TECHNICAL NOTE 10605

Routine-grade robustness with the Advanced Electron Ionization source: confirmation of contaminants in food products at trace levels by GC-MS/MS

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Keywords

Advanced electron ionization, AEI, robustness, pesticides, triple quadrupole mass spectrometry, GC-MS/MS, SmartTune

Goal

The aim of this study was to demonstrate the robust and routine performance of the Thermo Scientific™ TSQ™ 9000 triple quadrupole GC-MS/MS system with Advanced Electron Ionization source for the analysis of pesticide residues in food matrix.

Introduction

In today's modern, high-throughput analytical laboratory, instrument downtime can have a significant impact on laboratory productivity. Analysts working in such fast-paced environments are required to investigate large numbers of samples and to deliver accurate and valid results consistently. Having to disrupt this process causes sample turn-around times to increase and, as a result, the cost per sample to surge.

The advent of gas (and liquid) chromatography with triple quadrupole mass spectrometry (GC-MS/MS and LC-MS/MS) increased selectivity and drove detection limits down, reducing the requirement for sample clean-up and leading to quicker, cheaper methods (ex. QuEChERS[1]). However, these sample preparation methods often allow for more of the matrix to make its way into the chromatographic system and the ionization source, affecting the system robustness and increasing the maintenance intervals. Without a highly sensitive and robust ion source, detector responses can quickly drop off, leading to quality control (QC) failures, higher detection limits, and ultimately a failure to deliver acceptable and compliant results. Ensuring that the analytical systems used for these workflows are rugged enough to deal with the challenges faced is of the utmost importance to the user.

In this study, the performance of the TSQ 9000 GC-MS/MS triple quadrupole mass spectrometer with the new Advanced Electron Ionization (AEI) source is assessed. For this, peak area repeatability of selected pesticides was analyzed in approximately 900 injections of a complex sample extract. In addition to this, an easy-to-use, automated system, set up with the new SmartTune feature, is highlighted as a unique tool used to simplify the user experience and speed up analysis.

Experimental

Sample preparation

Carrot/potato baby food extracts (following the citrate buffered QuEChERS protocol using Thermo Scientific™ HyperSep™ dispersive solid phase extraction (dSPE) products)[2] were post spiked with a mixture of pesticides at a final concentration of 10 pg/µL (equivalent to 10 µg/kg in sample). Spiking solution concentrations were kept as high as reasonably practicable to keep dilution effects negligible. The final sample extract solvent was acetonitrile.

GC-MS/MS analysis

A TSQ 9000 triple quadrupole GC-MS/MS instrument equipped with an AEI source and coupled with a Thermo Scientific™ TRACE™ 1310 GC system was used. The AEI source provides a highly efficient electron ionization of analytes and a more tightly focused ion beam that provides an unparalleled level of sensitivity.

Liquid injections of sample extracts were performed using a Thermo Scientific™ TriPlus™ RSH™ autosampler, and chromatographic separation was achieved by a Thermo Scientific™ TraceGOLD™ TG-5SilMS 30 m × 0.25 mm I.D. × 0.25 µm film capillary column with 5 m integrated SafeGuard. Additional details of the instrument parameters are displayed in Table 1.

After initial source cleaning, repeat injections of the sample were made. After every 100 sample injections, the PTV liner was replaced along with the injector septum, approximately 10 cm trimmed from the head of the guard column followed by automatic tuning of the system using the SmartTune feature. A single analytical GC capillary column was used with no additional maintenance performed on either the GC or the MS.

Table 1. Gas chromatograph and mass spectrometer parameters.

