APPLICATION BRIEF 000019

Improving the routine testing of difficult-to-analyze pesticide residues by using the Thermo Scientific TraceGOLD TG-Contaminants column with GC-MS/MS technology

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Goal

Address a key challenge to contract testing laboratories (CTLs) by offering a rapid, robust analytical solution for difficult-to-analyze compounds:

- Showcase the capabilities of a new column technology for retention and separation in the shortest possible time frame
- Highlight the robustness of the injector module in heavy matrices
- Demonstrate that the Thermo Scientific™ TSQ™ 9000 Triple Quadrupole GC-MS/MS System with AEI source has the required sensitivity to meet European Union (EU) regulations in multiple matrices

This brief will establish the improved performance offered by this configuration for a selection of compounds.

Introduction

With the increasing number of directives and regulations, many sectors of food and environmental industries are subcontracting their analysis needs to CTLs. Examples of these measures and what they have established include: Directive 2000/06/EC (a framework in the field of water policy), Directive 2000/118/EC (protection of groundwater against pollution and deterioration), Directive 96/23/EC (a framework for residue monitoring in animals and animal products), Regulation (EC) No 396/2005 (maximum residue levels for pesticides in food), Regulation (EC) No 1881/2006 (maximum levels for contaminants in food), Regulation (EU) No 37/2010 (a list of maximum residue limits (MRLs) for permitted substances), and many others.

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Approximately one thousand active substances are currently used in pesticide formulations. In addition, metabolites, degradation products, and ''old'' (persistent) pesticides must also be considered by pesticide residue analysts.

Gas chromatography combined with mass spectrometry (GC-MS) provides 70-80% of the required parameters for pesticide analysis, with liquid chromatography (LC-MS), ion chromatography (IC-MS), or specific detectors covering the remaining parameters. This method utilizes GC-MS with a limit of detection of 0.5 pg on the column. The recommended extraction technique depends on the matrix, and include: liquid-liquid extraction (LLE) or solid-phase extraction (SPE) for water, accelerated solvent extraction (ASE) for biota samples, and the QuEChERS method for food samples. Samples prepared using any of these methods can be analyzed on the same GC column.

Strategy

With the goal of creating a multi-residue method with a run-time under 20 minutes, a column with low polarity was selected and the retention was adapted in order to efficiently retain the volatile compounds while minimizing the retention of late eluting compounds, such as pyrethroids, and other molecules that tend to tail.

This new multi-residue GC-MS/MS method detects up to 350 pesticides, including organophosphorus, organochlorine, pyrethroids, triazine, azole, and PAH or PCB and is run on a Thermo Scientific™ TraceGOLD™ TG-Contaminants GC column. The Thermo Scientific™ Thermospray Injector (TSI) is extremely robust, allowing users to inject significant sample volumes for improved detection.

All 350 contaminants were detected at concentrations between 0.2-0.5 pg/µL. In this application brief, we focus on known difficult-to-analyze compounds. Table 1 provides information on the chemical class and possible cause(s) to the analysis challenges. In terms of sensitivity and limit of quantitation (LOQ), natural water in environmental regulations or organic food in food safety applications pose the most analytical challenges. The chromatograms presented are in accordance with lowest regulation levels.

If a peak occurs at the specific retention time, (for example, PCB 28/31 or benzo-b (or “j”, or “k”) -fluoranthene, or HBCCD peaks could coelute) the sum of peaks can be used as a quantification result, or the sample could be reinjected for confirmation on a column which is specifically designed for those purposes.[1]

Table 1: Selection of compounds that are known to be difficult-to-analyze

Type	Family	Chemical formula	Common name	CAS number	Comments and customer feedback
Insecticide, acaricide	Organophosphate	$C_4H_7Cl_2O_4P$	Dichlorvos (DDVP)	62-73-7	Volatile, mainly sensitive to evaporation step/ sample prep
Acaricide, insecticide, nematocide	Organophosphorus	$C_5H_{12}NO_3PS_2$	Dimethoate	60-51-5	Often transferred from GC to LC
Herbicide, algicide	Chlorotriazine	$C_7H_{12}ClN_5$	Simazine	122-34-9	Tailing peak, sensitive to column condition
Fungicide	Aromatic	$C_8Cl_4N_2$	Chlorothalonil	1897-45-6	Very sensitive to column condition, difficult to quantify
Herbicide	Uracil	$C_9H_{13}BrN_2O_2$	Bromacil	314-40-9	Peak tailing
Fungicide	Phthalimide	$C_9H_4Cl_3NO_2S$	Folpet	133-07-3	Sensitive to column condition, reactive
Fungicide	Dicarboximide	$C_{13}H_{13}Cl_2N_3O_3$	Iprodione	36734-19-7	Very sensitive to column condition, even on a new column
Fungicide	Conazole	$C_{15}H_{17}Cl_2N_3O_2$	Propiconazole	60207-90-1	Very sensitive to column condition as all azoles
Herbicide	Amide, oxazole	$C_{18}H_{24}N_2O_4$	Isoxaben	82558-50-7	Often transferred from GC to LC
Insecticide, acaricide	Formamidine	$C_{19}H_{23}N_3$	Amitraz	33089-61-1	Low response, very sensitive to column condition
Fungicide	Dicarboximide	$C_{22}H_{18}N_2O_4$	Famoxadone	131807-57-3	Often transferred from GC to LC
Insecticide	Pyrethroid	$C_{22}H_{19}Br_2NO_3$	Deltamethrin	52918-63-5	Low response, peak tailing
Insecticide	Pyrethroid	$C_{23}H_{19}ClF_3NO_3$	L-Cyhalothrin	91465-08-6	Very low LQ required
Insecticide	Rotenoids	$C_{23}H_{22}O_6$	Rotenone	83-79-4	Low response, peak tends to widen and disappear

