Application note | 002225

Food safety

# Reducing running costs for GC-MS/MS analysis of pesticide residues using hydrogen carrier gas


## Authors

Łukasz Rajski[1], Daniel Kutscher[1], Adam Ladak[2]

[1]Thermo Fisher Scientific, Bremen, Germany

[2]Thermo Fisher Scientific, Hemel Hempstead, United Kingdom



## Keywords

Helium saving, hydrogen carrier gas, HeSaver-$H_2$Safer, TSQ 9610 Triple Quadrupole GC-MS/MS, pesticides, SRMs, timed-SRM, QuEChERS


## Goal

This application note demonstrates the performance of the Thermo Scientific™ TSQ™ 9610 Triple Quadrupole GC-MS/MS system for the analysis of more than 180 pesticide residues using hydrogen carrier gas.

## Introduction

Helium is the standard carrier gas for gas chromatography thanks to its high chromatographic efficiency and inertness. This is particularly important when considering applications involving mass spectrometric detection (GC-MS), where these characteristics ensure the best performance in terms of sensitivity. This has resulted in well-established, validated, and regulated GC and GC-MS methods using helium as the carrier gas. However, helium is a limited and non-renewable natural resource,[1] and recent price increases and supply issues caused by shortages have led laboratories and instrument manufacturers to investigate possible mitigation options, such as switching to alternative carrier gases or reducing the consumption of helium.

A possible alternative carrier gas, long established in regulated methods involving capillary GC combined with other detection systems such as flame ionization detection (FID), is hydrogen. Hydrogen has a diffusivity comparable to helium and is even preferable because its viscosity is about half, allowing lower inlet pressure for a given gas velocity, and maintaining the optimum separation efficiency at higher flow rates,

thus offering shorter analysis time. Additionally, hydrogen generators can create the required amount exactly when needed, offering laboratories a safe, steady, and renewable supply of hydrogen without the need to store a flammable gas. Therefore, using hydrogen instead of helium is an attractive solution because of its analytical and practical advantages; however, there are still important considerations before it can be used. Due to its flammability, a GC system using hydrogen needs to be equipped with a hydrogen sensor in the GC oven, capable of turning off the heating and the gas supply in case of detected leaks. Many existing validated methods are based on helium and must be re-optimized and re-validated in the case of carrier gas conversion. This is particularly important for GC-MS methods as the use of hydrogen affects the vacuum conditions in the ion source and therefore the ionization process, often with consequent decrease of the response. Despite these shortcomings, many GC and GC-MS applications are successfully run by using hydrogen, with clear advantages in terms of speed and cost of analysis.

A common application of gas chromatography coupled to triple quadrupole mass spectrometry is the analysis of pesticide residues in food samples. This is essential to monitor if pesticides are being applied on crops in compliance with regulations (label instructions) to protect the health of consumers. This application note demonstrates the performance of the Thermo Scientific™ TSQ™ 9610 Triple Quadrupole GC-MS/MS system equipped with a Thermo Scientific™ Advanced Electron Ionization (AEI) source for the analysis of more than 180 pesticide residues, many only accessible for analysis using GC-MS/MS.

## Instrumentation

The Thermo Scientific™ TRACE™ 1610 GC connected to the TSQ 9610 mass spectrometer was equipped with a Thermo Scientific™ iConnect™ HeSaver-$H_2$Safer™ SSL Injector module. The HeSaver-$H_2$Safer technology decouples the gas used for pressurizing the inlet and splitting the sample from the actual carrier gas supplied only to the column for the gas chromatographic separation of the analytes. It can be used in conjunction with helium or hydrogen carrier gas and decreases the carrier gas consumption considerably. The pressurizing gas can be an inexpensive alternative (e.g., nitrogen or argon), replacing the valuable carrier gas for the split and purge flows, and it is efficiently prevented from entering the column during separation. The pressurizing gas has also the benefit to eliminate the contact between the analytes and reactive carrier gas (hydrogen) in the hot injector, and consequently decreases the possibility of unwanted reactions. When the HeSaver-$H_2$Safer mode is used, a significant cost savings and prolonged cylinder lifetime can be realized when using helium, whereas the main advantage of the limited gas consumption for hydrogen is related to operational safety. The maximum amount of hydrogen flowing in the system is limited so that there is no risk to reach hazardous concentrations even in case of column breakage, and therefore a hydrogen sensor in the GC oven is not necessary.

The TSQ 9610 mass spectrometer was operated in timed-SRM mode. All the transitions were carefully optimized with Thermo Scientific™ AutoSRM software to obtain the highest possible sensitivity. The GC-MS method details are listed in Table 1, whereas the transitions, collision energies, and retention times can be found in Appendix 1. For the data acquisition and treatment, Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software was used.

The compound identification criteria were taken from the DG SANTE guidance document.[2] According to this document, two ion transitions are required to identify a given pesticide. The chromatographic peaks of those transitions must fully overlap, and signal-to-noise ratio must be equal or greater than 3. The ion ratio should be within ±30% (relative) of average of calibration standards. The retention time shift should not be greater than ±0.1 min. The aim was to check the performance at the default Maximum Residues Limit (MRL) of 0.01 mg/kg, applicable for baby food, without considering the MRLs mentioned in the Commission Directive 2006/125/EC of 5 December 2006.

A full list of transitions used with hydrogen as the carrier gas is included in Appendix 1. In a previously published method using helium, in general three transitions were monitored per analyte. However, the method presented here applied, in the great majority of cases, only two transitions. Moreover, the retention time window with hydrogen was set narrower than the window applied for helium (0.3 min vs. 0.7 min). The differences in the total transitions number and in the retention time window width influenced the dwell time applied per analyte, which could be extended. In the method with helium carrier gas, the shortest dwell time was 3.28 ms, whereas the current method with hydrogen carrier uses 8.48 ms, thus helping to increase the sensitivity and compensate for losses typically occurring with the use of hydrogen as the carrier gas.

Table 1. GC-MS method parameters

| TRACE 1610 GC | |
|---|---|
| **Injector** | |
| Injector type | iConnect Split/Splitless (SSL) injector upgraded with the HeSaver-$H_2$Safer (P/N MI-190000-0022) |
| Temperature [°C] | 260 |
| Pressuring gas | Nitrogen |
| Split mode | Splitless |
| Split flow [mL/min] | 50 (Nitrogen) |
| Splitless time [min] | 1 |
| Septum purge flow [mL/min] | 5 (Nitrogen) |
| Vacuum compensation | On |
| Liner | Thermo Scientific™ LinerGOLD™ Single Taper Liner with Wool (P/N 453A1925-UI) |
| Injection volume [µL] | 1 |
| **Oven** | |
| Analytical column | Thermo Scientific™ TraceGOLD™ TG-5SilMS (20 m × 0.18 mm × 0.18 µm) (P/N 26096-5780) |
| Carrier gas | Hydrogen |
| Carrier gas flow [mL/min] | 1.2 |
| **Oven temperature program** | |
| Ready delay [min] | 1.3 |
| Temperature 1 [°C] | 40 |
| Hold [min] | 1.5 |
| Rate [°C/min] | 25 |
| Temperature 2 [°C] | 90 |
| Hold [min] | 1.5 |
| Rate [°C/min] | 25 |
| Temperature 3 [°C] | 180 |
| Hold [min] | 0 |
| Rate [°C/min] | 5 |
| Temperature 4 [°C] | 280 |
| Hold [min] | 0 |
| Rate [°C/min] | 10 |
| Temperature 5 [°C] | 300 |
| Hold [min] | 5 |
| **TSQ 9610 GC-MS/MS** | |
| Ion source | Advanced Electron Ionization (AEI) Source |
| Transfer line temperature [°C] | 300 |
| Ion source temperature [°C] | 320 |
| Emission current [µA] | 10 |
| Electron energy [eV] | 50 |

## Sample preparation

During this study, two matrices (baby food and honey) were tested, and the results evaluated for a total of 181 pesticides.