TRACE 1310 GC System Parameters	
Injection volume:	1 µL
Liner:	Siltek™ six baffle PTV liner (P/N 453T2120)
Inlet:	70 °C
Carrier gas:	He, 1.2 mL/min
Inlet mode:	Splitless (split flow 50 mL/min after 2 min)
Column:	TraceGOLD TG-5SilMS with SafeGuard (30 m × 0.25 mm, 0.25 µm, with 5 m integrated guard column – P/N 26096-1425)

PTV Parameters:	**Rate (°C/s)**	**Temperature (°C)**	**Time (min)**	**Flow (mL/min)**
Injection	–	70	0.10	–
Transfer	5.0	300	2.00	–
Cleaning	14.5	320	5.00	75.0

Oven Temperature Program

Ramp	RT (min)	Rate (°C/min)	Temperature (°C)	Hold Time (min)
Initial	0	–	40	1.50
1	1.5	25.0	90	1.50
2	5	25.0	180	0.00
3	8.6	5.0	280	0.00
Final	28.6	10.0	300	5.00
Run time	35.6	–	–	–

TSQ 9000 Mass Spectrometer Parameters	
Transfer line:	250 °C
Ionization type:	EI
Ion source:	320 °C
Acquisition mode:	Timed SRM
Tuning parameters:	AEI SmartTune
Collision gas and pressure:	Argon at 70 psi
Peak width:	0.7 Da at FWHM (both Q1 and Q3)

Data processing

Data were acquired, processed, and reported using Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software.

Results and discussion

The experiments conducted aimed to assess the robustness of the TSQ 9000 AEI GC-MS/MS system for a large number of repeat injections of a real pesticide residue sample matrix extracted with acetonitrile following QuEChERS.

When performing analysis by GC-MS/MS, the detector response is used to quantify the analytical component. This detector is usually an electron multiplier which, as the name suggests, multiplies the electrons generated at the dynode. The gain factor applied to these multipliers indicates the factor to which the signal has been enhanced; for example, a multiplier gain of 3 × 10^5 (3E5) would theoretically generate 300,000 electrons from a single ion event. In order to maintain a relatively consistent peak area as ion sources become dirty and electron multipliers age, the gain factor and voltage applied to the multiplier increase (values adjusted during system tuning).

To assess the robustness of the ion source, the peak areas of the target analytes have been divided by the gain factor used for data acquisition. The derived value, referred to as the ion flux, can be directly related to the number of analyte ions that are transmitted from the ion source. Figure 1 shows the ion flux for five selected pesticides as selected reaction monitoring (SRM) transmitted ion transitions. In addition to a very stable ion flux response across the entire data set, the ion ratios (defined as qualifier response/quantifier response expressed as a percentage) were also very stable throughout the entire experiment (equivalent to one month of uninterrupted acquisition), as demonstrated in Figure 2.

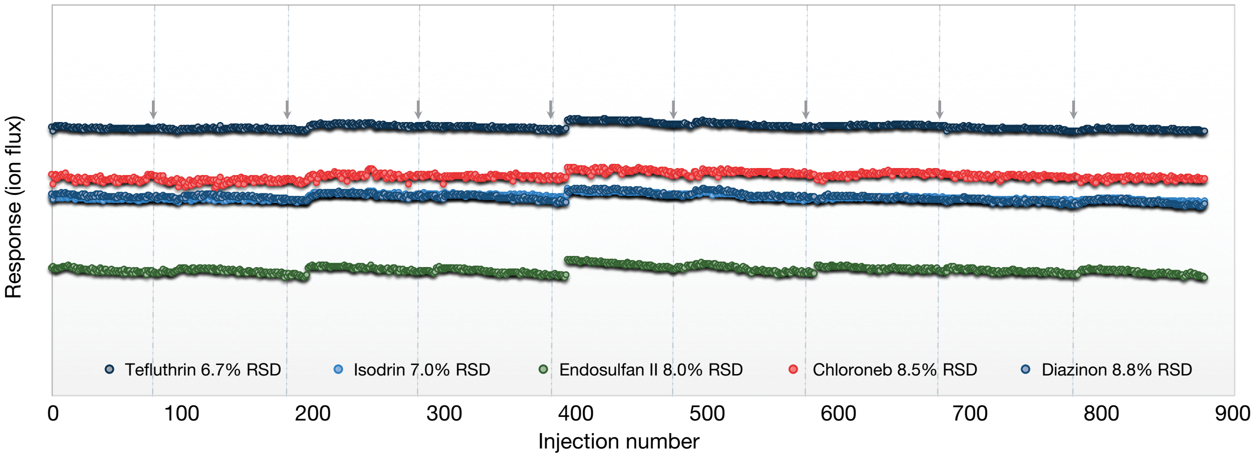


Figure 1. Robustness data showing approximately 900 sequential injections of matrix sample extract spiked with pesticides at 10 ppb [µg/kg]. Injector maintenance and tuning intervals are marked with an arrow. No internal standard correction was used, and no source maintenance was performed during the whole injection series.