Method

Gas chromatography products and methods

Thermo Scientific™ TRACE™ 1310 Gas Chromatograph with Thermo Scientific™ Instant Connect Thermospray SSL Injector Module

Thermo Scientific™ LinerGOLD™ Splitless Precision Liner, Quartz Wool, 5 mm (P/N 453T2999-UI)

TraceGOLD TG-Contaminants column, 15 m × 0.25 mm ID × 0.1 µm (P/N 26056-0350)

Thermo Scientific™ GuardGOLD™ 10 m x 0.53 mm ID (P/N 26050-1053) with Thermo Scientific™ Mini Capillary Union (P/N 290GU499)

Injection volume	3 µL (DCM)
Injector temperature	200 °C
Splitless time	1 min
Column flow	1.2 mL/min

Mass spectrometry products and methods

TSQ 9000 triple quadrupole system with AEI source (300°C) Electron ionization mode @ 70 eV T-SRM acquisition type

Performance

Following an environmental quality standards (EQS) protocol method, standards are injected over different concentration ranges (from 0.2-1 pg/µL to 500 pg/µL). Example chromatograms of difficult-to-analyze compounds at concentration between 0.2 pg/µL to 5 pg/µL (meeting or exceeding legislation requirements) are shown in Figures 1-14 along with a summary of the results of the corresponding calibration curves (Table 2).

