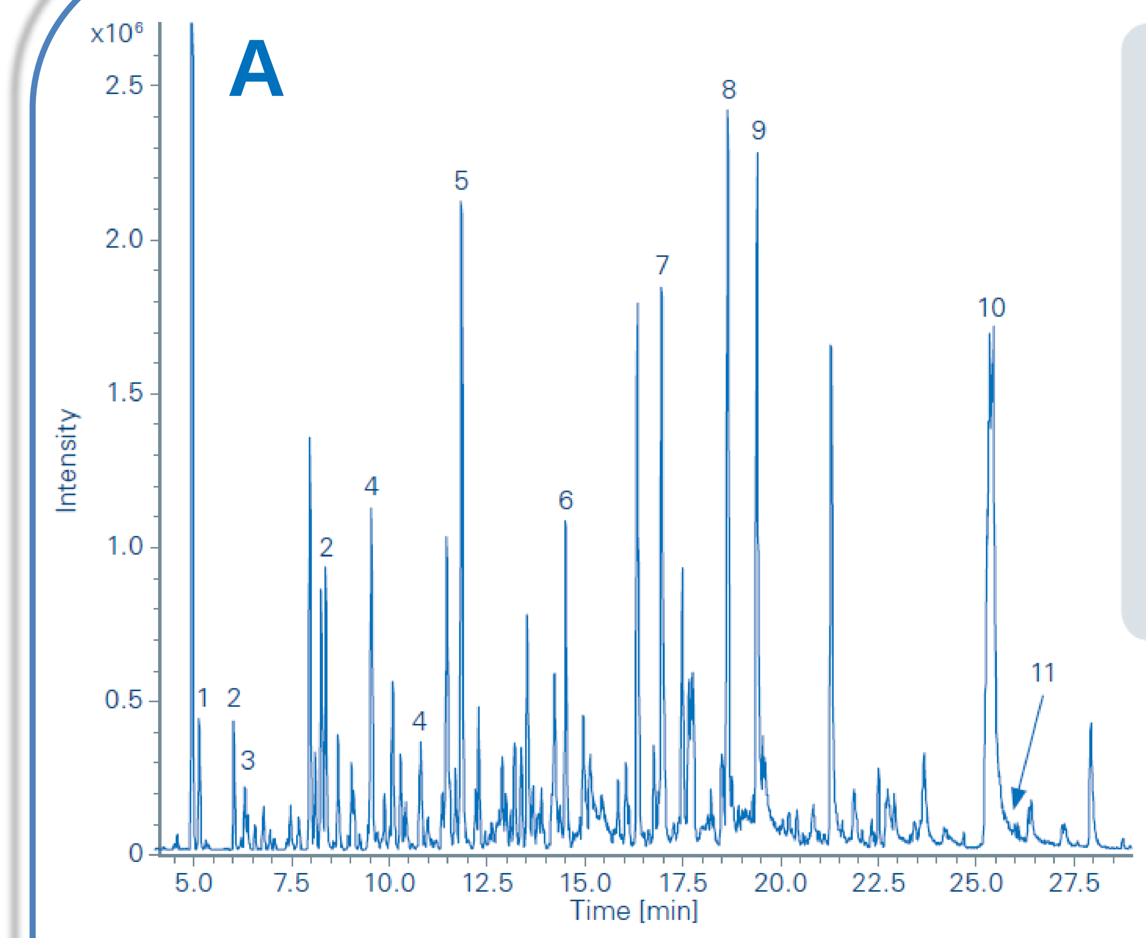
Introduction

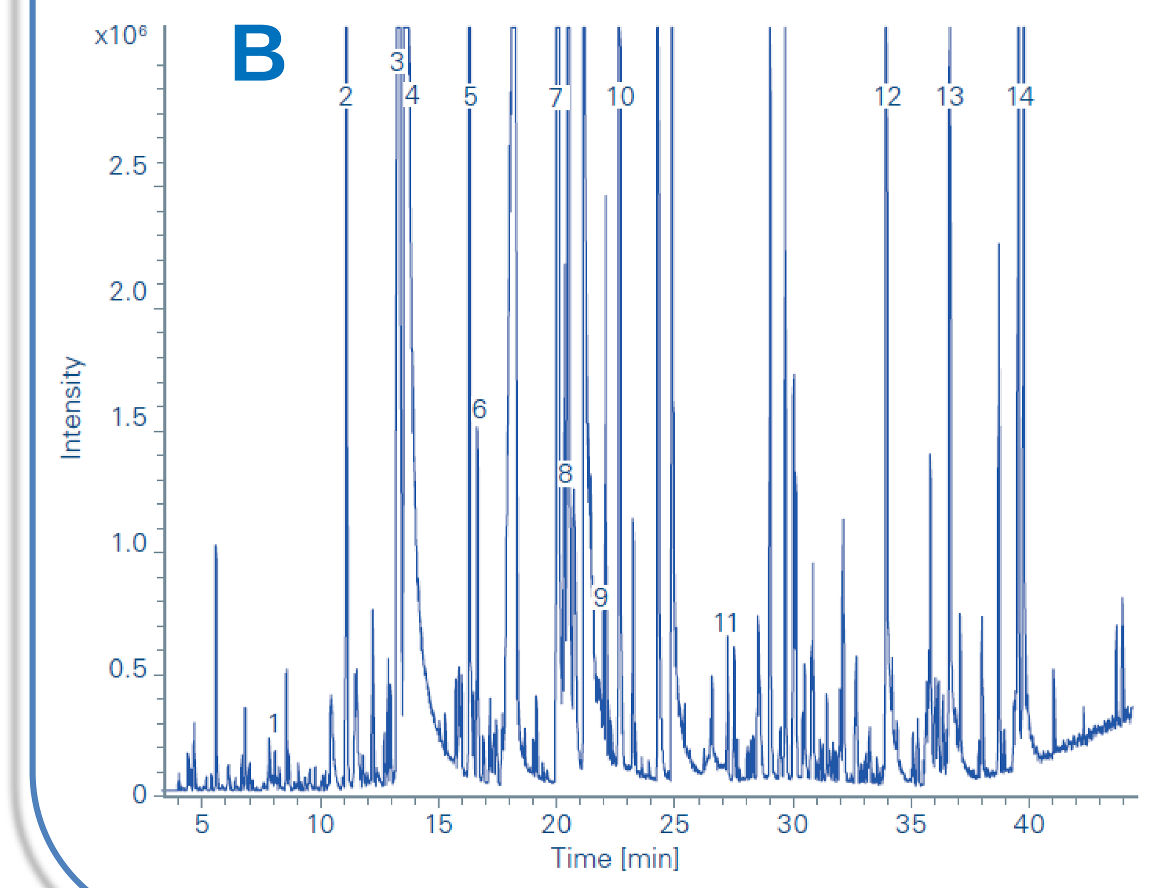
Polymeric materials are made in a wide array of forms to serve an equally wide scope of applications. To improve utility, plasticizers or flame-retardants are often added. Unfortunately, many of these compounds have been shown to be toxic. Halogenated flame retardants, for example are shown to have adverse health effects. Synthetic fabrics treated with these compounds may be in close and constant contact with the skin. Thus, it is important to be able to quickly and accurately detect the presence of such chemicals in consumer products and professional equipment.

Methods

Samples taken from five distinct types of fabric were analyzed by pyrolysis GC-APCI QTOF MS system (Fig. 3). Names and formulas of 85 commonly used flame retardants and plasticizers were obtained from a web search. A custom compound database was created to be utilized in a targeted suspect finder workflow. A very small piece of the fabric (100-200 μg) was inserted in the quartz sample tubes of the pyrolizer. After pyrolyzing at 750°C the products were directly transferred to the injector of the GC. A 50 min. temperature gradient was used to separate the compounds after