

SIFI – Simultaneous Collection of Full Scan and Selected Ion Recording Mass Spectral Data

Introduction

In 1997, PerkinElmer introduced the TurboMass™ Gas Chromatography/Mass Spectrometry (GC/MS) system; with it, the ability to collect full scan and selected ion recording (SIR, also called SIM for selected ion monitoring) data in a single analysis. SIFI™ (selected ion full ion), as it is known, is simultaneous SIR and full-scan data acquisition, allowing the user to obtain the library-searchable spectral information of full scan with the sensitivity of SIR. SIFI becomes more useful with the growing need to generate more information at higher sensitivity from existing GC/MS methods, without additional analyses.

SIFI is best applied to analyses with wide concentration ranges or in which selected components require increased sensitivity. Examples are highly fragmented pesticides in pesticide-screening analysis, particularly low-concentration compounds in environmental methods, and the highly-brominated congeners of polybrominated diphenyl ethers in WEEE/RoHS analysis.

Today, the state-of-the-art PerkinElmer® Clarus® 600 GC/MS, with high-speed electronics, achieves best-in-class data-collection rates, further improving SIFI capabilities. This technical note will demonstrate the following:

- SIFI operation
- SIFI GC/MS method development
- Full scan and SIFI spectral data to single mode data
- The sensitivity increase observed in the SIR function of SIFI data

Experimental

This study was carried out on the Clarus 600 T GC/MS. The GC conditions were constant throughout the study. A 1- μ L split injection of polychlorinated biphenyl (PCB) congeners mix was injected into a 280 °C injector port. The Elite-5MS (30 m x 0.25 mm x 0.25 μ m) column was temperature programmed from 120 °C to 280 °C at 20 °C/min, with a carrier gas flow of 1 mL/min (helium). A specific analyte from the PCB mix, 2-chlorobiphenyl, is considered throughout this study.

Table 1. The Clarus 600 Mass Spectrometer Operating Conditions.

Mass Spectrometer:	PerkinElmer Clarus 600 T
GC Inlet Line Temperature:	280 °C
Ion Source Temperature:	280 °C
Function Type:	SIFI
Full Scan Range:	140-265 <i>m/z</i>
Full Scan Time:	0.02 sec
InterScan Delay:	0.06 sec
SIR Dwell Time:	0.01 sec
SIR Interchannel Delay:	0.005 sec
Summary of SIR Functions:	4 ions/function
Function 2:	<i>m/z</i> 152, 153, 188, 190

An important consideration when designing MS data-collection functions is to collect data at a rate sufficient to accurately and reproducibly describe chromatographic peak shape – in GC/MS, 8-12 scans per peak. Additionally, the transitions between functions should not occur during the elution of an analyte peak. Pictured in Figure 1 is the MS method editor window of TurboMass GC/MS software. The graphical depiction of functions allows the user to visualize the timing of each function, creating a simple environment in which to develop methods.

In the MS method editor, each colored bar represents a different data-collection function. The green bar represents the solvent delay; up to 4 solvent delays can be placed throughout the run. During solvent delay, the filament current is off. The blue bar represents a full-scan function; the available mass range for full scan is *m/z* 1-1200. The red bar represents an SIR function; multiple ions can be collected in each function. An MS method may contain a combination of multiple functions; the type and timing of these functions is not limited, and overlapping is permitted.

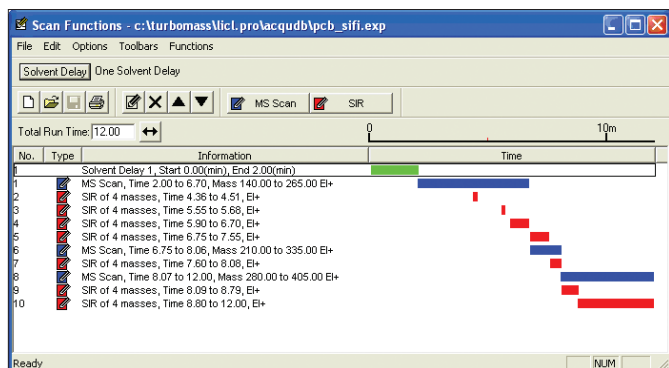


Figure 1. The TurboMass MS method development window.

The creation of SIFI data-acquisition functions requires the optimization of different parameters within the MS method. An example is a chromatographic peak 3 seconds wide, at base, and the analysis requires 10 scans per peak; then the total time available for each MS cycle is 0.3 seconds. Once the peak width and cycle time are determined, a balance needs to be found between 4 key parameters. In full scan acquisition, the scan time and inter-scan delay need optimization. In SIR, the dwell time and inter-channel delay for each ion require optimization.