Samples were prepared using the QuEChERS method.[3] In short, a 10 g portion of the sample was weighed in a 50 mL PTFE centrifuge tube, subsequently 10 mL of acetonitrile was added and the samples were shaken in an automatic axial extractor for 7 min. Afterwards, 4 g of magnesium sulphate, 1 g of sodium chloride, 1 g of trisodium citrate dihydrate, and 0.5 g of disodium hydrogen citrate sesquihydrate were added (Thermo Scientific™ QuEChERS EN 15662 Method Extraction Kit, P/N S1-10-EN-KIT), and the samples were again shaken in the automatic axial extractor for 7 min. The extract was then centrifuged (3,700 rpm) for 5 min. A 5 mL volume of the supernatant was transferred to a 15 mL PTFE centrifuge tube containing 750 mg of $MgSO_4$ and 125 mg of PSA. The extract was shaken in a vortex for 30 s and centrifuged again (3,700 rpm) for 5 min. The extract was transferred to an amber vial and acidified with 10 µL formic acid 5% per mL of extract.

## Consequences of switching the carrier gas type from helium to hydrogen

Substitution of helium with hydrogen has some important consequences for the chromatographic separation as well as for the MS detection. Maintaining the same column, carrier gas flow rate, and oven program, hydrogen provides shorter retention times than helium. That should be considered as an advantage because it improves the sample throughput. However, the retention time shift is not the same for all the analytes (in this study retention time shifts between 0.5 and 2 minutes were observed depending on the overall elution time of a given compound), so the new retention times must be confirmed first. This can be accomplished with additional injections of standard solutions with wider retention time windows, or in full scan MS mode.

Hydrogen provides a better chromatographic efficiency (often expressed as a higher number of the theoretical plates), which results in slightly narrower chromatographic peaks (compared to helium), however this had a negligible impact on the MS/MS method, as the number of the data points per chromatographic peak remained unchanged.

For some of the analytes, the presence of hydrogen affected the ionization process, and the spectrum obtained with hydrogen was different than the spectrum acquired with helium. Figure 1 shows a full mass spectrum for fipronil using both helium and hydrogen. Not only is the base peak different, but the relative intensities of the remaining major ions have also changed. This difference should not be considered a critical issue, as targeted methods used for pesticide residues analysis rely on compound identification based on retention time and ion ratios between compound specific transitions, and not on the fidelity to spectral libraries. Nevertheless, in some cases, a re-optimization of the SRM transitions must be performed to search for more sensitive alternatives. The sensitivity of the final method was sufficient to analyze the pesticides at 0.005 mg/kg. Figure 2 shows examples of the chromatographic peak obtained at this concentration level.

## Linearity

Linearity was checked in the concentration range 0.005–0.500 mg/kg. According to the DG SANTE guidance document, the linearity evaluation is based on the back calculated concentrations. To include a point into the calibration curve, its back-calculated concentration should not deviate from the true concentration by more than 20%. More than 97% of the 181 evaluated compounds showed a linear response within the investigated concentration range in both the tested matrices (more detailed information can be found in Appendix 2). Figure 3 highlights the linearity observed for chlorfenson in baby food and for triadimenol in honey, as a representative example.

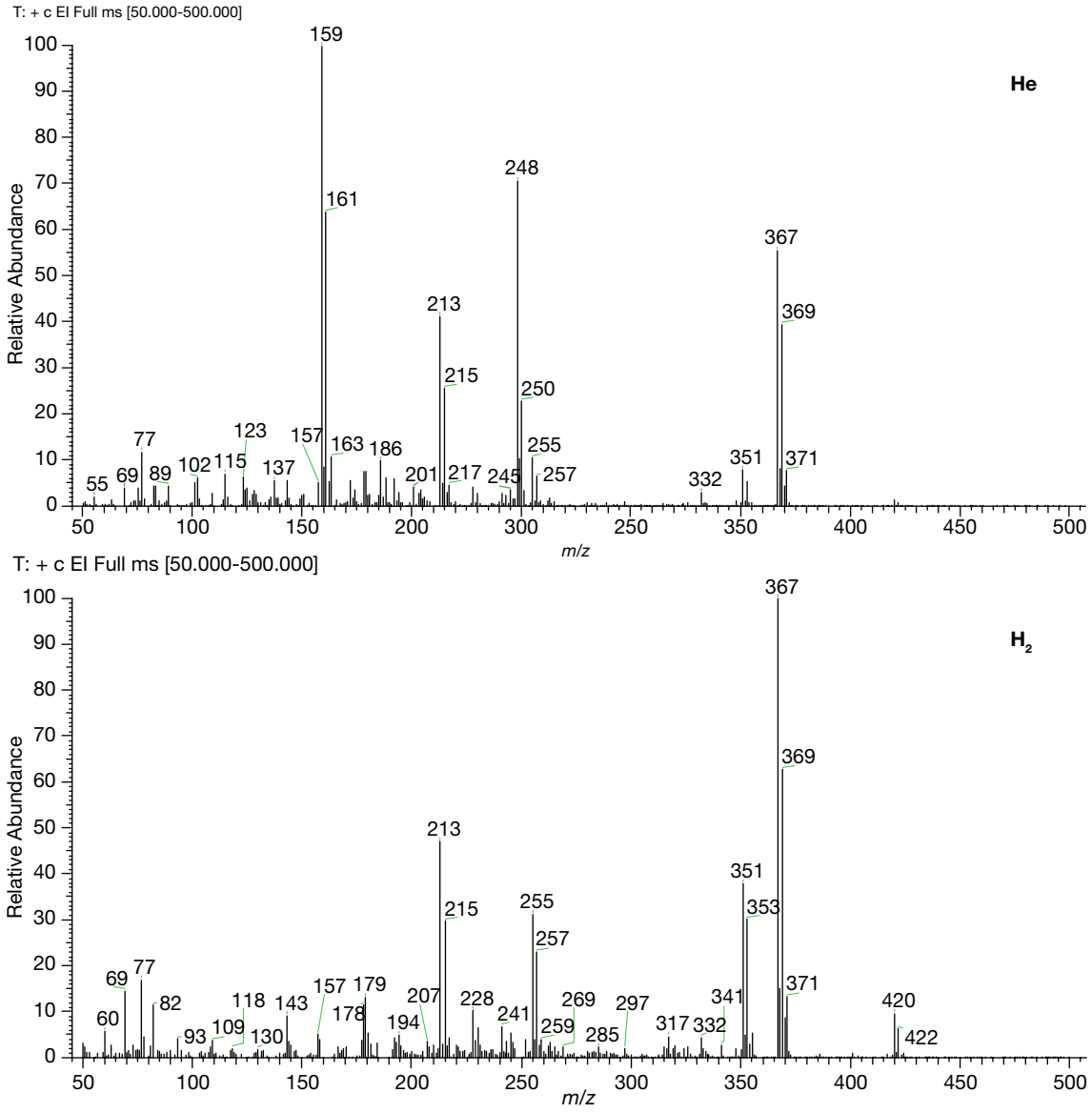


Figure 1. Fipronil, full scan spectra obtained with helium (top) and hydrogen (bottom) carrier gas

