

Using GCxGC/HRTOFMS with EI/FI/PI for component identification and time variation analysis of perfume

Introduction

Perfumes are known to be complex mixtures that typically contain a variety of compounds. Their scents are strongly affected by these compounds and their quantity ratios. Additionally, these ratios can change over time, thus changing the perfume's scent.

Two-dimensional gas chromatography/time-of-flight mass spectrometry (GCxGC-TOFMS) is an effective technique for measuring complex samples like perfumes. Using electron ionization (EI) allows for database searches. However, these searches may result in mis-assignments without the additional high-resolution molecular ion information that can be generated through soft ionization techniques.

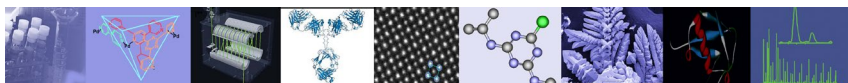
In this study, we used GCxGC-HRTOFMS with EI and the soft ionization techniques of FI (Field Ionization) and PI (Photoionization). Additionally, we measured the changes in intensity over time for the top note/middle note/base note compounds.

Experiment

A pure perfume oil was qualitatively analyzed by using GCxGC-HRTOFMS EI, FI and PI. For the time studies, 0.1 μL of pure oil for the same perfume was placed in a 22mL vial and heated at 35°C for 0 hour, 0.5 hour, 1 hour and 3 hours. Afterwards, the headspace was sampled by using a SPME fiber (50/30 μm DVB/CAR/PDMS, Stableflex) and then measured by using GCxGC-HRTOFMS FI.

Table 1. GCxGC and HRTOFMS Conditions

Condition	EI	FI	PI
-Instruments-	JMS-T200GC "AccuTOF GCx-plus" (JEOL Ltd.) ZX-2 (GCxGC module : ZOEX Corporation)		
-GCxGC conditions-			
Inlet mode	Liquid Injection ; Split 100:1 (280°C), SPME Injection ; Split 30:1 (250°C)		
1st column	Blank tube 4m x 0.25mm + BPX5, 30m x 0.25mm, 0.25 μm		
2nd column	Blank tube 1.5m x 0.1 mm + BPX50, 2m x 0.1mm, 0.1 μm + Blank 1m x 0.1mm		
Oven temp. program	40 °C (1 min) -> 5 °C/min -> 300 °C (5min), Total: 58 min		
Hot jet temp. program	190 °C (1 min) -> 5 °C/min -> 400 °C (15min)		
He carrier gas flow	1.4 mL/min (Constant flow)		
Modulator period	4 sec		
-Injection conditions-			
Liquid Injection	Injection volume ; 0.1 μL (0.5 μL syringe)		
SPME Injection	50/30 μm DVB/CAR/PDMS, Stableflex (2cm)		
SPME sample volume	0.5 μL in 22mL vial @35°C (20min)		
-MS conditions-			
Ion source	EI ion source	EI/FI/FD combination ion source	EI/PI combination ion source
Ionization mode	EI+	FI+	PI+
Ionization condition	Ionization voltage: 70 V Ionization current: 300 μA	Cathode voltage: -10 kV Emitter flashing: 40 mA, 8 msec (Wait time for flashing: 15 msec)	D ₂ lamp
Ion source temp.	250 °C	OFF	250 °C
GC interface temp.	280 °C		
Acquisition time	40 msec (25 Hz)		
Sampling time	0.25 nsec (4 GHz)		
m/z range	m/z 35-800		



Results

All terpenes were detected with good chromatographic separation. The 2D map for FI and PI showed near-identical retention time patterns as those observed in the EI 2D map. In most cases, the FI and PI data showed stronger molecular ion signals than the EI data. However, for the PI measurement, the Musk Ketone (R.T. = 42.950, 2.802) peak was not detected due to the fact that its ionization energy is higher than the irradiating photon energy generated from the deuterium lamp.

The peak detected at R.T. = 37.684, 2.719 (MS1 in the 2D map) showed an EI mass spectrum that matched well with the NIST library mass spectrum for methyl β -orcinolcarboxylate. Additionally, the EI, PI and FI accurate mass measurements showed the chemical formula determined for the molecular ion to be $C_{10}H_{12}O_4^+$, which further supports the NIST match.

