

Application News

Go Faster with Low-Pressure GC-MS Analysis

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User Benefits

- ◆ GCMS-QP2020 NX supports high throughput analysis using fast and low-pressure GC-MS
- ◆ Chromatographic peak definition improves with higher quadrupole scanning speed
- ◆ Save up to 80% of analysis time in routine screening analysis with fast and low-pressure GC-MS

Introduction

Gas chromatography mass spectrometry (GC-MS) is a well-developed and robust method used for the analysis of volatile and semi-volatile compounds in various application fields. The increasing demands for higher sensitivity and sample throughput have spurred decades of development and innovation. Innovations in GC column and GC hardware are constantly being sought out to improve the efficiency of GC-MS analysis. Considerable efforts in these areas have enabled a substantial reduction of GC-MS analysis time with minimal compromise on the chromatographic resolution. These techniques are known as fast GC-MS and low-pressure GC-MS (LPGC-MS) methods.

The fast GC-MS method is based on the usage of narrow-bore columns and has successfully transitioned from research to commercial use. Nowadays, it is increasingly being adopted for routine analysis. As for the LPGC-MS method, it is undergoing the transition phase and its development has only been recently spurred by the commercial availability of a low-pressure GC column kit. The kit eliminates the technical difficulty encountered in the adoption of the LPGC-MS method and is expected to broaden its utilization. These high sampling throughput methods are expected to drastically reduce the GC-MS analysis while maintaining similar accuracy in analysis.

In this article, we will demonstrate the robustness of the Shimadzu single quadrupole system, GCMS-QP2020 NX, to support the utilization of fast GC-MS and LPGC-MS methods, with a focus on the latter. When coupled with the high scanning speed capability of the Shimadzu GCMS-QP2020 NX, the LPGC-MS method could be utilized for rapid screening in various application fields.

Measurement Conditions and Samples

Pesticide standard mixtures were purchased from Restek. The standard GC column used was SH-I-5Sil MS 30 m × 0.25 mm ID and 0.25 μm film thickness (P/N: 221-75954-30). The column used for fast GC was SH-I-5Sil MS 20 m × 0.15 mm ID and 0.15 μm film thickness (P/N: 227-36030-01). The low-pressure GC column, LP-Rtx-5MS, consists of a restrictor column of 5 m × 0.18 mm ID coupled with an analytical column of 15 m × 0.53 mm ID and 1 μm film thickness and a 1 m integrated transfer line on the outlet end was used.

For standard GC-MS analysis, pre-set GC and MS parameters from Method 3 of the Shimadzu Smart Pesticide Database were used. The MS parameters were retained for both fast GC-MS and LPGC-MS analysis while the GC parameters were translated using the Restek EZGC Method Translator™ tool⁽¹⁾. Scan acquisition mode was used for all analysis and varying scan speed was used for LPGC-MS analysis.

Table 1. Standard GC conditions for detection of compounds in pesticide standard mixtures

Standard GC	
GC	
Injection Temp	250 °C
Injection Mode	Splitless, 1.0 min sampling time
Oven Temperature	105 °C (3 min), 10 °C/min to 130 °C, 4 °C/min to 200 °C, 8 °C/min to 290 °C (6 min)
Flow Control	Helium, linear velocity (44.1 cm/s)

Table 2. Fast GC conditions for detection of compounds in pesticide standard mixtures

Fast GC	
GC	
Injection Temp	250 °C
Injection Mode	Splitless, 2.0 min sampling time
Oven Temperature	105 °C (1.7 min), 17.6 °C/min to 130 °C, 7 °C/min to 200 °C, 14.1 °C/min to 290 °C (3.4 min)
Flow Control	Helium, linear velocity (51.9 cm/s)

Table 3. LPGC conditions for detection of compounds in pesticide standard mixtures

LPGC	
GC	
Injection Temp	250 °C
Injection Mode	Splitless, 0.5 min sampling time
Oven Temperature	105 °C (1 min), 35 °C/min to 320 °C (1 min)
Flow Control	Helium, linear velocity (130 cm/s)

Table 4. MS conditions for detection of compounds in pesticide standard mixtures

LPGC	
MS	
Interface Temp	280 °C
Ion Source Temp	230 °C
Ionization Mode	Electron Ionization
Data Acquisition Mode	Scan
Event Time	0.3 sec
Scan Speed	1428 u/sec
Mass Range	<i>m/z</i> 50-460

■ Results and Discussion

How Much Faster Can We Go?