In the case of a 3-second wide peak, the default Turbo-Mass full-scan settings use a single-mode acquisition with a cycle time of 0.3 seconds; this includes a scan time of 0.2 seconds and an inter-scan delay of 0.1 seconds, achieving 10 scans per peak. The determination of cycle time in a SIFI function includes the sum of the scan, inter-scan delay, as well as the dwell and inter-channel delay for each SIR ion. The exact values for each of these parameters will be defined by the relative importance between spectral data and detection limits dictated by each specific application.

The objective of this experiment is to utilize the MS in a mode which would push the limit of the system electronics. The result is that the cycle time of the MS method is as short as possible. The short cycle time limits the time available for scan and dwell acquisition and thus sacrifices response in exchange for very high speed. In this case, we are able to achieve 8 full-scan spectra and 8 SIR data points in one second.

The mass spectrometer conditions utilized in this study are summarized in Table 1. During single-mode (full scan or SIR) acquisition, the scan range, scan time, SIR ions and SIR dwell time remained constant, while the inter-scan delay and inter-channel delay were modified to achieve consistent MS cycle time.

Results

SIFI acquisition is comprised of a full scan and SIR data collection running simultaneously. Testing the capabilities of SIFI requires comparison of the data acquired during each SIFI function to an identical function collected in single-mode operation. The consistency between single-mode operation and SIFI will be demonstrated with two experiments:

- Experiment 1: Comparison of spectral data between SIFI and single mode operation
- Experiment 2: Comparison of peak area between SIFI and single mode operation

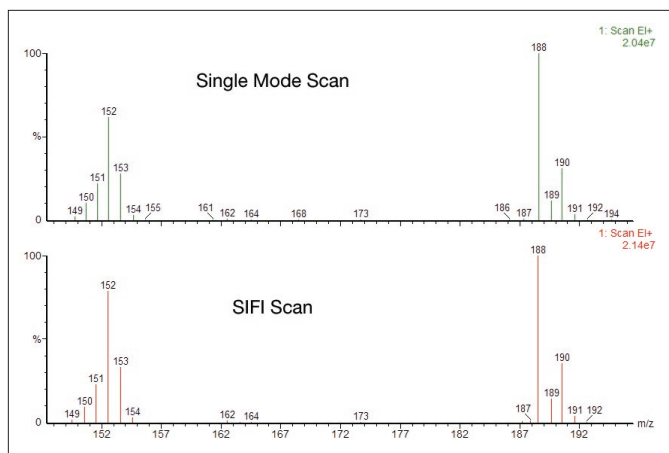


Figure 2. Spectral comparison of 2-chlorobiphenyl between scan and SIFI mode.

In Experiment 1, the spectral data from single-mode full-scan data collection is compared to the spectral data from SIFI. Figure 2 pictures the experimental spectra of 2-chlorobiphenyl from full scan (top), with the SIFI full scan data (bottom). The ion-ratio data is examined in more detail in Table 2; the ion-ratio data from 7 duplicate analyses are averaged and compared. Looking at both the ion intensity and ion-ratio data, you can see no significant difference – the percent difference between single mode and SIFI, for major ion fragments, is 5.5% or less.

Table 2. Ion Intensity and Ratio Comparison of 2-Chlorobiphenyl in 7 Duplicate-Scan and SIFI Analyses (Experiment 1).

<i>m/z</i>	Full Scan Avg. Ion Intensity	Full Scan (SIFI) Avg. Ion Intensity	% Diff.
153	5899857	6586571	5.5%
190	6954857	7459000	3.5%
152	14120000	15508571	4.7%
188	20685714	21630000	2.2%

<i>m/z</i>	Avg. Ion Ratio	Avg. Ion Ratio	% Diff.
153	28.5%	30.4%	3.2%
190	33.6%	34.4%	1.2%
152	68.5%	71.5%	2.1%
188	100.0%	100.0%	0.0%

Continuing with Experiment 1, the SIR ion-ratio data from single-mode and SIFI acquisition require comparison. Again, 2-chlorobiphenyl was the test compound. Figure 3 shows the mass spectral data from each analysis. Each of the overlaid chromatograms is an extracted ion chromatogram displaying the intensity of a single ion.

Examination of the chromatograms in Figure 3 shows that the peak area of each extracted ion is very similar. A statistical analysis of the difference in ion intensity between operational modes is presented in Table 3 (Page 4). It shows 7 duplicate analyses of 2-chlorobiphenyl. This data confirms that the peak area and the ion-ratio data are the same in single-mode and SIFI acquisition.