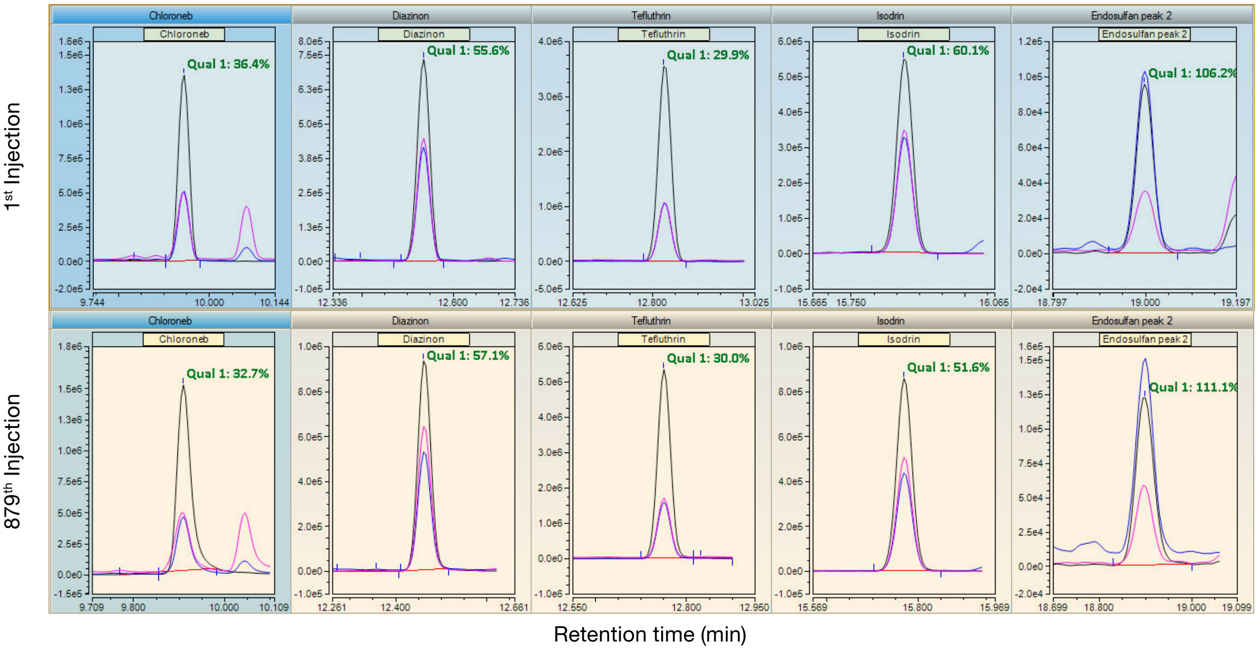


Figure 2. Example chromatography and ion ratios for the selected peaks as shown in Figure 1 in the first and last injections of the acquired data set. [Black = Quan, Blue = Qual 1, Purple = Qual 2]

Of the 150 pesticides assessed, >90% exhibited a relative standard deviation (ion flux) of <20% over the full ~900 injection data set (Figure 3). In comparison, SANTE acceptance criteria[3] for precision requires a minimum of five replicates at the target LOQ and at 2–10× the target LOQ or the MRL (as shown).