Most current GC-MS methods are established based on the conventional setup of GC-MS, particularly on the usage of standard GC columns. A typical GC column has a length ranging from 25 to 60 m, an inner diameter of 0.25 to 0.32 mm, and a film thickness of 0.25 to 3 μm. On average, a standard GC-MS analysis requires 30 to 60 minutes and provides adequate chromatographic resolution and sensitivity for identification.

Increasing demands for higher efficiency in terms of analysis time have spurred the development of fast GC-MS methods. The fast GC-MS method is expected to shorten analysis time while maintaining a similar chromatographic resolution seen in the standard GC-MS method. This has been achieved with the implementation of various modifications of GC columns and hardware. A fast GC column is shorter, has a narrower internal diameter and a thinner film thickness as compared to a standard GC column. The column length ranges from 10 to 20 m while the inner diameter is ≤ 0.15 mm and the film thickness is typically between 0.1 and 0.4 μm. Due to these modifications,

the GC hardware must be able to sustain a high maximum operational head pressure. In addition, high linear temperature ramps are essential to maintain a high separation efficiency as the analysis time is drastically reduced. Consequently, an automatic pressure regulator is required to maintain constant average linear velocity over the entire temperature program.

At the same time, the LPGC-MS method is also developed to reduce analysis time and thus increase sample throughput. Commercially available low-pressure GC column kit consists of a 15 m × 0.53 mm ID and 1 μm film thickness analytical column (MS side) attached to a restrictor of 5 m × 0.18 mm ID (GC inlet side). The restrictor enables a normal head pressure at the GC inlet while the analytical column has an outlet pressure of a near-vacuum condition. This condition increases the linear velocity of the carrier gas and thus shortens the analysis time. Like the fast GC-MS method, high linear temperature ramps are required to ensure a smooth implementation of the LPGC-MS method.

Shimadzu GCMS-QP2020 NX which utilizes the Nexis GC-2030 is equipped with new advanced flow controllers (AFC) to deliver the necessary pressure and carrier gas flow requirements to perform fast GC-MS and LPGC-MS analysis. In this Application News, we evaluated the time-saving performance of these methods with a standard mixture consisting of 110 types of pesticides (Figure 1).

As a starting point for reference, pre-set GC-MS method in Shimadzu Smart Pesticide Database which utilizes a standard GC column required an analysis time of 40 min for a good chromatographic resolution and sensitivity. When the method was translated to a fast GC column using the method translator tool with emphasis on speed optimization, the analysis time required was 23 min. Additional optimizations are possible to further reduce the analysis time but are not within the intention of this article. With an LPGC column, the analysis time required was 8 min. The usage of the LPGC column drastically reduced the overall analysis time by 80 % and 65 % when compared to standard and fast GC columns, respectively. The last eluting pesticide compound, deltamethrin, eluted at 35.4, 21.1, and 7.7 min with standard, fast, and low-pressure GC columns, respectively.