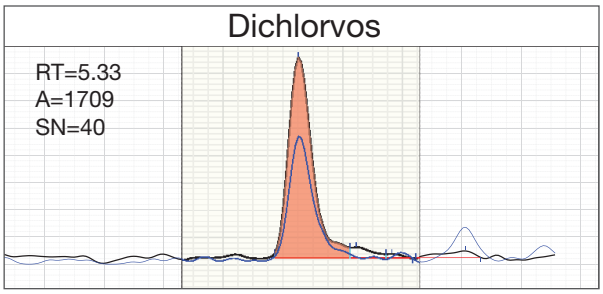

Figure 1. Data showing two SRM transitions (0.2 pg/µL) for Dichlorvos

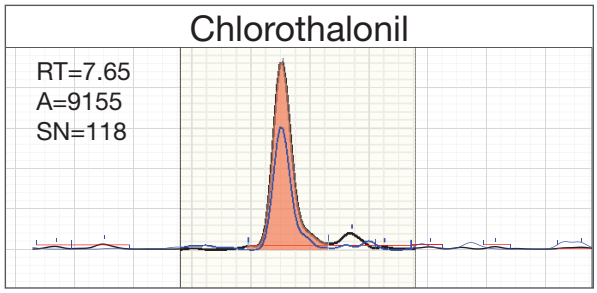

Figure 4. Data showing two SRM transitions (0.5 pg/µL) for Chlorothalonil

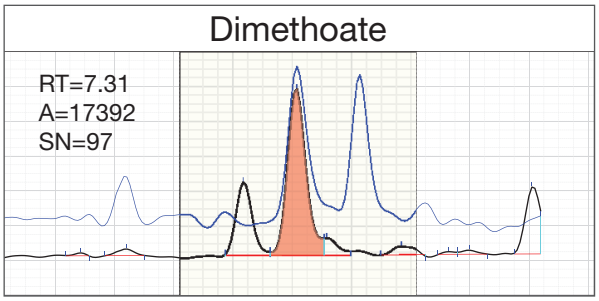

Figure 2. Data showing two SRM transitions (2 pg/µL) for Dimethoate

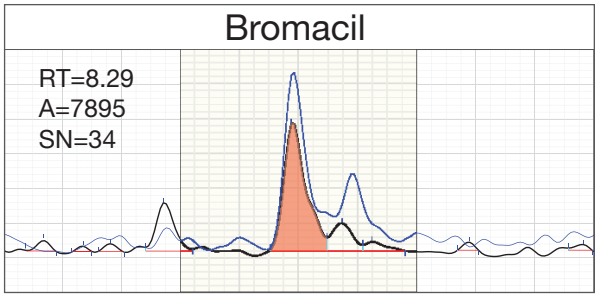

Figure 5. Data showing two SRM transitions (2 pg/µL) for Bromacil

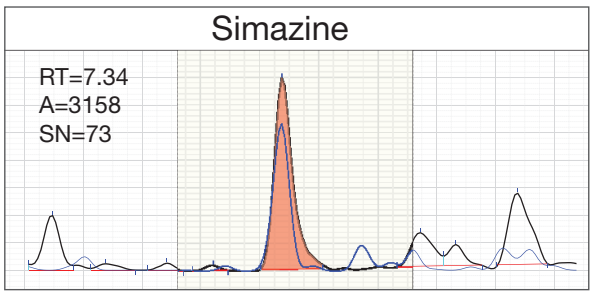

Figure 3. Data showing two SRM transitions (0.5 pg/µL) and for Simazine

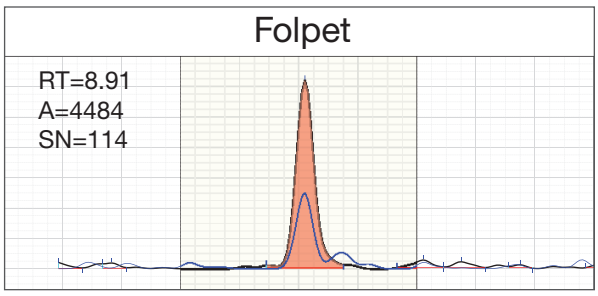

Figure 6. Data showing two SRM transitions (2 pg/µL) for Folpet

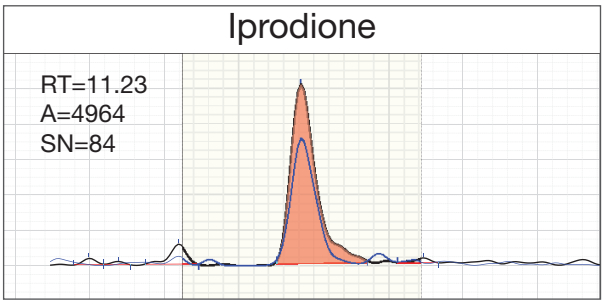

Figure 7. Data showing two SRM transitions (1 pg/µL) for Iprodione

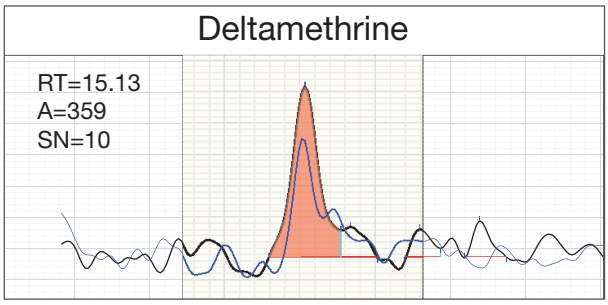

Figure 11. Data showing two SRM transitions (0.5 pg/µL) for Deltamethrine

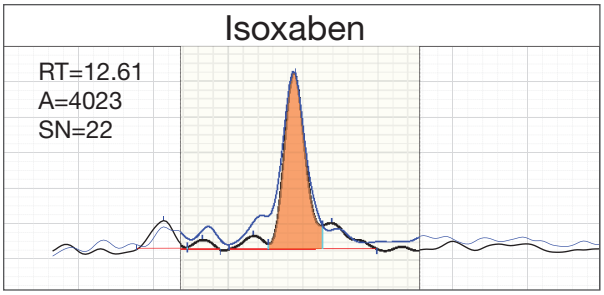

Figure 8. Data showing two SRM transitions (5 pg/µL) for Isoxaben

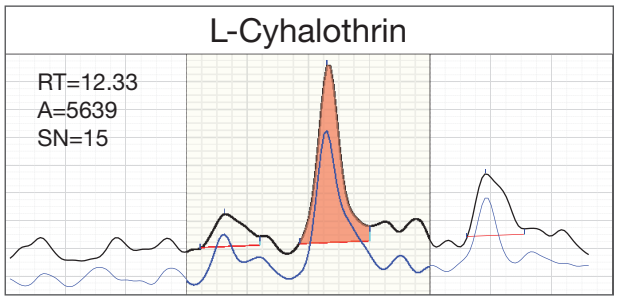

Figure 12. Data showing two SRM transitions (0.5 pg/µL) for L-Cyhalothrin

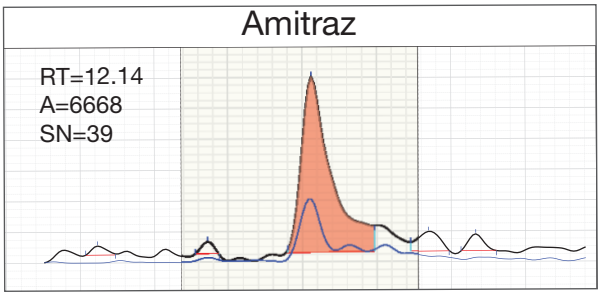

Figure 9. Data showing two SRM transitions (1 pg/µL) and for Amitraz

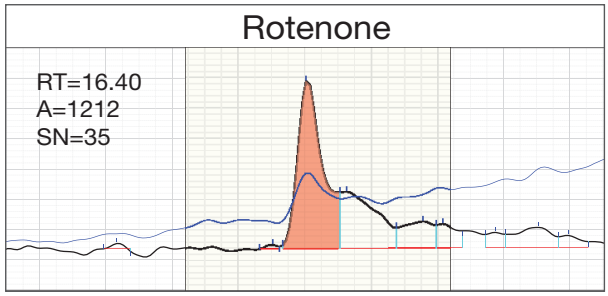

Figure 13. Data showing two SRM transitions (5 pg/µL) for Rotenone

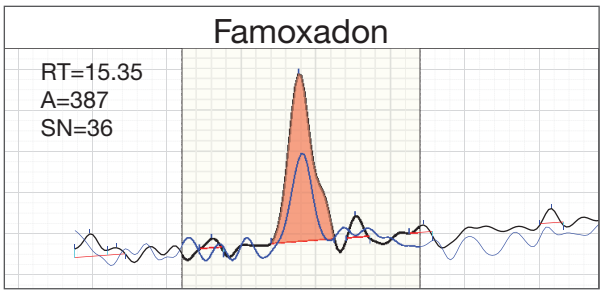

Figure 10. Data showing two SRM transitions (1 pg/µL) for Famoxadon

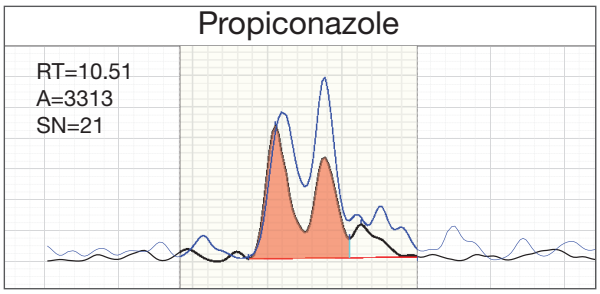

Figure 14. Data showing two SRM transitions (0.5 pg/µL) for Propiconazole

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Table 2. Results from a 13-point calibration curve (0.2 pg/L to 500 pg/µL) for a selection of difficult-to-analyze compounds