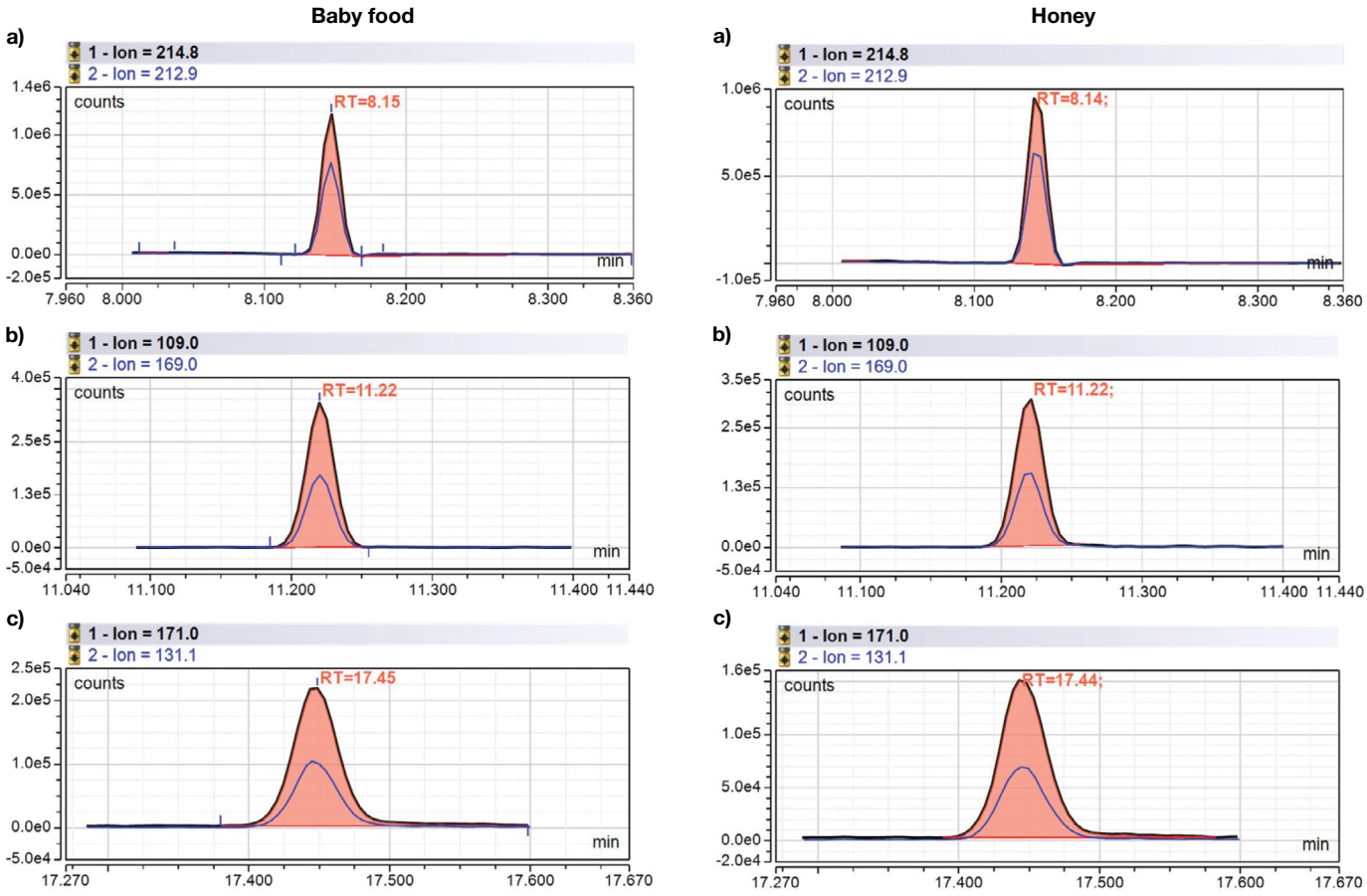


Figure 2. Examples of peaks obtained at 0.005 mg/kg in baby food and honey, using hydrogen as carrier gas: a) pentachlorobenzene, b) fenthion, c) tebufenpyrad

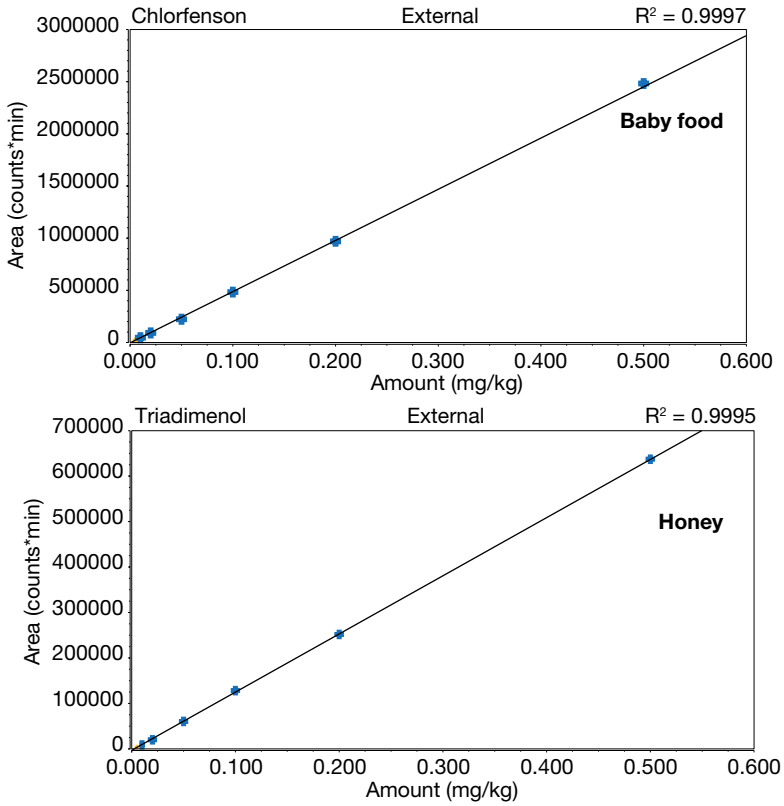


Figure 3. Calibration curve of chlorfenson in baby food and triadimenol in honey, with hydrogen as carrier gas; concentration range 0.005–0.500 mg/kg

## Repeatability

Repeatability was evaluated at two concentration levels: 0.01 mg/kg and 0.05 mg/kg. The samples were injected in quintuplicate and subsequently the relative standard deviation was calculated. In both matrices, 98% of the evaluated pesticides showed an RSD equal or lower than 10%. At 0.05 mg/kg the results were slightly better, with 99% of the analytes showing RSD ≤10%. Although the SANTE guideline allows for RSD values of up to 20% for a given compound, it is important to consider that this number applies to the full workflow, including extraction and clean-up of the sample. Therefore, an analytical method must allow for some margin to always ensure compliance. Figure 4 shows the distribution of the RSD results (for more details see Appendix 2), including data obtained on baby food with helium carrier gas as reference (grey bar). As can be seen, the performance with hydrogen is highly comparable to the performance with helium.

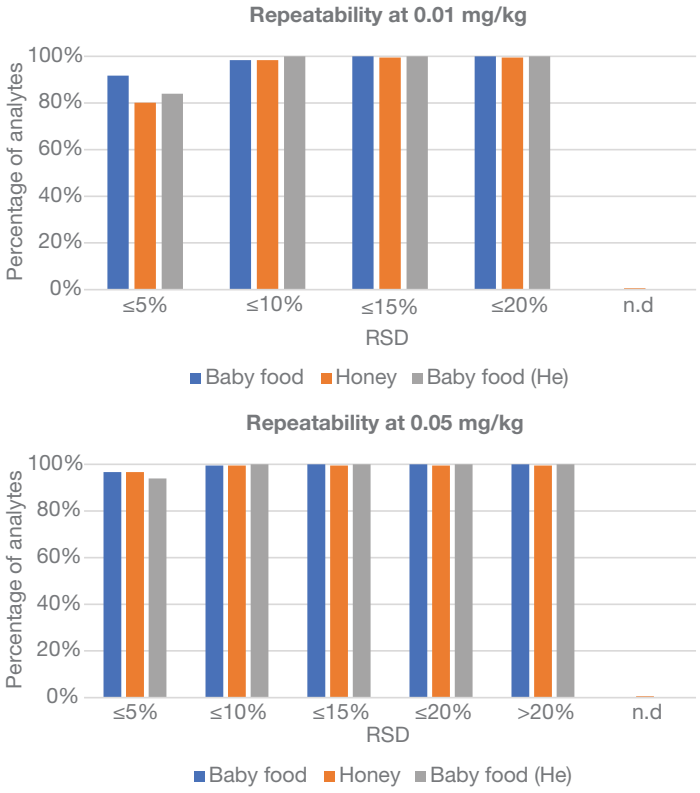


**Figure 4. Repeatability (n = 5) of 181 pesticides in two matrices (baby food and honey) with hydrogen as carrier gas, compared with repeatability of pesticides in baby food using carrier helium**

## Implication on gas consumption

Although the data presented in this study clearly demonstrates compliance with SANTE guidelines, the use of hydrogen as carrier gas may not be the ideal solution in all cases. Optimum performance is often only achieved with helium. The use of the HeSaver-$H_2$Safer technology offers an alternative to the use of carrier hydrogen, especially for GC-MS methods. Thanks to the limited carrier gas consumption of a few mL/min, it offers the flexibility to maintain helium as the carrier gas with significant savings, mitigating helium shortage issues.