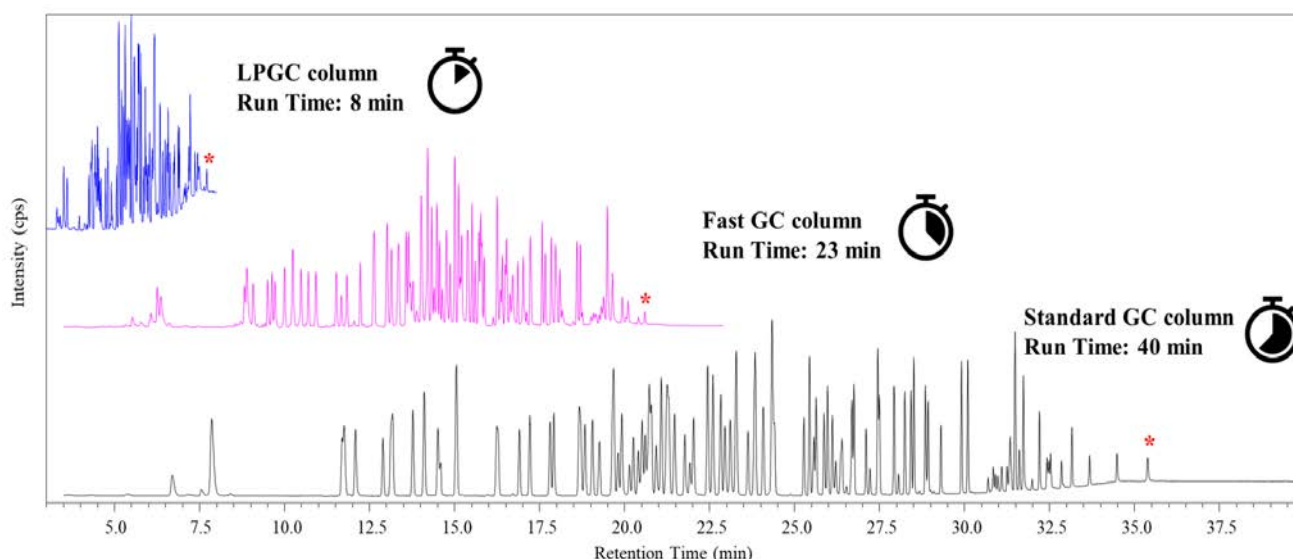


Figure 1. Total ion chromatograms for the analysis of pesticide standard mixture with low-pressure, fast, and standard GC columns. The red asterisks marked the position of the last eluting compound, deltamethrin.

Mass Spectrometer Requirement for LPGC-MS

The utilization of LPGC-MS reduced the analysis time drastically but traded efficiency for speed. Due to the short analysis time, analytes elute closer to one another as compared to the conventional GC-MS method. A 10-fold increase in the number of analytes eluted can be expected. As seen in Figure 2a, approximately 40 analytes eluted within the retention time range of 5 to 6 min.

Fortunately, MS can provide the selectivity required for compound identification via library search. With LPGC-MS, the MS detector also needs to be fast enough to detect the rapidly eluting analytes. A high scan speed helps to ensure that the relative intensities of the fragment ions do not change significantly from point to point over a narrow peak. Shimadzu GCMS-QP2020 NX can provide a scan speed of up to 20,000 u/sec. Data collected at 20,000 u/sec contains more data points as compared to data collected at 1,438 u/sec, as seen in Figure 2a. This helps to improve peak definition and increase the accuracy and precision of analysis. For example, in Figure 2b, the peaks of tetramethrin isomers are more well-defined in the data collected at 20,000 u/sec (dark-coloured plot). As a result,

quantitative analysis of tetramethrin based on m/z 164 ion would provide a more accurate and precise analysis compared to 1,438 u/sec. Since the identification and quantitation of bifenthrin can be determined using m/z 181 ion, it can be selectively analyzed despite co-eluting with the tetramethrin isomers.

The performance of 20,000 u/sec in the Shimadzu GCMS-QP2020 NX is enabled by the Advanced Scanning Speed Protocol (ASSP™) technology. ASSP™ technology optimizes the quadrupole rod bias voltage to minimize sensitivity deterioration at a high scan speed of 10,000 u/sec or faster. As seen in Figures 2a and 2b, the intensities of profiles collected at 20,000 u/sec are comparable to those obtained with 1,438 u/sec. Since ASSP™ technology can maintain the sensitivity at high scan speed, the fidelity of the mass spectra is retained as well. This enables the usage of the mass spectra for compound identification via library match even at high scan speed of 20,000 u/sec. In Figures 2c and 2d, the extracted mass spectra of tetramethrin-2 collected at 1,438 and 20,000 u/sec were almost identical and were matched to NIST mass spectral library with a similarity score of > 85 % for both mass spectra.