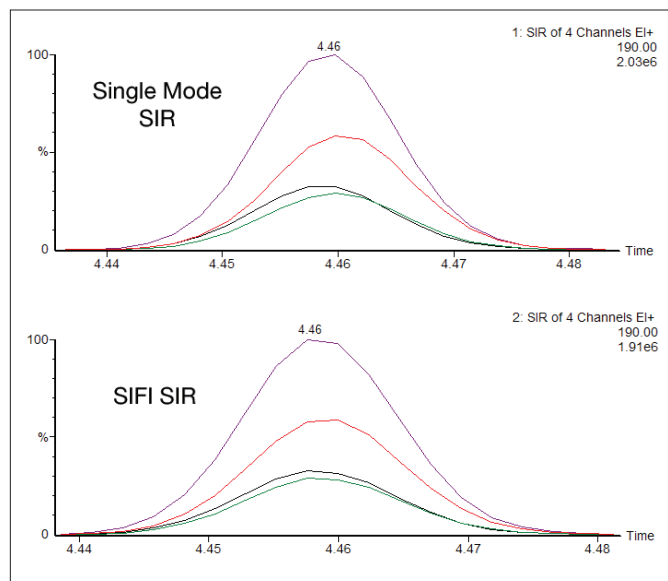


Figure 3. Ion-ratio comparison between single-mode SIR and SIFI analysis.

Table 3. Ion Intensity and Ratio Comparison of 2-Chlorobiphenyl in 7 Duplicate Single-Mode SIR and SIFI Analyses.

<i>m/z</i>	SIR Avg. Ion Intensity	SIR (SIFI) Avg. Ion Intensity	% Diff.
153	379929	421129	5.1%
190	433357	473229	4.4%
152	768729	861957	5.7%
188	1332000	1461286	4.6%

<i>m/z</i>	Avg. Ion Ratio	Avg. Ion Ratio	% Diff.
153	28.5%	28.8%	0.5%
190	32.5%	32.4%	0.2%
152	57.7%	59.0%	1.1%
188	100.0%	100.0%	0.0%

In addition to testing the spectral data generated, it is also necessary to verify that the peak area in each mode is consistent (Experiment 2). Figure 4 graphically displays a peak-area comparison between a single full-scan and SIFI analysis.

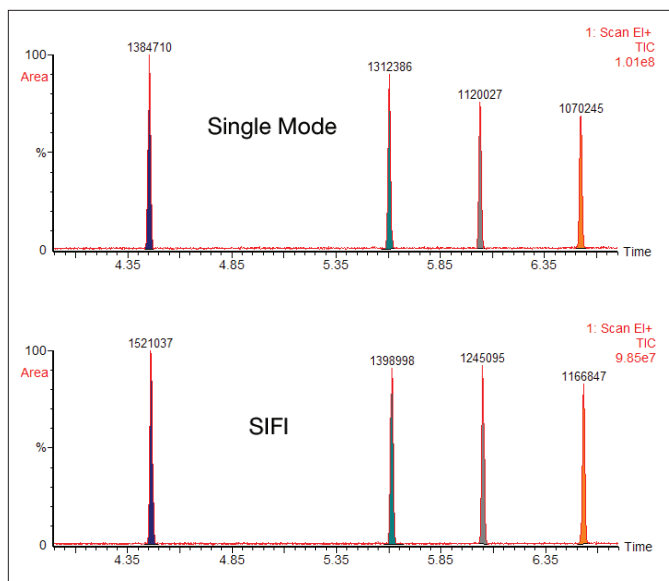


Figure 4. Peak area comparison between full-scan-only mode and full-scan SIFI data.

Table 4 compares 10 duplicate analyses of 2-chlorobiphenyl and demonstrates no significant difference between single mode and SIFI peak area. Additionally, the percent relative standard deviation within each of the 10 duplicate analyses is also well below 5%, demonstrating consistency in peak area throughout the test.

Table 4. Area Comparison Between 10 Duplicate Analyses in Each Mode of Operation Scan, SIR, and SIFI.