Helium gas consumption with a standard SSL injector and the GC-MS method described in this note is 1.3 liters per sample. However, this volume can be reduced to 0.32 liters per sample when the HeSaver-$H_2$Safer mode is used. Thus, the helium consumption with the HeSaver-$H_2$Safer mode would be four times lower than with the standard SSL injector. If the instrument was running 365 days per year and 24 hours per day, one helium cylinder would last almost 2 years. The Thermo Scientific™ Helium Saver Calculator tool[4] offers an easy-to-use and intuitive interface to estimate helium consumption and cost impact on individual laboratories activities. GC parameters regarding column dimensions, carrier gas and split flow settings, as well as helium and nitrogen costs are adjustable to reflect a given laboratory's methodology and regional gas cost to provide estimates on helium cylinder lifetime and cost savings. It is worth highlighting that the use of the HeSaver-$H_2$Safer technology does not affect sensitivity or retention times and does not involve any method re-optimization when switching from a standard SSL injector.[5]

## Conclusions

It has been demonstrated that the TSQ 9610 GC-MS/MS is capable of identifying and quantifying pesticides at 0.01 mg/kg concentration level when hydrogen is used as the carrier gas. The proposed method provides a viable alternative for laboratories performing the testing for pesticide residues in a wide range of food matrices and looking at ways to circumvent helium price increases or potential supply shortages. While the use of hydrogen may have a negative impact on detection sensitivity (and hence the ability to meet established detection limit requirements), the use of the AEI ion source together with a few changes in the choice of transitions can offset these and allow to achieve comparable performance at reduced running costs.

Key findings of the application are summarized in the following:

- The use of the HeSaver-$H_2$Safer technology allows for a safe and compliant use of hydrogen as an alternative carrier gas in GC/GC-MS applications without the need to install a hydrogen sensor and removes any risk of unwanted reactions with the sample in the hot SSL injector. Additionally, it offers the flexibility to maintain helium as the carrier gas with a significant savings, with the benefit to avoid method re-optimization while mitigating helium shortage issues.
- When used with hydrogen, the limited carrier gas consumption offered by the HeSaver-$H_2$Safer mode permits a very controlled system demand for hydrogen, making this solution ideal for laboratories working with hydrogen generators.
- Migrating the GC-MS/MS method from helium to hydrogen requires an adaptation of method parameters to address (i.e., retention time shift and different fragmentation patterns).
- All target pesticides met the regulatory RSD requirement of less than 20%. The relative standard deviation for N=5 repeats of each sample type at 0.01 mg/kg was equal or lower than 10% for 98% of the evaluated compounds.
- 97% of pesticides in baby food and 98% in honey showed a linear response in the concentration range 0.005–0.500 mg/kg.
- For laboratories requiring best detection sensitivity, or searching for non-target pesticides, the SSL upgraded to HeSaver-$H_2$Safer technology allows the use of carrier helium with a reduced consumption by a factor of four, maintaining the method.

### References


1. The Science Of Helium And Why Global Supplies Are Running Low: Short Wave : NPR
2. Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis In Food And Feed, SANTE 11312/2021.
3. Thermo Fisher Scientific, Application Note 000437: Confident analysis of ultra-trace pesticides residues in baby food using triple quadrupole GC-MS. https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-000437-gc-ms-pesticides-baby-food-an000437-en.pdf
4. Thermo Fisher Scientific Helium Saver Calculator. https://www.thermofisher.com/it/en/home/industrial/chromatography/chromatography-learning-center/chromatography-consumables-resources/chromatography-tools-calculators/helium-saver-calculator.html
5. Thermo Fisher Scientific, Product Spotlight SL001922: Reduction of helium usage for the analysis of pesticide residues in botanical dietary supplements using GC-MS/MS with the HeSaver-$H_2$Safer technology. https://assets.thermofisher.com/TFS-Assets/CMD/brochures/sl-001922-gc-ms-ms-hesaver-h2safer-botanical-pesticides-sl001922-en.pdf


## Appendix 1. List of the target compounds, retention times, and monitored transitions

### Part 1

| Pesticide | RT [min] | Window [min] | Precursor mass 1 | Product mass 1 | Collision energy 1 | Precursor mass 2 | Product mass 2 | Collision energy 2 | Precursor mass 3 | Product mass 3 | Collision energy 3 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2,3,5,6-Tetrachloroaniline | 8.72 | 0.3 | 230.8 | 157.9 | 18 | 230.8 | 159.8 | 18 | | | |
| 2,4'-Methoxychlor | 15.65 | 0.3 | 121.1 | 78 | 20 | 197.1 | 165.1 | 15 | 227.1 | 121 | 10 |
| 3,4-Dichloroaniline | 7.66 | 0.3 | 160.9 | 99 | 20 | 160.9 | 126 | 10 | | | |
| 4,4'-Methoxychlor olefin | 15.19 | 0.3 | 238.1 | 152.1 | 34 | 238.1 | 223.1 | 10 | | | |
| Acetochlor | 10.35 | 0.3 | 146.1 | 130 | 24 | 223.1 | 132 | 20 | | | |
| Acrinathrin | 19.38 | 0.3 | 181 | 152 | 22 | 208.1 | 180.9 | 8 | 289 | 93.1 | 8 |
| Alachlor | 10.48 | 0.3 | 188.1 | 130 | 32 | 188.1 | 160.1 | 8 | | | |
| Aldrin | 11.16 | 0.3 | 254.9 | 219.9 | 20 | 262.7 | 192.9 | 32 | | | |
| Allidochlor | 6.67 | 0.3 | 132 | 56.1 | 8 | 134 | 56 | 8 | | | |
| Anthraquinone | 11.18 | 0.3 | 208.1 | 152 | 22 | 208.1 | 180.1 | 10 | | | |
| Atrazine | 9.44 | 0.3 | 200.1 | 122 | 8 | 215.1 | 58.1 | 10 | | | |
| Azinphos-ethyl | 18.95 | 0.3 | 132 | 77 | 12 | 160 | 77 | 16 | | | |
| Azinphos-methyl | 17.88 | 0.3 | 132 | 77 | 12 | 160 | 50.9 | 34 | 160 | 77 | 16 |
| Benfluralin | 8.98 | 0.3 | 292 | 160 | 20 | 292 | 264 | 8 | | | |
| BHC, Alpha | 9.13 | 0.3 | 180.9 | 144.9 | 14 | 216.9 | 181 | 8 | | | |
| BHC, Beta | 9.42 | 0.3 | 216.9 | 180.9 | 8 | 218.9 | 183 | 8 | | | |
| BHC, delta | 9.89 | 0.3 | 180.9 | 144.9 | 14 | 218.9 | 182.9 | 8 | | | |
| BHC, gamma | 9.53 | 0.3 | 180.9 | 144.9 | 12 | 218.9 | 183 | 8 | | | |
| Bifenthrin | 17.11 | 0.3 | 165.1 | 163.6 | 24 | 181 | 165.9 | 10 | 181 | 179 | 12 |
| Biphenyl | 7.38 | 0.3 | 154.1 | 115 | 26 | 155.1 | 154.1 | 12 | | | |
| Bromfenvinphos-methyl | 12.04 | 0.3 | 294.9 | 79.1 | 30 | 294.9 | 109 | 16 | | | |
| Bromophos-ethyl | 12.47 | 0.3 | 302.8 | 284.8 | 14 | 358.8 | 302.8 | 14 | | | |