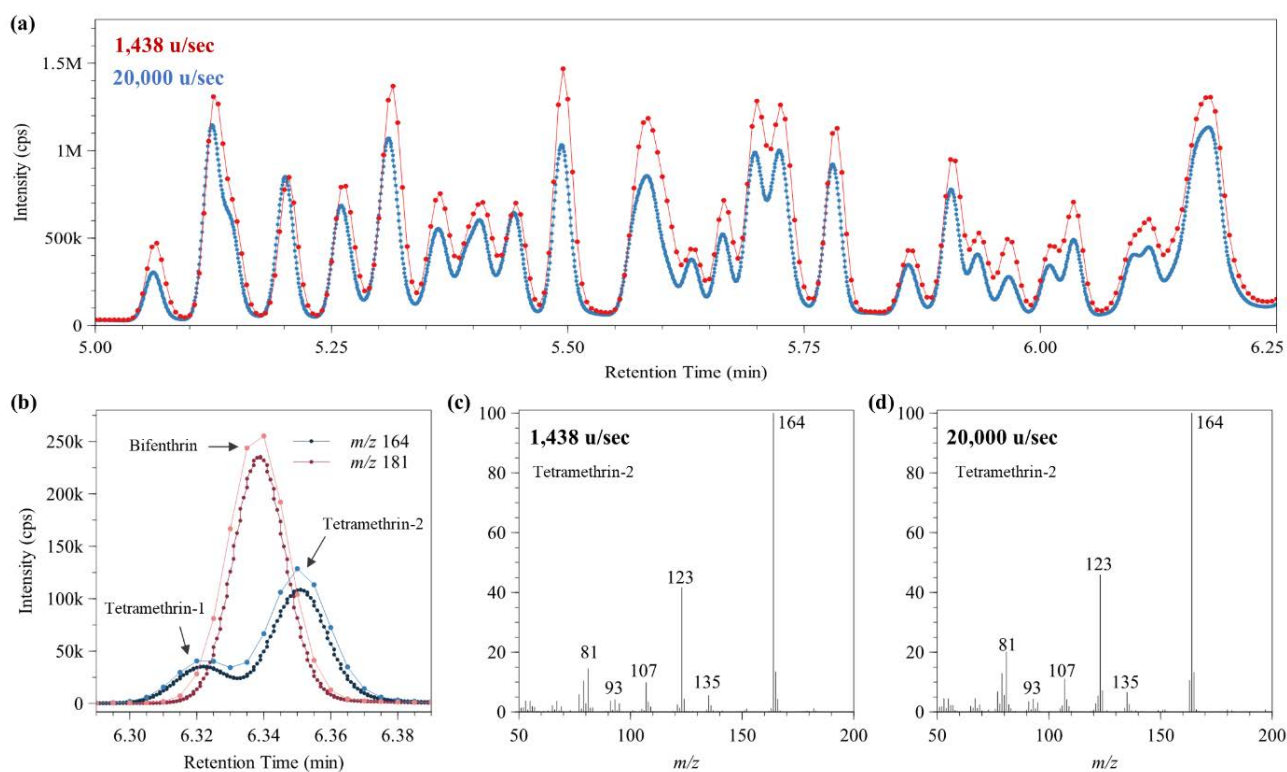


Figure 2. (a) Total ion chromatogram of pesticide standard mixture collected at 1,438 and 20,000 u/sec. (b) Extracted ion chromatogram of bifenthrin and tetramethrin isomers. The light-coloured plot was collected at 1,438 u/sec while the dark-coloured plot was collected at 20,000 u/sec. (c and d) Extracted mass spectra of tetramethrin-2 collected at 1,438 and 20,000 u/sec.

