Applications Note

AccuTOF-GCv Series

SPME-GCxGC/HRTOFMS Analysis of Tequila

Introduction

The JEOL "AccuTOF GCv 4G" is a third generation GC/HRTOFMS system with high speed data acquisition capabilities of up to 50Hz which makes it well suited as the detector for comprehensive 2-dimensional GC (GCxGC) measurements. Along with the high speed data acquisition, this MS system also provides high mass resolution, accurate mass measurements, and high sensitivity, all simultaneously. Consequently, this GCxGC/HRTOFMS system is a powerful tool for the qualitative analysis of complicated samples.

In this work, we measured commercially available tequila samples using GCxGC/HRTOFMS combined with solid-phase micro-extraction (SPME) preparation.

Fig. 1. GCxGC/HRTOFMS system.

Experimental

Sample information and measurement conditions are shown in Figure 2 and Table 1.

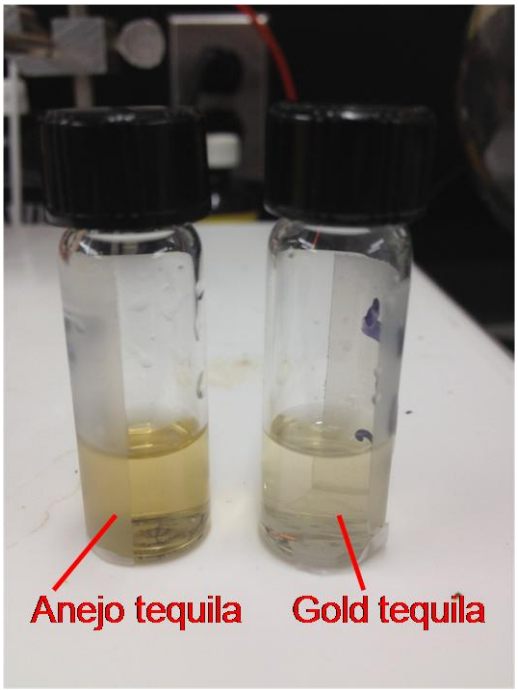

Fig. 2. Tequila samples.

Condition	SPME-GCxGC-EI
Sample	1. Anejo tequila 2. Gold tequila
SPME	50/30 um DVB/CAR/PDMS (SUPELCO)
SPME condition	10 min at room temparature
GCxGC system	ZX2 thermal modulator (ZOEX)
1st column	Rxi-5SilMS, 30 m x 0.25 mm, 0.25 um
2nd column	Rxi-17SilMS, 2 m x 0.15 mm, 0.15 um
Modulator loop	Deactivated fused silica, 1.5 m x 0.15 mm
Modulator period	10 sec
Modulator duration	400 msec
Inlet pressure	200 kPa
Inlet mode	Split 10:1
Oven temp.	50 C (1 min) -> 3 C/min -> 250 C
GC-TOFMS system	AccuTOF GCv 4G (JEOL)
Ionization mode	EI+
Ionization condition	Ionization voltage: 70 V Ionization current: 300 uA
Ion source temp.	250 C
GC-ITF temp.	280 C
m/z range	*m/z* 35-500
Acquisition time	20 msec (50 Hz)
Sampling time	0.25 nsec (4 GHz)
External calibrant	*m/z* 207.0329 (column background)

Table 1. Measurement condition.

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We analyzed two tequila samples (Figure 2), anejo and gold tequila. The anejo tequila is an aged tequila that is more expensive than the typical gold tequila. The SPME sample preparation step consisted of immersing the SPME fiber in the pure tequila for 10 minutes at room temperature. Afterwards, the SPME sample was measured using GCxGC/EI method (Table 1).

Results

The 2-dimensional total ion chromatograms (2D TICs) for each tequila sample are shown in Figures 3 and 4, respectively. Both TICs showed the presence of a wide variety of components in the sample.

The red circles in each 2D TIC, referred to as "Blobs," show the detected chemical components and include