On the other hand, the peak detected at R.T. = 39.417, 2.008 (MS2 in the 2D map) showed relatively high fragment ion intensities for the EI measurements. The NIST search for this mass spectrum showed several compounds with a match factor higher than 800 with different chemical compositions. To narrow down the possibilities, it was necessary to confirm the molecular ion using FI and PI. The results for these techniques showed an exact mass m/z value within 1.5 mDa of the calculated exact mass for $C_{16}H_{28}O$. This elemental composition narrowed down the EI library search candidates to Ambrox.

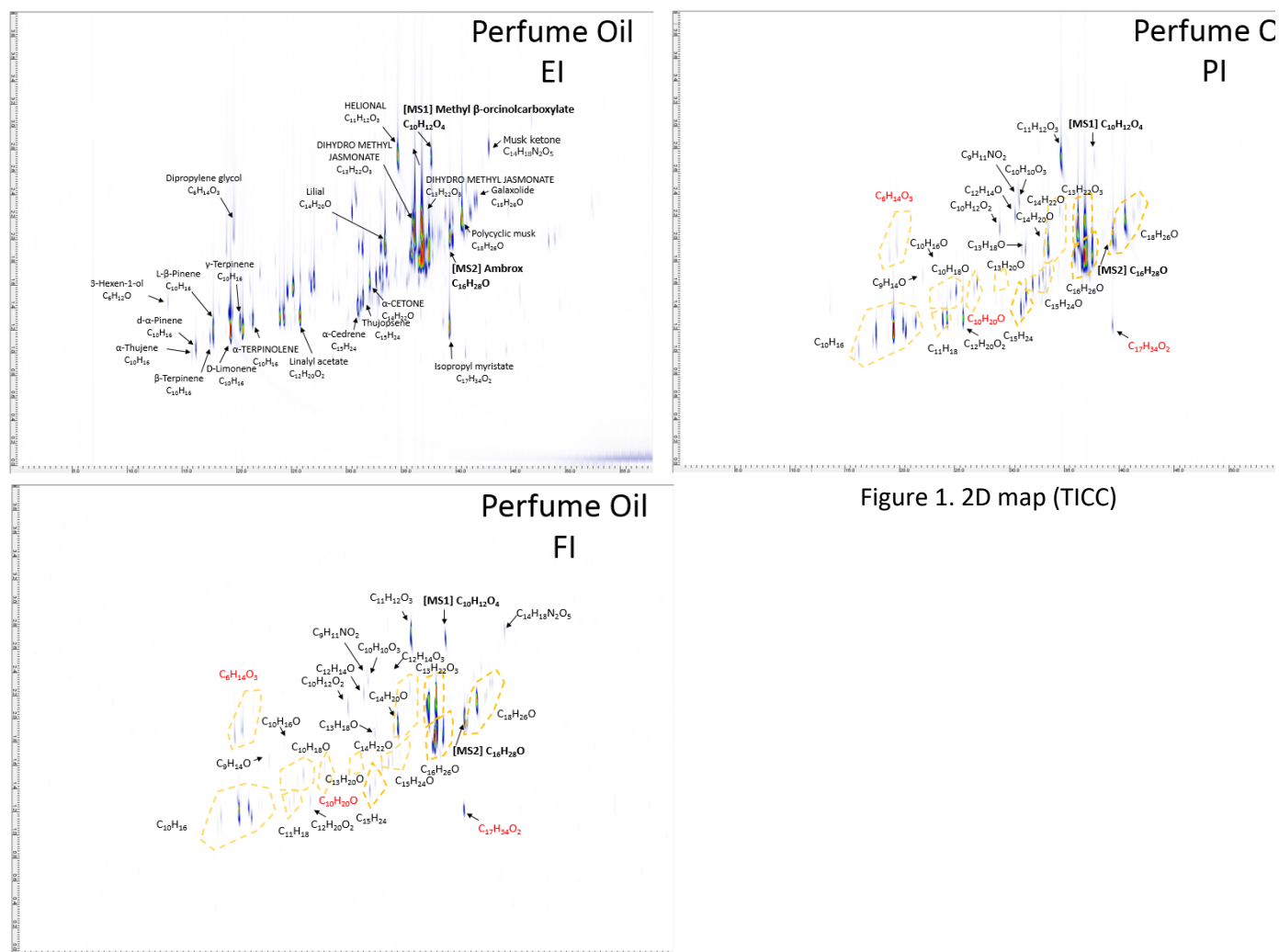


Figure 1. 2D map (TICC)