Deconvolution Approach for LPGC-MS data

As the usage of LPGC-MS resulted in the rapid elution of analytes, qualitative profiling of co-eluting peaks within a complex matrix may necessitate the use of spectral deconvolution to extract pure mass spectra for library match. This is provided that the target compounds are not completely overlapping. The degree of convolution of analytes like transluthrin and vinclozolin, as in Figure 3a, can be visualized with a surface plot. The surface plot provides visualization of the chromatogram waveform along all mass channels. Direct correlation of the chromatogram waveform to the deconvolution result, as seen in Figure 3b, can help to determine the accuracy of deconvolution.

Various deconvolution approaches or algorithms are available to deconvolve co-eluting components. AMDIS is a well-known software that deconvolves based on the chromatogram waveform. Apart from that, the multivariate curve resolution approach resolves co-eluting components by using dimensionality reduction and bilinear models. The data collected with the Shimadzu GC-MS system regardless of scan speeds can be analyzed by these approaches. Pure mass spectra can be obtained from the deconvolution results to enable a high-confidence library match. More information on the multivariate curve resolution approach can be found in Technology Brief MST-206⁽²⁾.

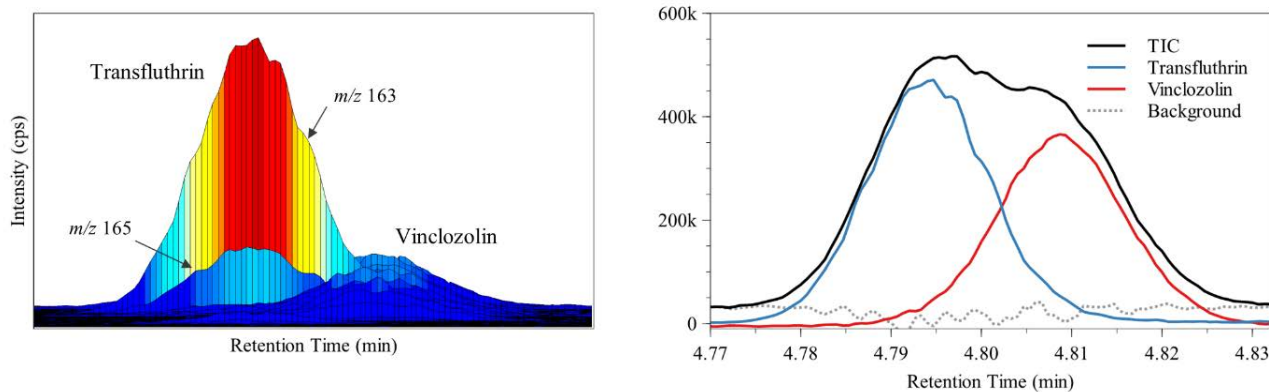


Figure 3. (a) Surface plot of co-eluting transfluthrin and vinclozolin indicating the mass chromatogram profiles for all mass channels (b) Deconvolution result consisting of transfluthrin and vinclozolin components as well as a background noise signal, obtained using SmartDalton™.

■ Conclusion

The Shimadzu GCMS-QP2020 NX can readily adopt LPGC-MS and fast GC-MS methods. The LPGC-MS method can reduce standard GC-MS analysis time by up to 80 % with minimal loss of efficiency. When analyzed with high scan speed, the collected LPGC-MS data showed improved peak definition, which can increase both the accuracy and precision of analysis. In addition, co-eluting analytes in the data can also benefit from various types of deconvolution approaches for pure mass spectra extraction. The pure mass spectra can improve library match scores and lead to a more accurate compound annotation. This solution can be readily adopted for high-throughput screening.

■ References

- (1) EZGC Method Translator (<https://ez.restek.com/ezgc-mtfc>)
- (2) Technology Brief MST-206

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