

Component Identification of Mineral Oil Hydrocarbons and Additives in Cardboard Packaging using GCxGC–HRTOF–MS with EI and PI

Introduction

Migration of mineral oil from packaging into food has become a health concern, especially since mineral oil affects the liver and lymph nodes. There are two types of mineral oil: mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH). Both types are generally measured using online coupled liquid chromatography–gas chromatography–flame ionization detection (LC/GC/FID) only to separate and detect target fractions, and it may miss other important, unexpected compounds.

By contrast, two-dimensional gas chromatography–high-resolution time-of-flight mass spectrometry (GCxGC–HRTOF–MS) is a comprehensive technique for analyzing complex samples. Using EI with this method allows for NIST database searches. Moreover, using a combination of high-resolution molecular-ion information generated via soft-ionization techniques with an EI NIST database search can result in more-reliable assignments. In this study, we used GCxGC–HRTOFMS with EI and photoionization (PI) soft-ionization techniques to identify compounds in cardboard.

Experiment

Sample preparation methods are shown in Figure 1. We sampled 1 g of the inside surface of the cardboard packaging for a commercial pancake batter mix into a vial, added 10 mL hexane and ethanol (1:1 volume ratio), and soaked it overnight. Then we collected the solvent into another vial and added 0.5 mL water. Next, we collected the top supernatant and added Na₂SO₄. After 1 hour, we collected the final supernatant and measured it via GCxGC–HRTOF–MS. Measurement conditions are shown in Table 1.

Figure 1. Sample preparation methods.

Inside surface of cardboard packaging (1g)
for a commercial pancake batter mix

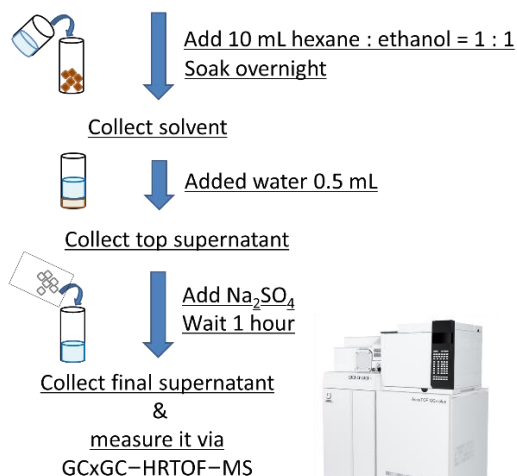
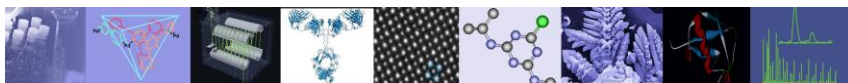


Table 1. Measurement conditions.

Condition	GCxGC/EI	GCxGC/PI
GCxGC system	Blank tube 1 m x 0.25 mm + Rxi-5Sil MS (Restek, Cat# 13623), 30 m x 0.25 mm, 0.25 μm	
1st column	Blank tube 1 m x 0.15 mm + Rxi-17Sil MS(Restek, Cat# 43820), 1.5 m x 0.15 mm, 0.15 μm	
2nd column	+ Blank 1 m x 0.15 mm	
Modulator period	7 sec	
He flow	1.2 mL/min (Constant flow)	
Inlet (mode)	COC (Track Oven)	
Oven temp.	70° C (1 min) -> 10° C/min -> 350° C (20 min)	
Hot jet	170° C (1 min) -> 10° C/min -> 400° C (25 min)	
Injection volume	EI: 2 μL / PI: 2 μL	
GC-TOFMS system	EI/PI combination ion source	
Ion source	EI/PI combination ion source	
Ionization mode	EI+	PI+
Ionization condition	Ionization voltage: 70 V Ionization current: 300 μA	D ₂ lamp
Ion source temp.	250° C	
GC-ITF temp.	320° C	
m/z range	m/z 10–800	
Acquisition time	40 msec (25 Hz)	
Sampling time	0.25 nsec (4 GHz)	