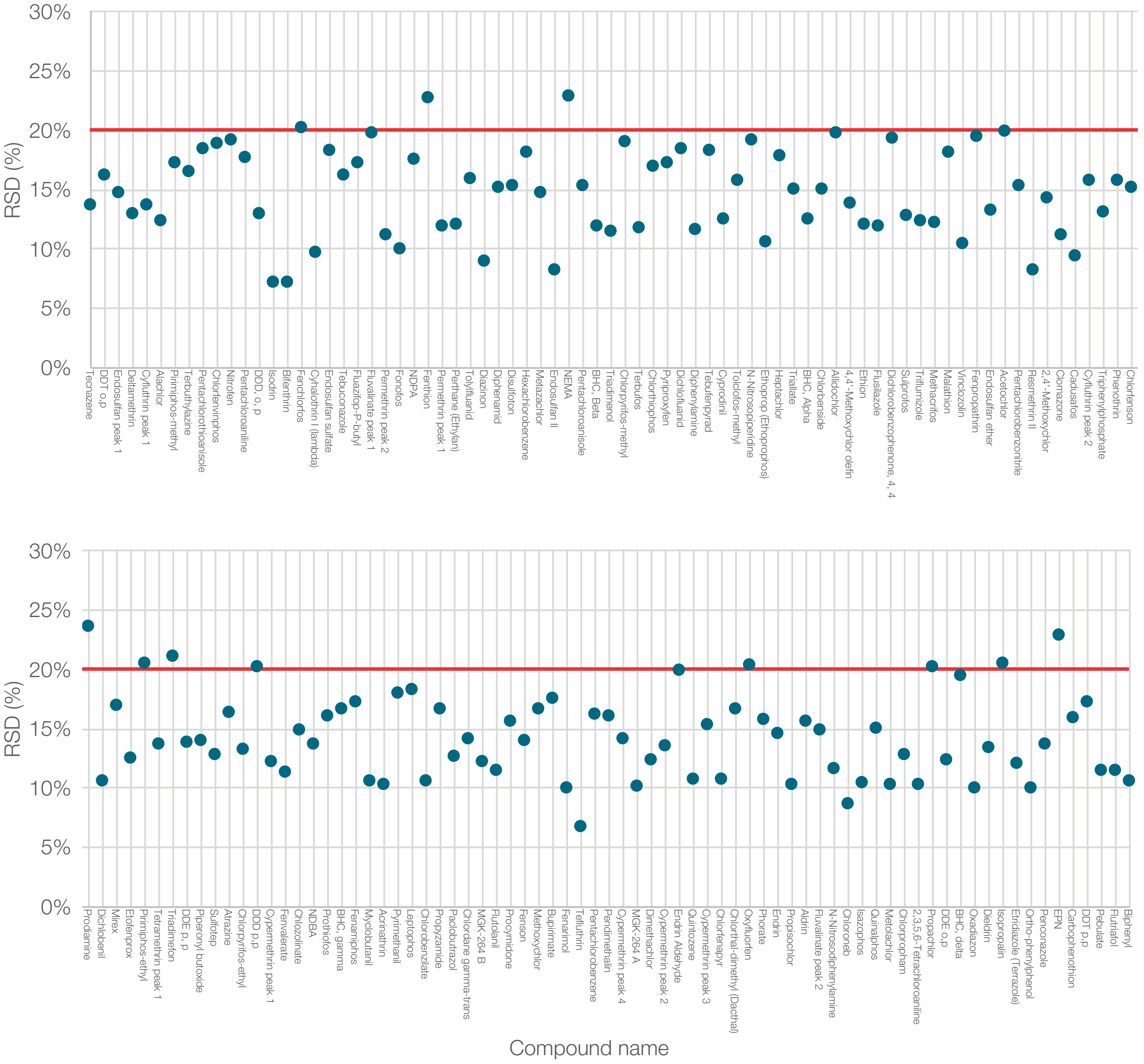


Figure 3. %RSD of the ion flux generated from each of the 150 pesticide residues assessed. The red line marks the 20% threshold.