Compound	Coefficient of determination (R^2)	Relative deviation at level shown (% difference)	Relative deviation at 10pg/µL (% difference)	Relative deviation at 500pg/µL (% difference)
Dichlorvos	0.998	-1.9	3.8	-0.8
Dimethoate	0.997	-4	-3.3	-1
Simazine	0.996	-15	-4.6	-1.2
Bromacil	0.997	15	-9.3	-0.8
Chlorothalonil	0.994	28.7	-14.2	-2
Folpet	0.997	-2.4	-2.3	-0.8
Iprodione	0.998	23.7	-8.9	-0.8
Amitraz	0.994	9.3	-22.6	-1.4
Isoxaben	0.999	-22.2	3.4	-0.5
Famoxadon	0.999	-10	46	-0.1
Deltamethrine	0.998	64	33	-0.5
Rotenone	0.999	-18.9	-11.6	-0.4
L-Cyhalothrin	0.997	63.2	-11.7	-1
Propiconazole S1S2	0.993	-23.4	-14.8	-1.4

Conclusion

The TraceGOLD TG-Contaminants column demonstrates an excellent ability to separate compounds of interest while minimizing tailing.

This single method enables the analysis of up to 350 multi-class contaminants in less than 20 minutes.

The combination of the TraceGOLD TG-Contaminants column, the TSI injector, and the TSQ 9000 system with AEI source provides a robust workflow with improved sensitivity for all compounds at a 0.5 pg/µl level or lower.

The strong linearity shown between 0.2 pg/µL and 500 pg/µL allowed detection and quantitation of many contaminants in a range of matrices, demonstrating that samples prepared by multiple approaches can be analyzed using this method.

This integrated and optimized workflow offers an innovative, rapid and robust analytical solution for contract testing laboratories, enabling the analysis of a wider class of contaminants in less time, at a lower cost, and without compromising performance.

Reference

1. Application Brief 22136: Resolving critical PCB isomers (28/31 and 128/167) using the Trace TR-PCB 8MS column, Thermo Fisher Scientific, Les Ulis, France and Runcorn, UK, 2021.

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

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