## Appendix 1. List of the target compounds, retention times, and monitored transitions

### Part 2

| Pesticide | RT [min] | Window [min] | Precursor mass 1 | Product mass 1 | Collision energy 1 | Precursor mass 2 | Product mass 2 | Collision energy 2 | Precursor mass 3 | Product mass 3 | Collision energy 3 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Bromophos-methyl (Bromophos) | 11.56 | 0.3 | 328.9 | 313.8 | 14 | 330.8 | 315.8 | 14 | | | |
| Bromopropylate | 16.91 | 0.3 | 184.9 | 156.9 | 12 | 340.8 | 185 | 14 | | | |
| Bupirimate | 13.6 | 0.3 | 273.1 | 108 | 14 | 273.1 | 193.2 | 8 | | | |
| Carbophenothion | 15.1 | 0.3 | 157 | 45 | 12 | 342 | 157 | 10 | | | |
| Carfentrazon-ethyl | 15.2 | 0.3 | 290 | 99.9 | 36 | 311.9 | 150.7 | 18 | 340.1 | 312.1 | 10 |
| Chlorbenside | 12.42 | 0.3 | 125 | 89 | 16 | 268 | 125 | 10 | | | |
| Chlordane alpha-cis | 12.71 | 0.3 | 271.9 | 236.9 | 14 | 374.8 | 265.9 | 20 | | | |
| Chlordane gamma-trans | 12.41 | 0.3 | 271.8 | 236.8 | 12 | 372.8 | 265.9 | 14 | | | |
| Chlorfenapyr | 13.83 | 0.3 | 248.9 | 112 | 24 | 327.9 | 246.9 | 14 | | | |
| Chlorfenson | 13.01 | 0.3 | 111 | 75 | 14 | 175 | 111 | 10 | | | |
| Chlorobenzilate | 14.19 | 0.3 | 139 | 111 | 12 | 251 | 139 | 14 | | | |
| Chloroneb | 8.11 | 0.3 | 190.9 | 113 | 14 | 193 | 53.1 | 32 | | | |
| Chlorpropham | 8.9 | 0.3 | 127 | 65 | 20 | 171 | 127 | 8 | 213 | 127 | 14 |
| Chlorpyrifos-ethyl | 11.17 | 0.3 | 198.9 | 171 | 14 | 313.9 | 257.9 | 12 | | | |
| Chlorpyrifos-methyl | 10.35 | 0.3 | 285.9 | 92.9 | 20 | 287.9 | 92.9 | 20 | | | |
| Chlorthal-dimethyl (Dacthal) | 11.25 | 0.3 | 300.9 | 222.9 | 22 | 300.9 | 272.9 | 12 | | | |
| Chlorthiophos | 14.53 | 0.3 | 268.9 | 205 | 14 | 324.9 | 268.9 | 12 | | | |
| Chlozolinate | 12.01 | 0.3 | 186 | 145 | 14 | 188 | 147 | 14 | 259 | 187.9 | 12 |
| Clomazone | 9.47 | 0.3 | 125 | 89 | 16 | 204 | 107 | 18 | | | |
| Coumaphos | 20.11 | 0.3 | 209.9 | 119 | 22 | 209.9 | 182 | 10 | 226 | 163 | 18 |
| Cycloate | 8.79 | 0.3 | 154.1 | 55.1 | 18 | 154.1 | 83.1 | 8 | | | |
| Cyhalothrin I (lambda) | 18.85 | 0.3 | 180.9 | 152 | 22 | 197.1 | 141.1 | 10 | 207.9 | 180.9 | 8 |
| Cyprodinil | 11.83 | 0.3 | 224.1 | 197.1 | 20 | 224.1 | 208.1 | 18 | | | |
| DDD p,p | 14.35 | 0.3 | 235 | 165 | 20 | 235 | 199 | 14 | 237 | 165 | 20 |
| DDD, o, p | 13.45 | 0.3 | 235 | 165 | 20 | 237 | 165 | 20 | | | |
| DDE o,p | 12.54 | 0.3 | 246 | 176.1 | 28 | 248 | 176.1 | 30 | | | |
| DDE p, p | 13.32 | 0.3 | 246 | 176.1 | 28 | 315.9 | 246 | 14 | | | |
| DDT o,p | 14.4 | 0.3 | 212 | 151 | 30 | 212 | 176 | 25 | | | |
| DDT p,p | 15.38 | 0.3 | 235 | 165.1 | 22 | 236.8 | 165 | 22 | | | |
| Deltamethrin | 24.66 | 0.3 | 252.8 | 92.9 | 16 | 252.8 | 172 | 8 | | | |
| Diazinon | 9.71 | 0.3 | 137.1 | 84.1 | 12 | 199 | 92.9 | 14 | | | |
| Dichlobenil | 7.06 | 0.3 | 170.9 | 99.9 | 24 | 170.9 | 136 | 12 | | | |
| Dichlorobenzophenone, 4, 4 | 11.42 | 0.3 | 139 | 74.9 | 26 | 141 | 113 | 10 | | | |
| Dicloran (Bortran) | 9.28 | 0.3 | 160 | 124.1 | 8 | 206 | 176 | 10 | | | |
| Dieldrin | 13.32 | 0.3 | 262.9 | 192.9 | 30 | 262.9 | 227.8 | 16 | | | |
| Diphenamid | 11.59 | 0.3 | 167.1 | 165.1 | 20 | 239.1 | 167.1 | 8 | | | |
| Diphenylamine | 8.73 | 0.3 | 168.1 | 167.1 | 14 | 169.1 | 168.1 | 12 | | | |
| Disulfoton | 9.82 | 0.3 | 88 | 59.8 | 6 | 142 | 81 | 10 | | | |
| Edifenphos | 15.12 | 0.3 | 172.9 | 109 | 8 | 310 | 109 | 26 | | | |
| Endosulfan ether | 10.14 | 0.3 | 238.9 | 204 | 12 | 240.9 | 206 | 14 | | | |
| Endosulfan alpha | 12.7 | 0.3 | 194.9 | 160 | 8 | 240.8 | 205.8 | 14 | | | |
| Endosulfan beta | 14.09 | 0.3 | 158.9 | 123 | 12 | 194.9 | 159 | 8 | | | |
| Endosulfan sulfate | 15.13 | 0.3 | 238.7 | 203.9 | 12 | 271.7 | 236.8 | 12 | | | |