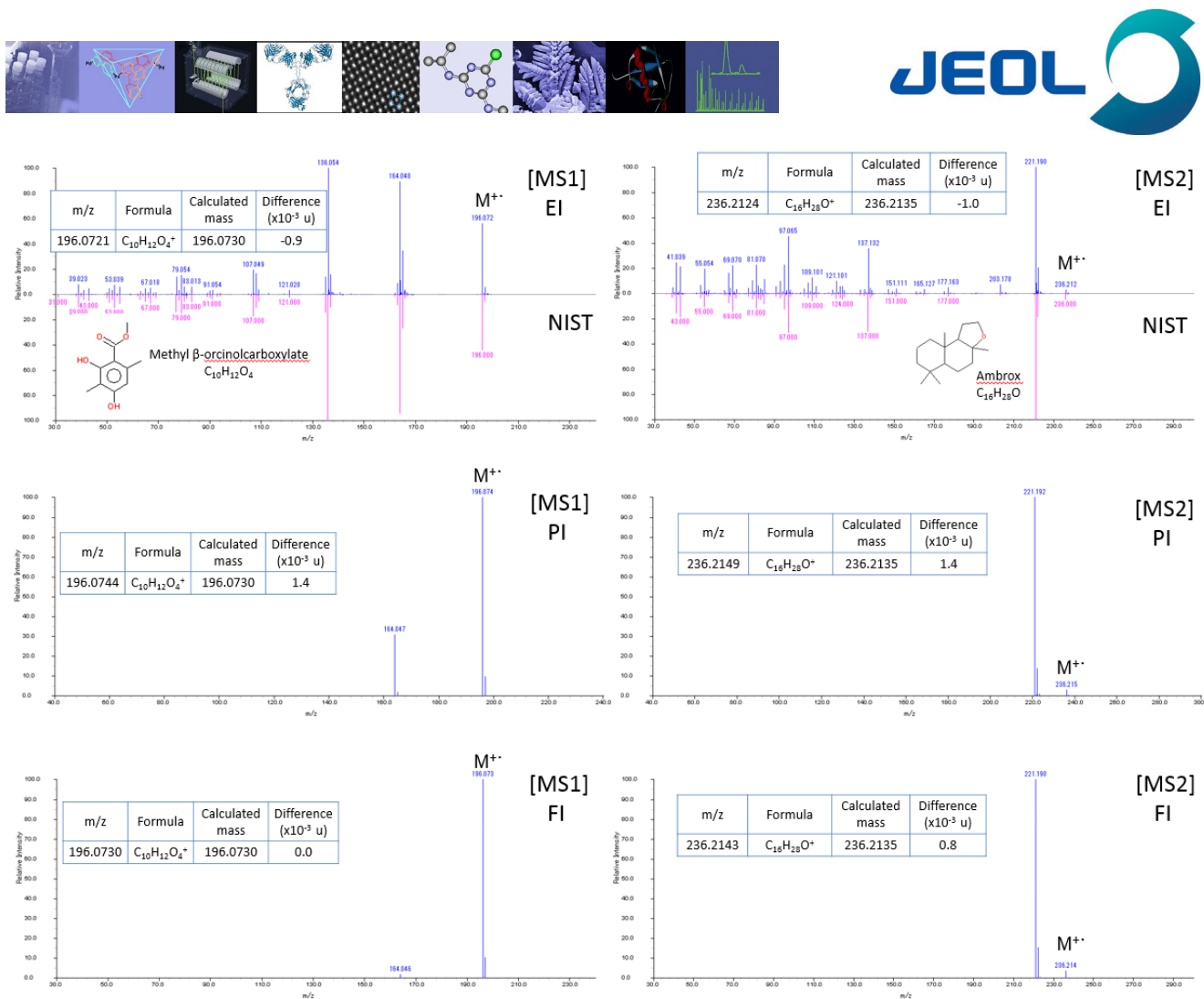
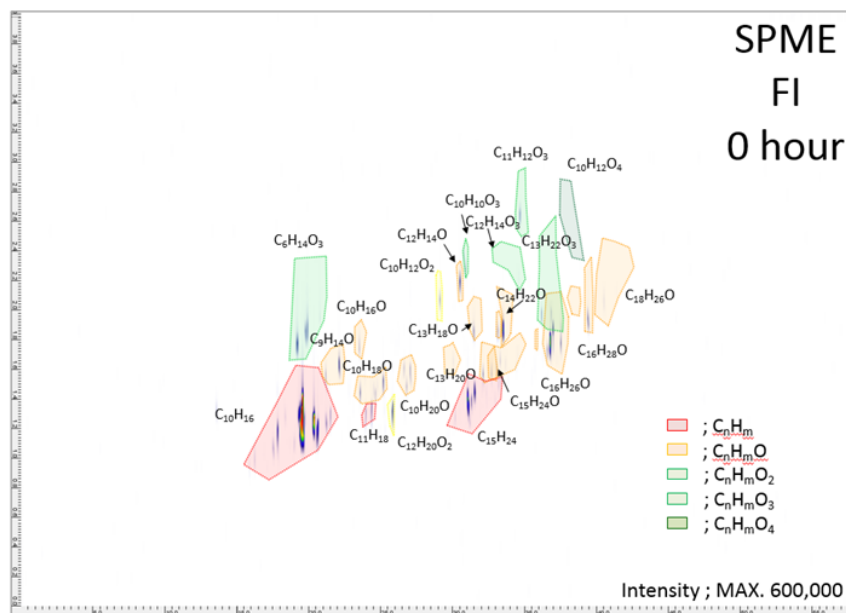