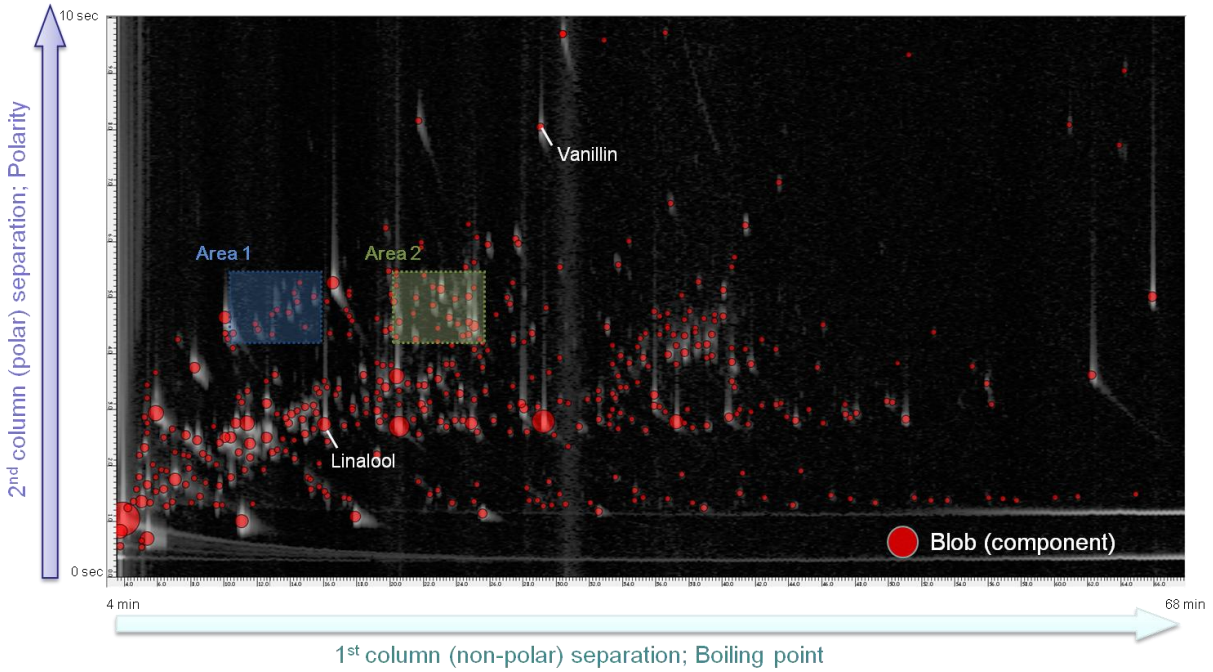

Fig. 3. GCxGC/EI TIC chromatogram of an anejo tequila.

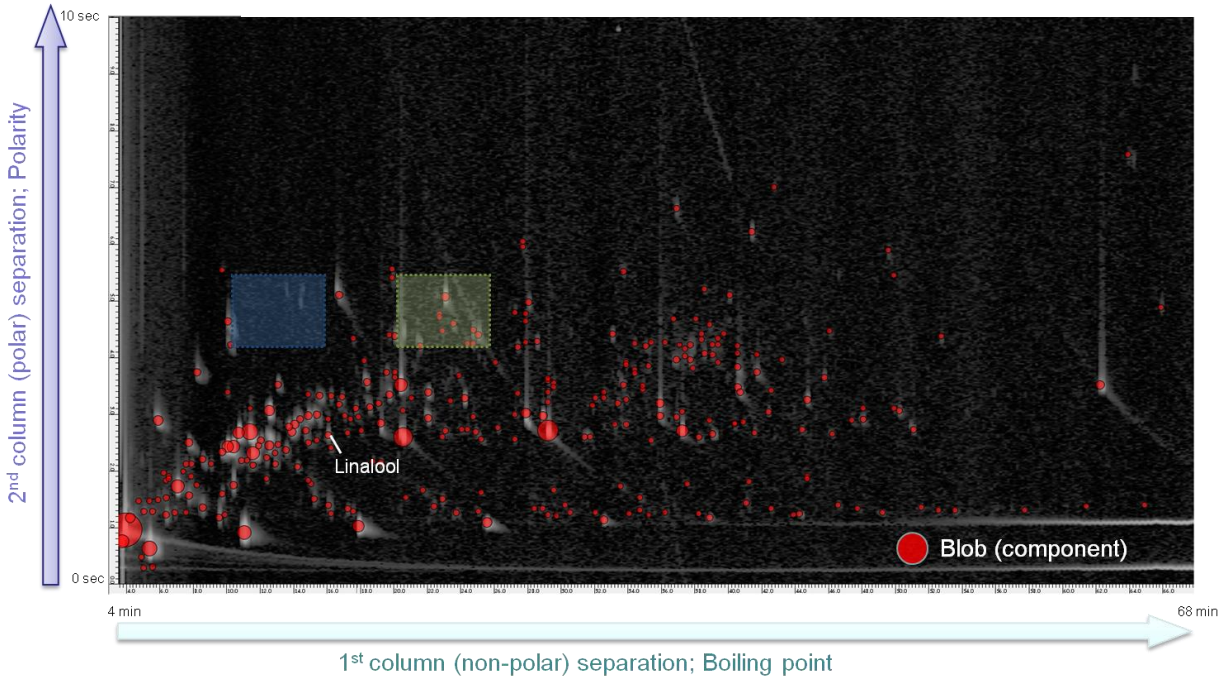

Fig. 4. GCxGC/EI TIC chromatogram of a gold tequila.

the EI mass spectrum for each component. The "Blob" size reflects the sum of the ion peak intensities for each chemical component.