## Appendix 1. List of the target compounds, retention times, and monitored transitions

### Part 3

| Pesticide | RT [min] | Window [min] | Precursor mass 1 | Product mass 1 | Collision energy 1 | Precursor mass 2 | Product mass 2 | Collision energy 2 | Precursor mass 3 | Product mass 3 | Collision energy 3 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Endrin | 13.81 | 0.3 | 244.9 | 173 | 22 | 262.8 | 192.9 | 30 | 280.8 | 244.9 | 8 |
| Endrin Aldehyde | 14.48 | 0.3 | 249.8 | 214.9 | 24 | 278.9 | 242.9 | 10 | | | |
| Endrin-Ketone | 16.37 | 0.3 | 316.8 | 208.9 | 28 | 316.8 | 281 | 10 | | | |
| EPN | 16.85 | 0.3 | 157 | 77 | 22 | 169 | 77 | 22 | 169 | 141 | 8 |
| Ethalfluralin | 8.98 | 0.3 | 264 | 160 | 12 | 292 | 160 | 18 | 292 | 264 | 8 |
| Ethion | 14.46 | 0.3 | 230.9 | 128.9 | 22 | 230.9 | 174.9 | 12 | | | |
| Etofenprox | 22.24 | 0.3 | 163.1 | 107.1 | 16 | 163.1 | 135.1 | 10 | | | |
| Fenarimol | 18.68 | 0.3 | 139 | 74.9 | 26 | 139 | 111 | 14 | 219 | 107 | 10 |
| Fenchlorfos | 10.63 | 0.3 | 284.9 | 269.9 | 14 | 286.9 | 271.9 | 14 | | | |
| Fenitrothion | 10.87 | 0.3 | 277 | 109 | 14 | 277 | 260 | 6 | | | |
| Fenpropathrin | 17.33 | 0.3 | 181 | 126.8 | 28 | 181 | 151.9 | 22 | | | |
| Fenson | 11.51 | 0.3 | 141 | 50.9 | 30 | 141 | 77 | 8 | | | |
| Fenthion | 11.24 | 0.3 | 278 | 109 | 18 | 278 | 169 | 14 | | | |
| Fenvalerate | 23.25 | 0.7 | 125 | 89 | 18 | 167 | 125 | 10 | | | |
| Fipronil | 11.97 | 0.3 | 366.9 | 212.9 | 28 | 368.9 | 214.9 | 30 | | | |
| Fluazifop-P-butyl | 14.12 | 0.3 | 282.1 | 91.1 | 18 | 282.1 | 238.1 | 16 | | | |
| Fluchloralin | 9.74 | 0.3 | 306 | 264 | 8 | 326 | 63 | 12 | | | |
| Fludioxonil | 13.16 | 0.3 | 248 | 127 | 26 | 248 | 154 | 18 | | | |
| Fluquinconazole | 20.12 | 0.3 | 340 | 108.1 | 36 | 340 | 298 | 16 | | | |
| Fluridone | 22.51 | 0.7 | 328.1 | 189.1 | 38 | 328.1 | 258.8 | 24 | | | |
| Flusilazole | 13.53 | 0.3 | 233.1 | 151.9 | 14 | 233.1 | 164.9 | 16 | | | |
| Flutolanil | 13.11 | 0.3 | 173 | 95 | 28 | 281 | 173 | 10 | | | |
| Flutriafol | 12.86 | 0.3 | 123 | 75 | 24 | 219.1 | 95 | 34 | 219.1 | 123 | 12 |
| Fluvalinate peak 1 | 23.65 | 1 | 250 | 55.1 | 16 | 250 | 199.9 | 18 | | | |
| Fluvalinate peak 2 | 23.8 | 1 | 250 | 55.1 | 16 | 250 | 200 | 16 | | | |
| Fonofos | 9.64 | 0.3 | 137 | 109 | 6 | 246 | 109 | 14 | | | |
| Heptachlor | 10.56 | 0.3 | 271.8 | 236.8 | 12 | 273.8 | 238.8 | 14 | | | |
| Hexachlorobenzene | 9.17 | 0.3 | 283.8 | 213.8 | 30 | 283.8 | 248.8 | 16 | | | |
| Hexazinone | 15.55 | 0.3 | 171.1 | 71.1 | 14 | 171.1 | 85.1 | 12 | | | |
| Iodofenfos | 13 | 0.3 | 376.8 | 361.8 | 16 | 378.8 | 363.8 | 14 | | | |
| Iprodione | 16.72 | 0.3 | 314 | 245 | 10 | 315.7 | 247 | 10 | | | |
| Isazophos | 9.86 | 0.3 | 118.9 | 76 | 18 | 256.9 | 161.9 | 4 | | | |
| Isodrin | 11.7 | 0.3 | 146.9 | 111.1 | 10 | 192.9 | 123 | 28 | | | |
| Isopropalin | 11.73 | 0.3 | 280.1 | 180.2 | 10 | 280.1 | 238.2 | 8 | | | |
| Lenacil | 15.27 | 0.3 | 153 | 82.1 | 16 | 153 | 135.6 | 12 | | | |
| Leptophos | 17.86 | 0.3 | 171 | 77.1 | 18 | 171 | 124.3 | 10 | | | |
| Linuron | 10.96 | 0.3 | 187 | 124 | 20 | 248 | 61.1 | 8 | | | |
| Malathion | 11.07 | 0.3 | 127 | 99 | 6 | 158 | 125 | 6 | | | |
| Metalaxyl | 10.6 | 0.3 | 234.1 | 146.1 | 20 | 234.1 | 174.1 | 10 | | | |
| Metazachlor | 11.82 | 0.3 | 132.1 | 117.1 | 14 | 133.1 | 132.1 | 12 | 209 | 132.1 | 16 |
| Methacrifos | 8.07 | 0.3 | 124.9 | 47.1 | 12 | 207.9 | 180.1 | 6 | | | |
| Methoxychlor | 17.13 | 0.3 | 227.1 | 141.1 | 32 | 227.1 | 169.1 | 22 | | | |
| Metolachlor | 11.12 | 0.3 | 238.1 | 133.1 | 26 | 238.1 | 162.1 | 10 | | | |

## Appendix 1. List of the target compounds, retention times, and monitored transitions

### Part 4

| Pesticide | RT [min] | Window [min] | Precursor mass 1 | Product mass 1 | Collision energy 1 | Precursor mass 2 | Product mass 2 | Collision energy 2 | Precursor mass 3 | Product mass 3 | Collision energy 3 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Mevinphos | 7.65 | 0.3 | 127 | 95 | 14 | 192 | 127 | 10 | | | |
| MGK-264 A | 11.63 | 0.3 | 164.1 | 80.1 | 24 | 164.1 | 93.1 | 10 | 164.1 | 98.1 | 10 |
| MGK-264 B | 11.88 | 0.3 | 164.1 | 67.1 | 6 | 164.1 | 98.1 | 12 | | | |
| Mirex | 18.19 | 0.3 | 272 | 236.8 | 14 | 273.8 | 238.8 | 14 | | | |
| Myclobutanil | 13.44 | 0.3 | 179 | 90 | 28 | 179 | 125 | 14 | | | |
| N-(2,4-Dimethylphenyl) formamide | 7.96 | 0.3 | 149.1 | 106.1 | 16 | 149.1 | 120.1 | 14 | 149.1 | 121.1 | 6 |
| Nitralin | 16.27 | 0.3 | 274 | 216 | 8 | 316.2 | 274 | 8 | | | |
| Nitrofen | 13.88 | 0.3 | 202 | 139 | 24 | 283 | 162 | 20 | | | |
| Nonachlor-cis | 14.26 | 0.3 | 406.8 | 299.9 | 14 | 410.8 | 301.8 | 14 | | | |
| Nonachlor-trans | 12.79 | 0.3 | 271.8 | 236.8 | 14 | 406.8 | 299.8 | 14 | | | |
| Norflurazon | 15.19 | 0.3 | 145 | 95 | 16 | 303 | 145 | 20 | | | |
| Ortho-phenylphenol | 8.17 | 0.3 | 170.1 | 115 | 34 | 170.1 | 141.1 | 22 | | | |
| Oxadiazon | 13.44 | 0.3 | 175 | 112 | 12 | 258 | 175 | 6 | | | |
| Oxyfluorfen | 13.62 | 0.3 | 252 | 146 | 30 | 300 | 223 | 14 | | | |
| Paclobutrazol | 12.6 | 0.3 | 138 | 103.1 | 14 | 236 | 125 | 12 | 236 | 167 | 10 |
| Parathion (ethyl) | 11.31 | 0.3 | 154.9 | 125 | 6 | 291 | 109 | 12 | | | |
| Parathion-methyl | 10.45 | 0.3 | 233 | 109 | 10 | 263 | 109 | 12 | | | |
| Pebulate | 7.86 | 0.3 | 128 | 72 | 6 | 128.1 | 57.1 | 8 | | | |
| Penconazole | 11.93 | 0.3 | 159 | 123 | 20 | 248.1 | 157 | 22 | | | |
| Pendimethalin | 11.82 | 0.3 | 252.1 | 161.1 | 14 | 252.1 | 162.1 | 8 | 252.1 | 191.3 | 8 |
| Pentachloroaniline | 10.12 | 0.3 | 262.9 | 191.9 | 20 | 266.9 | 193.9 | 20 | | | |
| Pentachloroanisole | 9.24 | 0.3 | 264.8 | 236.9 | 10 | 279.9 | 236.8 | 22 | | | |
| Pentachlorobenzene | 8.16 | 0.3 | 247.9 | 212.9 | 18 | 249.8 | 214.8 | 16 | | | |
| Pentachlorobenzonitrile | 9.51 | 0.3 | 272.9 | 237.9 | 16 | 274.8 | 239.9 | 18 | | | |
| Pentachlorothioanisole | 10.91 | 0.3 | 295.7 | 245.9 | 30 | 295.7 | 262.9 | 12 | | | |
| Permethrin | 20.2 | 0.6 | 183.1 | 165.1 | 10 | 184.1 | 91.1 | 20 | 184.1 | 141.1 | 15 |
| Perthane (Ethylan) | 14.01 | 0.3 | 223.1 | 167 | 12 | 223.1 | 179 | 20 | | | |
| Phenothrin | 18.01 | 0.3 | 123.1 | 41.1 | 24 | 123.1 | 79.1 | 14 | 123.1 | 81.1 | 8 |
| Phorate | 9.09 | 0.3 | 121 | 65 | 10 | 260 | 75 | 8 | | | |
| Phosalone | 17.85 | 0.3 | 182 | 74.8 | 30 | 182 | 111 | 14 | | | |
| Phosmet | 16.65 | 0.3 | 160 | 76.9 | 22 | 160 | 133 | 10 | | | |
| Piperonyl butoxide | 16.26 | 0.3 | 176.1 | 103.1 | 22 | 176.1 | 131.1 | 12 | | | |
| Pirimiphos-ethyl | 11.65 | 0.3 | 304.1 | 168.1 | 12 | 318.1 | 166.1 | 12 | | | |
| Pirimiphos-methyl | 10.86 | 0.3 | 233 | 151.1 | 6 | 290.1 | 125 | 20 | | | |
| Pretilachlor | 13.22 | 0.3 | 162 | 132.1 | 20 | 202.1 | 174.2 | 8 | 262.1 | 202.1 | 6 |
| Prochloraz | 20.27 | 0.3 | 180 | 69 | 14 | 180.1 | 138.1 | 12 | 308 | 70 | 12 |
| Procymidone | 12.22 | 0.3 | 283 | 68.1 | 24 | 283 | 96.1 | 8 | | | |
| Prodiamine | 10.93 | 0.3 | 275.1 | 255.1 | 8 | 321.1 | 203 | 10 | 321.1 | 279.1 | 6 |
| Profenofos | 13.23 | 0.3 | 336.9 | 266.9 | 12 | 338.9 | 268.9 | 14 | | | |
| Profluralin | 9.58 | 0.3 | 318.1 | 55 | 12 | 318.1 | 199.1 | 12 | 347.1 | 330.1 | 6 |
| Propanil | 10.29 | 0.3 | 161 | 90 | 24 | 161 | 99 | 24 | 217 | 161 | 8 |
| Propargite | 16.03 | 0.3 | 135.1 | 77.1 | 26 | 135.1 | 107.1 | 12 | 150.1 | 135.1 | 8 |
| Propisochlor | 10.56 | 0.3 | 162.1 | 120.1 | 12 | 162.1 | 144.1 | 8 | | | |