Results

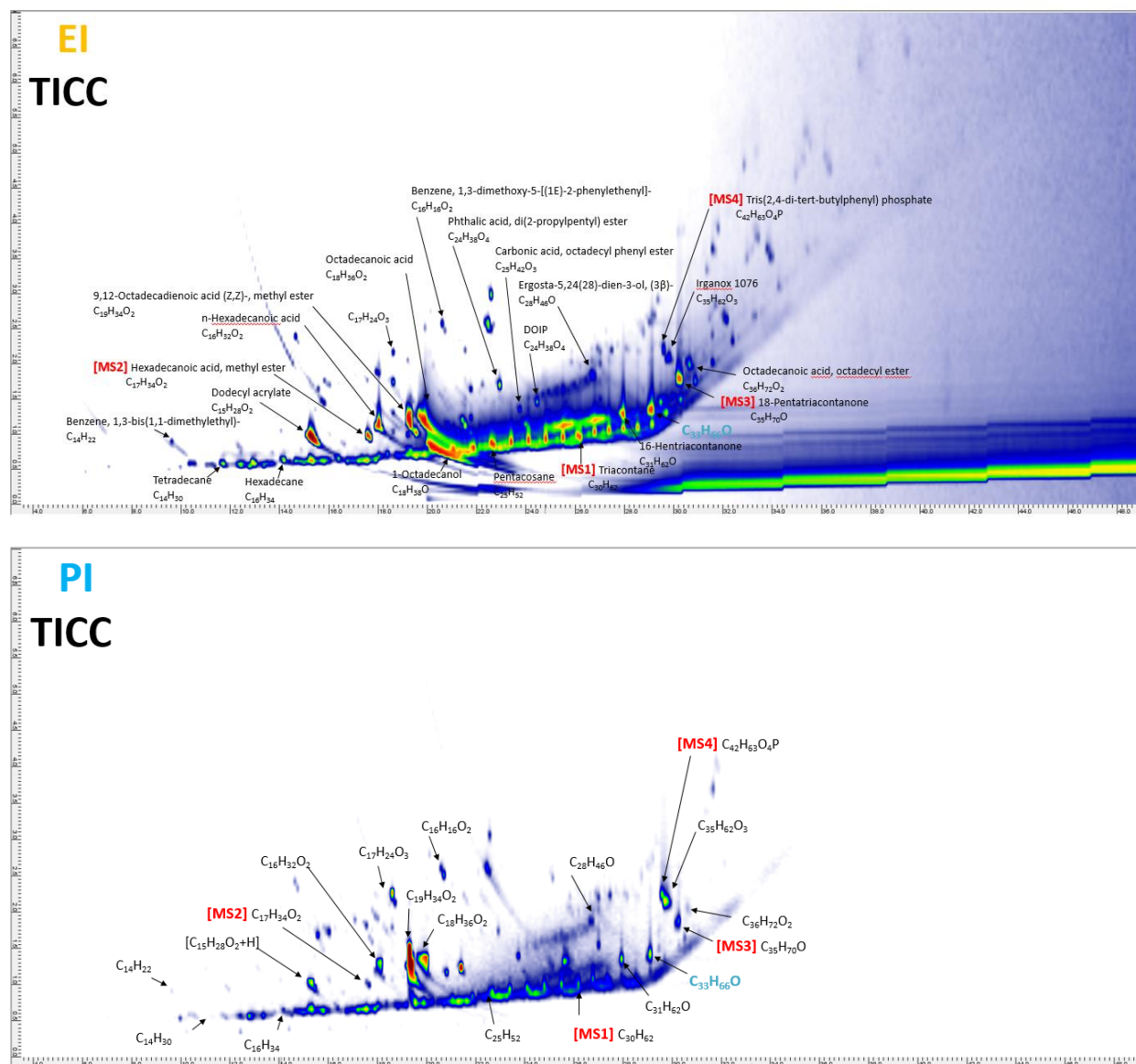


Figure 2. TICC 2D maps for EI and PI.

Total ion current chromatogram two-dimensional maps (TICC 2D maps) for EI and PI are shown in Figure 2. Both maps show near-identical retention time patterns. We obtained assigned compound results using a NIST library search of EI data and the estimated elemental composition of chemical formulas from PI data. We detected MOSHs C13–C40 using EI, and PI confirmed molecular ions in MOSHs C13–C35. Aromatic compounds, fatty acids, fatty-acid esters, fatty alcohols, sterols, ketones, phthalic acid esters, Irganox 1076 and tris(2,4-di-tert-butylphenyl) phosphate were also detected. The phthalic-acid esters, Irganox 1076 and tris(2,4-di-tert-butylphenyl) phosphate, are known as antioxidants/plasticizers in polymers.

Both EI and PI mass spectra of representative compounds that are marked [MS1]–[MS4] in Figure 2 are shown in Figure 3 as well.