As expected, the anejo tequila showed a more complex 2D TIC (i.e. more chemical components) than in the gold tequila 2D TIC image, which was the result of the longer anejo aging process. As an example of this, Area 1 (Blue region) and Area 2 (Green region) are highlighted in Figures 3 and 4.

Next, a NIST library search for all of the detected blobs was carried out for each sample. The NIST library search results are shown in Table 2. The anejo tequila had 409 chemicals detected in the 2D TIC with 236 of them (57.7%) identified with match factors of over 700, which is typically sufficient for reliable chemical identification. As for the gold tequila, 291 chemicals were detected with 141 of them (48.5%) identified with match factors of over 700.

In most cases, it is sufficient to use the NIST search results for identifying the compounds in the GCxGC TIC image. This step is easy to do as all blobs over the whole TIC image or for specific regions can be selected at once, and then a NIST library search can be carried out to find the best spectral matches. Afterwards, the GC Image software can then be used to automatically label each blob with the best match from the database search. Figure 5 shows the chemical identifications for a number of the blobs in the narrow Areas 1 and 2 TIC regions based on the NIST library search result.

	Component number	
NIST Library Match Factor	Anejo tequila	Gold tequila
Over 900	31	23
900-800	101	57
800-700	104	61
700-600	85	60
600-500	63	66
500-400	18	21
400-300	7	3
SUM	409	291

Table 2. NIST search library result.

Figure 6 shows a measured EI mass spectrum that was very similar to the NIST data for linalool, which showed a match factor of 922. Linalool is a naturally occurring monoterpene alcohol that is found in many plants. This compound is widely used as a flavoring agent for many kinds of foods. The molecular ion for linalool was not observed in the EI mass spectrum. However, the fragment ion resulting from the dehydration of the molecular ion ($[M-H_2O]^+$) was observed and showed a mass accuracy of 1.57 mDa compared to the calculated value for $C_{10}H_{16}$ while using an external one-point drift compensation for the mass calibration. Figure 5 shows a measured EI mass spectrum that was very similar to the NIST data for vanillan, which showed a match factor of 905.

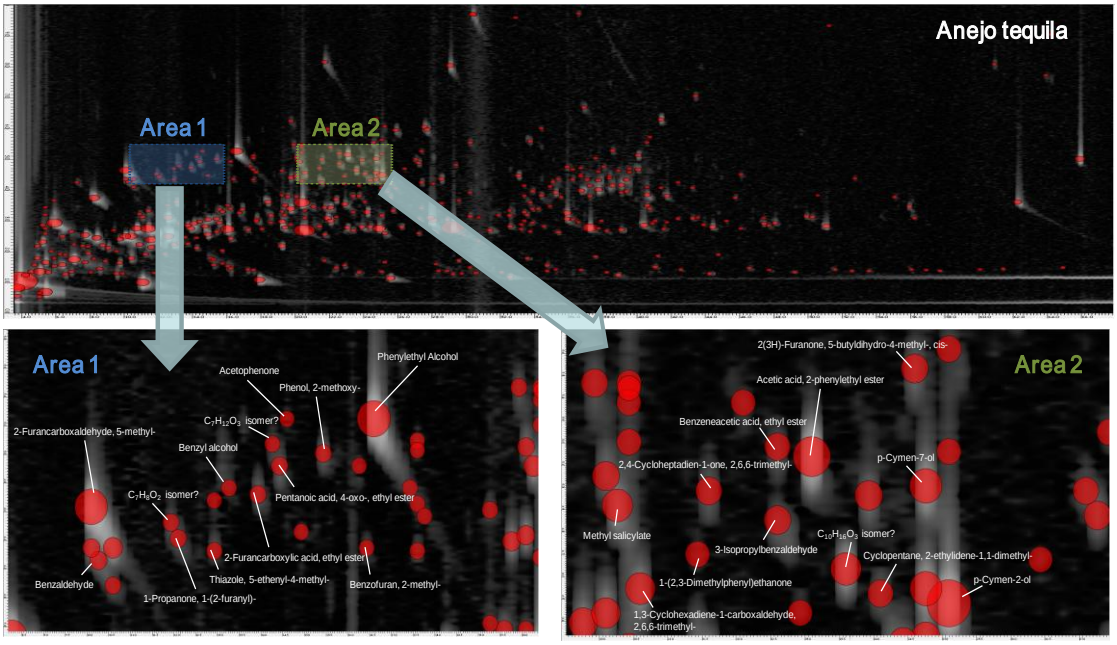

Fig. 5. Example of chemical identifications result.