SmartTune and Advanced Autotune

An important part of any GC-MS system is tuning. Ensuring the best sensitivity and that the mass calibration is accurate and the resolution achieved is adequate for the analysis to be confidently performed is essential. As quadrupole-based systems are scanning instruments, comprehensive tuning can be complex and time consuming.

The new dashboard for the Thermo Scientific™ ISQ™ 7000 single quadrupole GC-MS system and the TSQ 9000 GC-MS/MS system introduces the SmartTune feature for both Thermo Scientific™ ExtractaBrite™ and AEI source types, simplifying the tuning process and providing the user with a straight-forward, easy to follow tuning procedure with clear, visual indications of status and instruction (Figure 4).

Using the initial tuning parameters from a freshly cleaned ion source, subsequent tunes are compared against these values in order to maintain consistent instrument performance. Typically, a routine tune takes around 4–5 minutes to complete and generates a comprehensive report for easy tracking and compliance. In the event that a tune fails (for instance if a source is contaminated or the multiplier is exhausted), the system will automatically suggest guidance on remediation steps needed (Figure 5).

In addition to the SmartTune feature, the Advanced Autotune settings provide the experienced user with comprehensive control of all parameters. The systems are configurable with either SmartTune, Advanced Autotune, or both features enabled, streamlining workflows and simplifying the user experience.

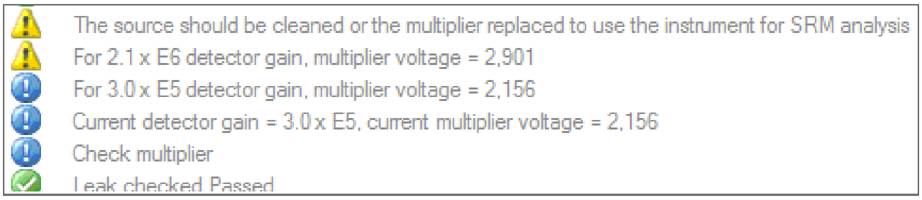
☐ First tune after installing a clean AEI ion volume.

Tuning completed successfully.

Tuning is complete.
Ready to run samples.
PASS
Check intensity passed.
Mass 219 intensity instrument value = 175,053,232
Mass 219 intensity tune results = 221,485,264
Check intensity
Check width passed

The tune file on the instrument is for an AEI ion source.

Figure 4. SmartTune dialogue window.



The source should be cleaned or the multiplier replaced to use the instrument for SRM analysis
For 2.1 x E6 detector gain, multiplier voltage = 2,901
For 3.0 x E5 detector gain, multiplier voltage = 2,156
Current detector gain = 3.0 x E5, current multiplier voltage = 2,156
Check multiplier
Leak checked Passed

Figure 5. SmartTune dialogue suggesting required remediation. In this instance the multiplier voltage has been artificially increased to simulate a dirty source/multiplier exhaustion scenario.

Conclusions

These preliminary results from this study demonstrate that the TSQ 9000 GC-MS/MS system configured with the AEI source provides an unmatched level of routine-grade robustness and represents a reliable analytical platform for routine high-throughput laboratories. Taken together, the experiments demonstrate:

- Ion flux stability over 900 sequential matrix injections, equivalent to one month's continuous data acquisition (33 samples per day for 27 consecutive days) and displaying consistent ion ratio response throughout.
- Relative standard deviations of <20% for over 90% of the 150 pesticides at a concentration of 10 ppb [µg/kg] using a single capillary column and no source maintenance.
- The SmartTune feature for fast, simple and reliable tuning for both the ExtractaBrite and AEI sources on both the ISQ 7000 and TSQ 9000 platforms, ensuring consistent performance with an easy interface.

References

1. http://quechers.cvua-stuttgart.de/
2. https://tools.thermofisher.com/content/sfs/brochures/WP-72048-MS-Sample-Preparation-WP72048-EN.pdf
3. SANTE/11813/2017. Guidance document on analytical quality control and method validation procedures for pesticides residues and analysis in food and feed. Supersedes SANTE 11945/2015. Implemented by 01/01/2018.

Find out more at **thermofisher.com/TSQ9000**