Figure 2. Mass spectra



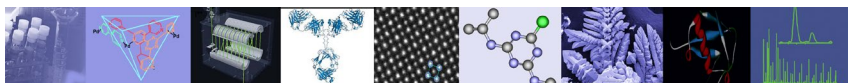
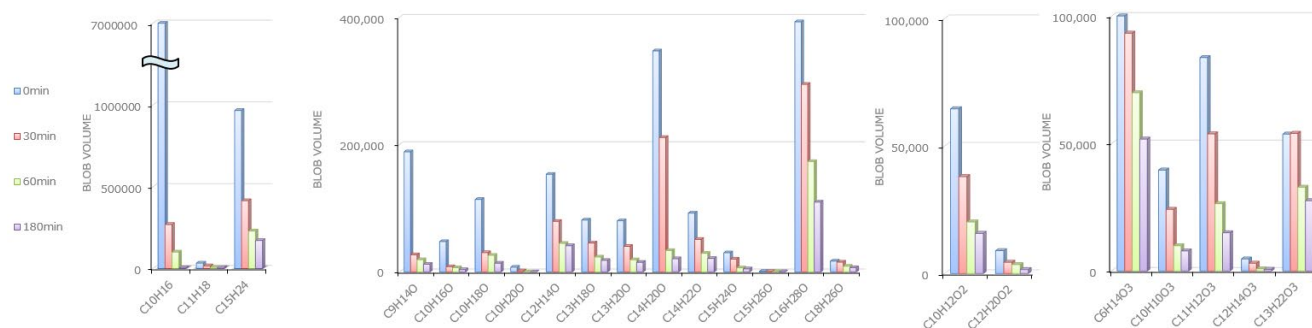


Table 2. Perfume Time Variation Study



The SPME-FI perfume time variation study results showed that the perfume components tended to have a large blob-volume change for smaller molecular-weight components over time. Additionally, the blob-volume change over time showed the trend: $C_nH_m > C_nH_mO > C_nH_mO_2 > C_nH_mO_3$.

Conclusion

The combination of EI fragmentation information with the exact-mass molecular ion information from FI and PI provided a means for narrowing down the NIST library search to help identify the compounds measured.

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