which the effluent was ionized by APCI and introduced into the Bruker Compact QTOF mass spectrometer. The newly created databases were used in combination with Bruker TASQ software to automatically process the data and detect the target compounds in the data sets.



	Compound	RT (min.)
1	Vinyl Acetate	5.23
2	Hydroxy propanone	6.12 + 8.44
3	Glyco aldehyde	6.4
4	Furaldehyde	9.61 + 10.85
5	Divinyl ester	11.91
6	2-Hydroxy-2-cyclopentene-1-one	14.55
7	Methoxy furanone	17.01
8	Dianhydro-α-d-glucopyranose	18.67
9	Methyl furoate	19.4
10	Levoglocosan	25.4
11	Melamine	25.98



	Compound	RT (min.)
1	Toluene	8.2
2	4-Hydroxybenzaldehyde	11.25
3	Aniline	13.36
4	Benzonitrile	14.05
5	m-Toluamide	16.34
6	p-Toluamide	16.7
7	Phenyl propyl ether	20.1
8	Methyl benzoate	20.3
9	Phenyl formamide	22.08
10	Benzimidazole	22.66
11	Ethyl terephtalate	27.26
12	Benzanilide	33.95
13	4,4'-Methylenedianiline	36.64
14	Amino phenyl benzamide	39.47 + 39.70

Fig. 1: A - High resolution pyrogram of the cotton T-shirt sample. Peaks 1 through 10 were determined to be breakdown products of the cotton fibers. Peak 11 is a small amount of the flame-retardant Melamine ($C_3H_6N_6$). **B** - 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 a plasticizer Ethyl Terephthalate.