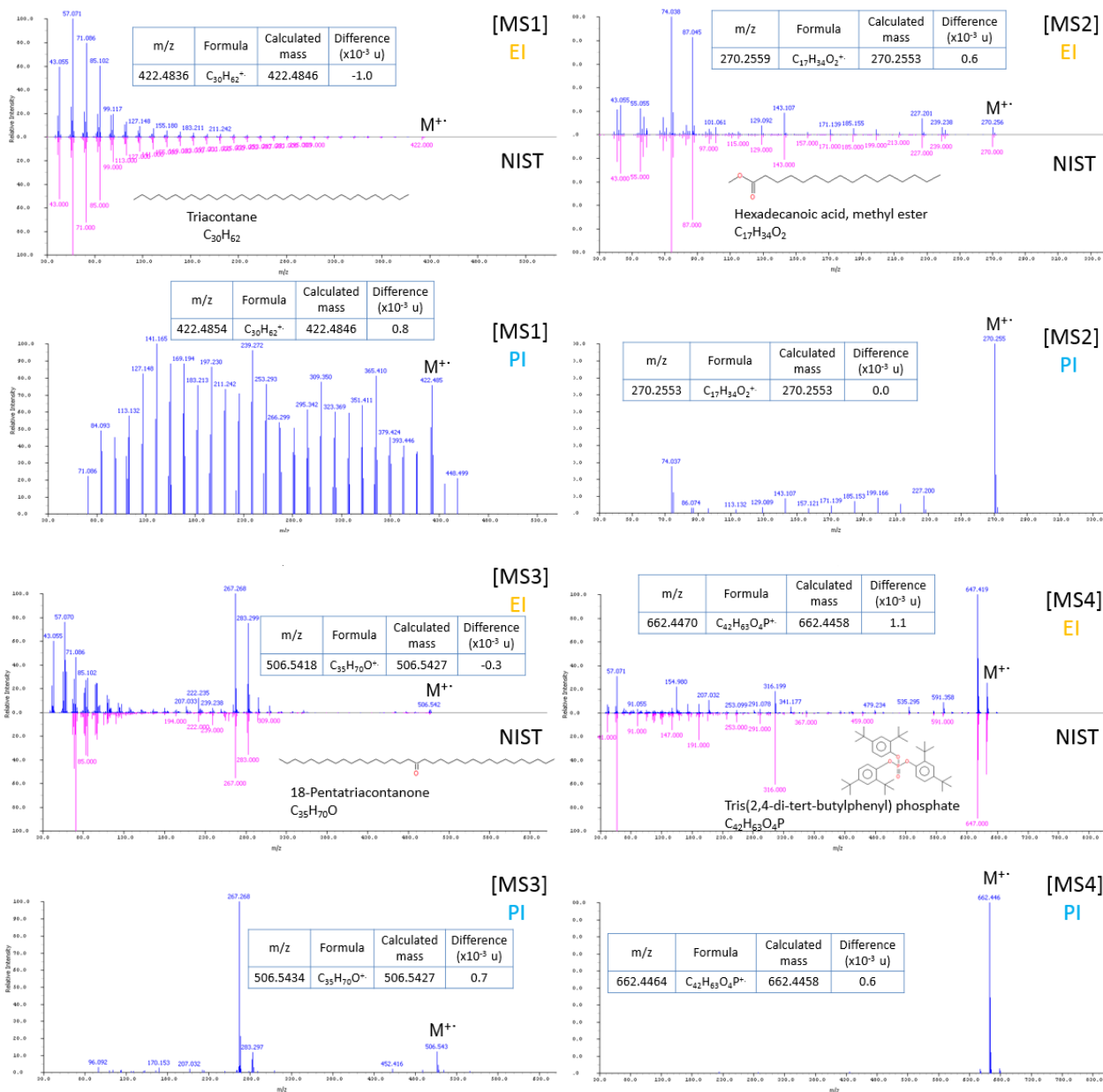
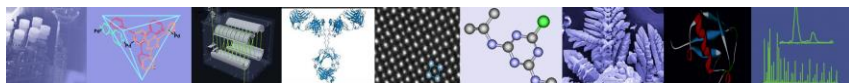
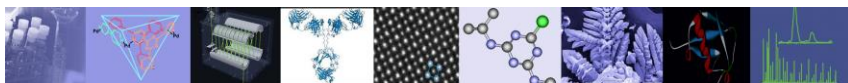


Figure 3. EI and PI mass spectra of representative compounds.

In most cases, the PI data show stronger molecular-ion signals than the EI data, as shown by the mass spectra. However, for the phthalic-acid esters the PI data show mainly fragment ions; no molecular ions were detected. If multiple compounds show an EI database match factor greater than 800, or the EI library search results do not show a high match factor, then it is very helpful to estimate the molecular-ion chemical formula to narrow down the possibilities.

For example, the library search results for the peak detected at RT = 29.050 min, 1.320 sec does not show a high match factor. However, the PI mass spectrum shows a molecular ion that supports C₃₃H₆₆O as the elemental composition. The EI mass spectrum shows fragment ions similar to 18-Pentatriacontanone [MS3], suggesting that this compound is likely 17-tritriacontanone (C₃₃H₆₆O).



Conclusion

The resulting 2D chromatograms for EI and PI show the same retention time patterns. In addition to mineral oil, tris(2,4-di-tert-butylphenyl)phosphite, tris(2,4-di-tert-butylphenyl)phosphate and 16-hentriacontanone, which are polymer additives, were detected in the cardboard. These compounds could also contaminate food by migrating from the packaging materials, just like mineral oils. Furthermore, the first-dimension RT of these compounds overlapped with MOSH, but the second dimension was able to provide separation. Additionally, 16-hentriacontanone had a small molecular-ion intensity in EI, so we used PI to determine the molecular-ion peak necessary for identification.

In summary:

- ✓ The combination of EI fragmentation information with the exact mass molecular-ion information from PI provided a way to narrow down the NIST library search to help identify the compounds measured.
- ✓ The EI/PI combination ion source easily switched the ionization technique by simply turning the EI filament on and off in the software.
- ✓ Using GCxGC–HRTOF–MS with both EI and PI is a powerful tool for qualitative analysis of non-targeted analytes.

11 Dearborn Road, Peabody, MA 01960
Tel: (978) 535-5900 • Fax: (978) 536-2205
ms@jeol.com • www.jeolusa.com