## Appendix 1. List of the target compounds, retention times, and monitored transitions

### Part 5

| Pesticide | RT [min] | Window [min] | Precursor mass 1 | Product mass 1 | Collision energy 1 | Precursor mass 2 | Product mass 2 | Collision energy 2 | Precursor mass 3 | Product mass 3 | Collision energy 3 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Propyzamide | 9.66 | 0.3 | 172.9 | 109 | 24 | 172.9 | 145 | 14 | 174.9 | 147 | 14 |
| Prothiofos | 13.12 | 0.3 | 266.9 | 220.9 | 18 | 309 | 238.9 | 14 | | | |
| Pyraclofos | 19.41 | 0.3 | 194 | 138 | 18 | 360 | 194.1 | 12 | | | |
| Pyrazophos | 18.99 | 0.3 | 221 | 148.7 | 14 | 221 | 193.1 | 8 | | | |
| Pyridaben | 20.19 | 0.3 | 147.1 | 117.1 | 20 | 147.1 | 119.1 | 8 | 147.1 | 132.1 | 12 |
| Pyridaphenthion | 16.62 | 0.3 | 199 | 92.1 | 14 | 340 | 199.1 | 8 | | | |
| Pyrimethanil | 9.74 | 0.3 | 198.1 | 118 | 32 | 198.1 | 158.1 | 18 | | | |
| Pyriproxyfen | 18.31 | 0.3 | 136.1 | 96 | 10 | 226.1 | 186.1 | 12 | | | |
| Quinalphos | 12.15 | 0.3 | 146 | 118.1 | 10 | 157.1 | 102 | 22 | | | |
| Quintozene | 9.46 | 0.3 | 213.8 | 178.9 | 14 | 294.8 | 236.9 | 14 | | | |
| Sulfotep | 8.99 | 0.3 | 237.9 | 145.9 | 12 | 322 | 145.9 | 22 | | | |
| Sulprofos | 14.86 | 0.3 | 156 | 108 | 30 | 322 | 156.1 | 10 | | | |
| Tebuconazole | 15.78 | 0.3 | 125 | 89 | 16 | 250 | 125 | 20 | | | |
| Tebufenpyrad | 17.47 | 0.3 | 276.1 | 171 | 10 | 318.1 | 131.1 | 14 | | | |
| Tecnazene | 8.54 | 0.3 | 214.8 | 178.9 | 8 | 258.9 | 201 | 12 | | | |
| Tefluthrin | 9.91 | 0.3 | 177 | 127 | 14 | 177 | 137 | 16 | | | |
| Terbacil | 9.85 | 0.3 | 160 | 76 | 12 | 161 | 144 | 12 | | | |
| Terbufos | 9.6 | 0.3 | 231 | 128.9 | 20 | 231 | 175 | 10 | | | |
| Terbuthylazine | 9.61 | 0.3 | 214.1 | 104.1 | 16 | 214.1 | 132.1 | 10 | | | |
| Tetrachlorvinphos | 12.62 | 0.3 | 328.9 | 109 | 18 | 330.9 | 109 | 18 | 332.9 | 109 | 14 |
| Tetradifon | 17.63 | 0.3 | 159 | 74.8 | 32 | 159 | 111 | 20 | | | |
| Tetrahydrophthalimide (THPI) | 8.03 | 0.3 | 151 | 79.9 | 6 | 151 | 122.1 | 8 | | | |
| Tolclofos-methyl | 10.46 | 0.3 | 265 | 219.9 | 20 | 265 | 250 | 12 | | | |
| Triadimefon | 11.37 | 0.3 | 208 | 111 | 20 | 208 | 126.7 | 12 | | | |
| Triadimenol | 12.24 | 0.3 | 128 | 65 | 18 | 128 | 100 | 10 | | | |
| Triallate | 9.94 | 0.3 | 86.1 | 43.3 | 6 | 268 | 183.9 | 18 | 268 | 226 | 12 |
| Triazophos | 14.86 | 0.3 | 161.1 | 134.1 | 8 | 257 | 162.1 | 6 | | | |
| Tricyclazole | 13.02 | 0.3 | 189 | 161 | 14 | 189 | 162 | 10 | | | |
| Triflumizole | 12.34 | 0.3 | 206 | 179 | 14 | 206 | 186 | 8 | | | |
| Trifluralin | 8.95 | 0.3 | 264 | 160 | 14 | 306.1 | 264.1 | 8 | | | |
| Vinclozolin | 10.43 | 0.3 | 186.8 | 124 | 18 | 212 | 172 | 14 | | | |