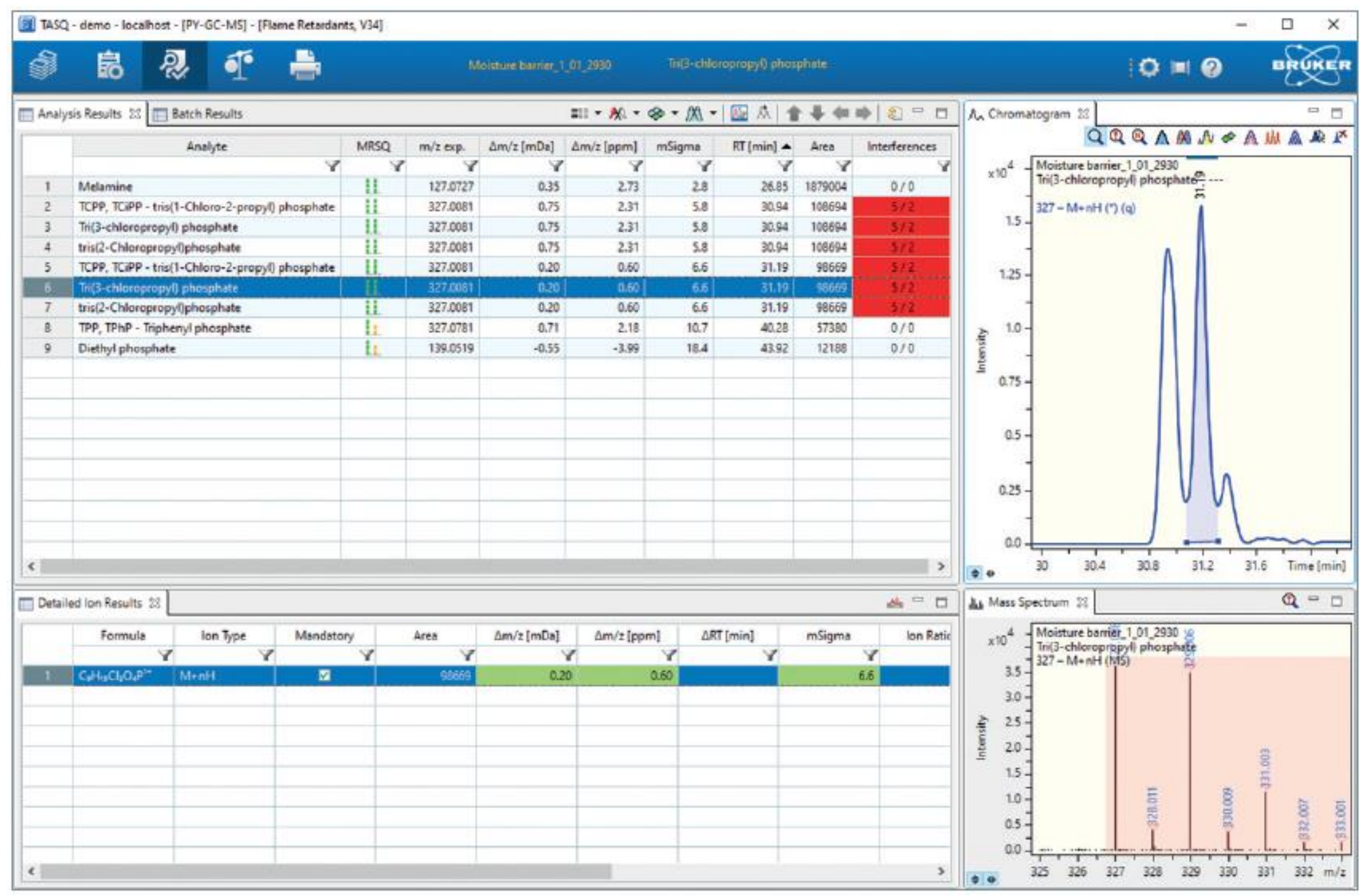


Fig. 2: Bruker TASQ software analysis review screen showing examples of target compounds detected in the protective gear moisture barrier fabric sample.

Fig. 3: 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.

Results

Using the high resolution QTOF MS system, all components eluting from the GC are detected with both mass accuracy (<2 ppm) and isotopic distribution (<2% error). High resolution and accurate mass measurement can be critical for confident and reliable detection of target analytes. As the pyrograms of synthetic materials are often complex, a powerful algorithms are needed to process the data and identify the compounds of interest. Using Bruker TASQ software (Fig. 2), the targeted plasticizers and flame retardants were detected in two of the five fabrics tested (Fig. 1A and Fig. 1B). A total of five targets could be detected using TASQ Suspect Finder workflow, most of which could not be visually noticed in the pyrograms. The Suspect Finder workflow does not require a target analyte standard or prior knowledge of its elution time, but only the molecular formula. Relying on the comparison of calculated and measured accurate masses and isotopic distribution patterns, this workflow proved capable of reliable detection of target analytes without extensive method development. This approach provides a significant advantage over the conventional nominal mass GC-MS methods, when standards of target compounds are unavailable.

Conclusions

- The combination of Bruker high-resolution QTOF mass spectrometry system with pyrolysis GC-APCI and TASQ Suspect Finder workflow provides a reliable solution for screening for flame retardants, plasticizers, and other additives in synthetic materials, even when standards of these target analytes are unavailable.

Synthetics Materials