Additionally, the molecular ion showed a mass accuracy of 0.88 mDa for the elemental composition of $C_8H_8O_3$. Vanillin is a phenolic aldehyde that was only detected in the anejo tequila (Figure 3). These results clearly show that even for 50Hz GCxGC measurement data, we can obtain normal EI mass spectral patterns that are directly comparable to NIST database mass spectra and high mass accuracy information to help further confirm the identity of unknown compounds through elemental composition calculations.

Conclusion

The AccuTOF GCv 4G allows 50Hz GCxGC measurements with high sensitivity, high mass resolution and high mass accuracy, all simultaneously. Additionally, we can do NIST library searches using GCxGC data in exactly the same way as for regular 1D GC/MS. The AccuTOF GCv 4G coupled with the 2D GC technique is an extremely useful tool for the qualitative analysis of complicated samples.

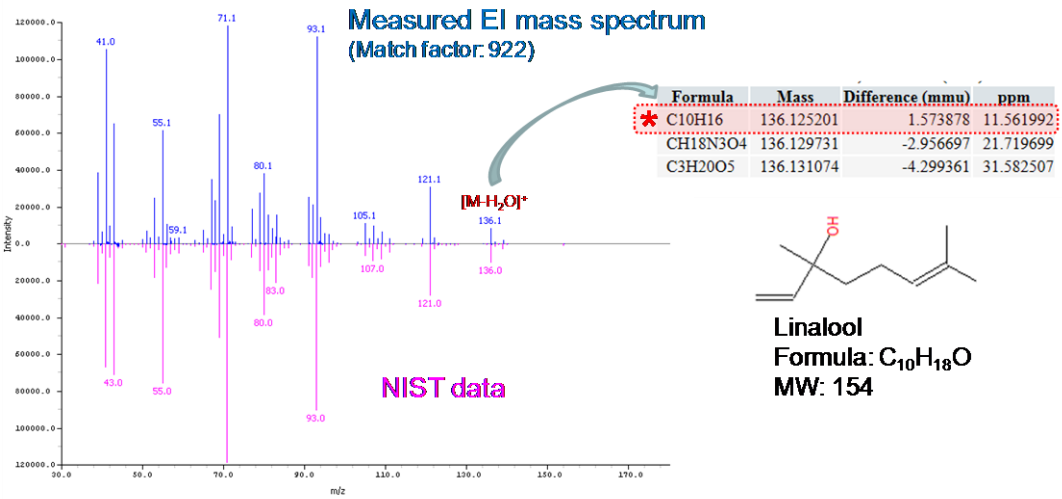

Fig. 6. Measured EI mass spectrum and NIST data of Linalool.

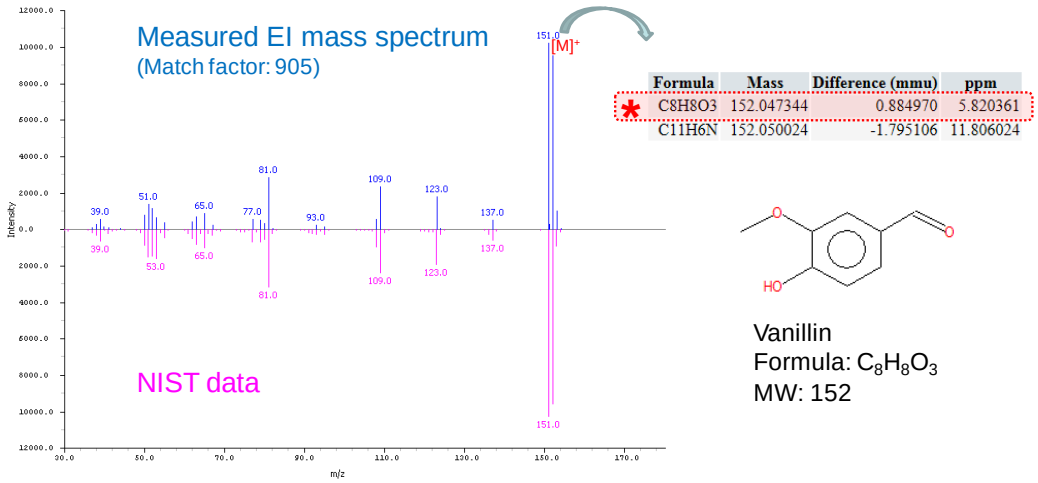

Fig. 7. EI mass spectrum and NIST data of Vanillin.