	Scan Response	Scan (SIFI) Response	
Avg. (n=10)	498754	513161	% Diff
%RSD	3.5%	2.4%	2.8%
	Scan Response	Scan (SIFI) Response	
Avg. (n=10)	63387	63041	% Diff
%RSD	2.5%	2.7%	0.5%

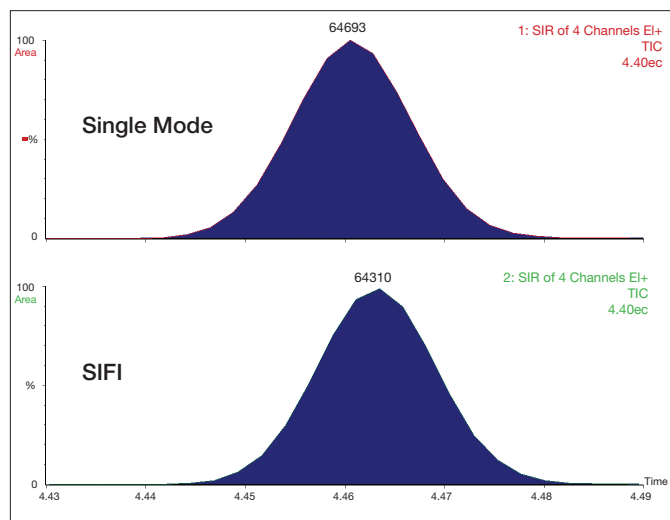


Figure 5. Peak area comparison between SIR only mode and SIR SIFI data.

The peak-area comparison was also performed on the SIR data; Figure 5 displays a single run from each mode of analysis. Table 4 shows greater detail for the SIR peak-area comparison; the duplicate analysis of 10 samples shows virtually no difference (0.5%) between the peak area in SIR and SIFI. Additionally, the percent relative standard deviation within each of the 10 duplicate analyses is less than 3%, showing very little difference in peak area, run over run.

The above results show that spectral data and peak area are consistent between both single-mode acquisition and SIFI acquisition, allowing the user to confidently acquire both the library-searchable full-scan data and improved-sensitivity SIR data with simultaneous SIFI.

The final data comparison of this study will demonstrate the improvement in detection limits as a result of including SIR data collection. RMS (root mean square) signal-to-noise evaluation allows the user to approximate the sensitivity of the system for a particular compound. Figure 6 compares the RMS signal to noise of 2-chlorobiphenyl between the SIR and full-scan-acquisition functions within the same run using SIFI acquisition. The chromatograms show a single analysis. Signal-to-noise data from 10 duplicate analyses is presented in the table. The increase in sensitivity achieved with SIR is dramatic – in this case, greater than 20x. Depending on the specific data-collection conditions, the improvement in detection limits as a result of SIR will be as much as 80x.

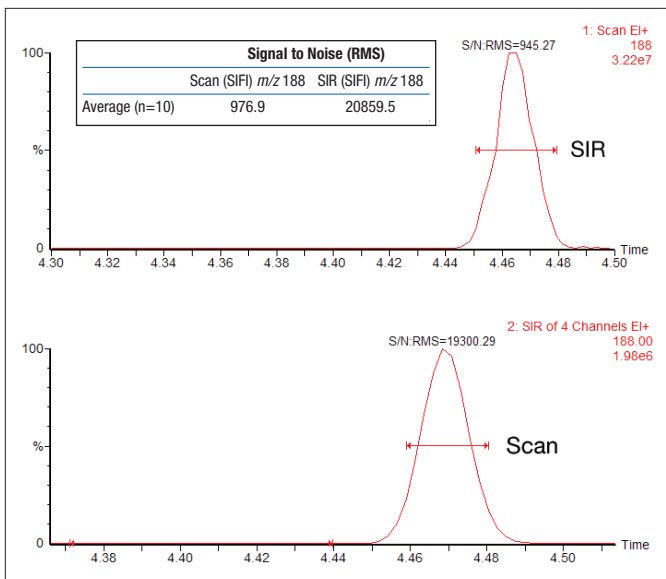


Figure 6. Comparison of the signal to noise of a SIFI acquisition obtained in each mode – full scan and SIM.

Conclusion

Selected ion full ion (SIFI) mass spectral data acquisition is a powerful tool in GC/MS analysis. This study has demonstrated the use of simultaneous overlapping of full scan and SIR functions, allowing users to collect data with full spectral information and increased sensitivity. SIFI methods are created within the simple graphical interface of TurboMass GC/MS software.

The data presented demonstrates that the spectral quality and peak-area response of SIFI have no statistical difference to data collected in single-operation mode. Additionally, a dramatic sensitivity improvement is achieved with the addition of SIR data; this was shown by comparing the signal to noise of 2-chlorobiphenyl full scan with the signal to noise of SIR.

The use of SIFI for GC/MS data acquisition provides the library-searchable mass spectral data characteristic of full-scan analysis with the improved detection limits and signal-to-noise characteristic of selected ion acquisition, in a single run.