## Appendix 2. Details of repeatability and linearity evaluation

### Part 1

| Pesticide | Repeatability (n = 5) | | | | | | Linear range [mg/kg] | |
|---|---|---|---|---|---|---|---|---|
| | 0.01 mg/kg | | | 0.05 mg/kg | | | | |
| | Baby food | Honey | Baby food (He) | Baby food | Honey | Baby food (He) | Baby food | Honey |
| 2,3,5,6-Tetrachloroaniline | 2% | 4% | 5% | 4% | 4% | 5% | 0.005–0.500 | 0.005–0.500 |
| 2,4'-Methoxychlor | 6% | 4% | 5% | 4% | 4% | 7% | 0.005–0.500 | 0.005–0.500 |
| 3,4-Dichloroaniline | 13% | - | 9% | 9% | - | 8% | 0.005–0.200 | – |
| 4,4'-Methoxychlor olefin | 1% | 1% | 4% | 1% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| Acetochlor | 4% | 4% | 3% | 4% | 2% | 2% | 0.005–0.500 | 0.005–0.500 |
| Acrinathrin | 5% | 3% | 6% | 3% | 1% | 5% | 0.005–0.500 | 0.005–0.500 |
| Alachlor | 3% | 3% | 5% | 3% | 1% | 3% | 0.005–0.500 | 0.005–0.500 |
| Aldrin | 3% | 2% | 3% | 2% | 4% | 3% | 0.005–0.500 | 0.005–0.500 |
| Allidochlor | 5% | 4% | 5% | 4% | 4% | 4% | 0.005–0.500 | 0.005–0.500 |
| Anthraquinone | 2% | 3% | 4% | 3% | 4% | 3% | 0.005–0.500 | 0.005–0.500 |
| Atrazine | 4% | 5% | 6% | 5% | 1% | 2% | 0.005–0.500 | 0.005–0.500 |
| Azinphos-ethyl | 1% | 4% | 7% | 4% | 5% | 5% | 0.005–0.500 | 0.005–0.500 |
| Azinphos-methyl | 5% | 3% | 6% | 3% | 3% | 5% | 0.005–0.200 | 0.005–0.500 |
| Benfluralin | 6% | 3% | 4% | 3% | 4% | 3% | 0.005–0.500 | 0.005–0.500 |
| BHC, Alpha | 2% | 2% | 4% | 2% | 3% | 3% | 0.005–0.500 | 0.005–0.500 |
| BHC, Beta | 2% | 2% | 4% | 2% | 2% | 3% | 0.005–0.500 | 0.005–0.500 |
| BHC, delta | 3% | 1% | 3% | 1% | 2% | 2% | 0.005–0.500 | 0.005–0.500 |
| BHC, gamma | 4% | 2% | 4% | 2% | 3% | 3% | 0.005–0.500 | 0.005–0.500 |
| Bifenthrin | 6% | 2% | 4% | 2% | 3% | 4% | 0.005–0.500 | 0.005–0.500 |
| Biphenyl | 4% | 5% | 4% | 5% | 2% | 8% | 0.005–0.500 | 0.005–0.500 |
| Bromfenvinphos-methyl | 3% | 2% | 5% | 2% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| Bromophos-ethyl | 1% | 1% | 3% | 1% | 3% | 3% | 0.005–0.500 | 0.005–0.500 |
| Bromophos-methyl (Bromophos) | 2% | 2% | 4% | 2% | 3% | 3% | 0.005–0.500 | 0.005–0.500 |
| Bromopropylate | 3% | 3% | 5% | 3% | 3% | 5% | 0.005–0.500 | 0.005–0.500 |
| Bupirimate | 1% | 2% | 6% | 2% | 3% | 4% | 0.005–0.500 | 0.005–0.500 |
| Carbophenothion | 2% | 2% | 5% | 2% | 1% | 4% | 0.005–0.500 | 0.005–0.500 |
| Carfentrazon-ethyl | 4% | 2% | 5% | 2% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| Chlorbenside | 2% | 1% | 4% | 1% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| Chlordane alpha-cis | 2% | 1% | 5% | 1% | 3% | 4% | 0.005–0.500 | 0.005–0.500 |
| Chlordane gamma-trans | 1% | 1% | 5% | 1% | 3% | 4% | 0.005–0.500 | 0.005–0.500 |
| Chlorfenapyr | 5% | 2% | 3% | 2% | 5% | 5% | 0.005–0.500 | 0.005–0.500 |
| Chlorfenson | 2% | 1% | 5% | 1% | 1% | 4% | 0.005–0.500 | 0.005–0.500 |
| Chlorobenzilate | 3% | 1% | 4% | 1% | 3% | 4% | 0.005–0.500 | 0.005–0.500 |
| Chloroneb | 2% | 5% | 3% | 5% | 4% | 5% | 0.005–0.500 | 0.005–0.500 |
| Chlorpropham | 3% | 2% | 3% | 2% | 3% | 2% | 0.005–0.500 | 0.005–0.500 |
| Chlorpyrifos-ethyl | 2% | 1% | 3% | 1% | 3% | 2% | 0.005–0.500 | 0.005–0.500 |
| Chlorpyrifos-methyl | 4% | 1% | 4% | 1% | 2% | 3% | 0.005–0.500 | 0.005–0.500 |
| Chlorthal-dimethyl (Dacthal) | 1% | 1% | 6% | 1% | 3% | 3% | 0.005–0.500 | 0.005–0.500 |
| Chlorthiophos | 1% | 1% | 4% | 1% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| Chlozolinate | 3% | 2% | 4% | 2% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| Clomazone | 3% | 2% | 4% | 2% | 2% | 3% | 0.005–0.500 | 0.005–0.500 |
| Coumaphos | 3% | 5% | 5% | 5% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| Cycloate | 3% | 4% | 4% | 4% | 4% | 6% | 0.005–0.500 | 0.005–0.500 |

## Appendix 2. Details of repeatability and linearity evaluation

### Part 2

| Pesticide | Repeatability (n = 5) | | | | | | Linear range [mg/kg] | |
|---|---|---|---|---|---|---|---|---|
| | 0.01 mg/kg | | | 0.05 mg/kg | | | | |
| | Baby food | Honey | Baby food (He) | Baby food | Honey | Baby food (He) | Baby food | Honey |
| Cyhalothrin I (lambda) | 3% | 4% | 5% | 4% | 3% | 5% | 0.005–0.500 | 0.005–0.500 |
| Cyprodinil | 4% | 2% | 3% | 2% | 1% | 4% | 0.005–0.500 | 0.005–0.500 |
| DDD p,p | 5% | 3% | 3% | 3% | 4% | 8% | 0.005–0.500 | 0.005–0.500 |
| DDD, o, p | 4% | 2% | 3% | 2% | 3% | 4% | 0.005–0.500 | 0.005–0.500 |
| DDE o,p | 1% | 3% | 2% | 3% | 2% | 3% | 0.005–0.500 | 0.005–0.500 |
| DDE p, p | 1% | 2% | 4% | 2% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| DDT o,p | 11% | 12% | 5% | 12% | 5% | 3% | 0.005–0.500 | 0.005–0.500 |
| DDT p,p | 14% | 10% | 6% | 10% | 6% | 7% | 0.005–0.500 | 0.005–0.500 |
| Deltamethrin | 4% | 6% | 4% | 6% | 2% | 5% | 0.005–0.500 | 0.005–0.500 |
| Diazinon | 3% | 2% | 3% | 2% | 2% | 2% | 0.005–0.500 | 0.005–0.500 |
| Dichlobenil | 4% | 5% | 5% | 5% | 5% | 8% | 0.005–0.500 | 0.005–0.500 |
| Dichlorobenzophenone, 4, 4 | 1% | 3% | 2% | 3% | 4% | 3% | 0.005–0.500 | 0.005–0.500 |
| Dicloran (Bortran) | 3% | 2% | 2% | 2% | 2% | 1% | 0.005–0.500 | 0.005–0.500 |
| Dieldrin | 2% | 1% | 6% | 1% | 6% | 4% | 0.005–0.500 | 0.005–0.500 |
| Diphenamid | 3% | 2% | 4% | 2% | 2% | 3% | 0.005–0.500 | 0.005–0.500 |
| Diphenylamine | 3% | 4% | 5% | 4% | 2% | 3% | 0.005–0.500 | 0.005–0.500 |
| Disulfoton | 6% | 2% | 4% | 2% | 2% | 1% | 0.005–0.500 | 0.005–0.500 |
| Edifenphos | 2% | 5% | 3% | 5% | 2% | 5% | 0.005–0.500 | 0.005–0.500 |
| Endosulfan ether | 2% | 3% | 3% | 3% | 3% | 3% | 0.005–0.500 | 0.005–0.500 |
| Endosulfan alpha | 6% | 1% | 3% | 1% | 3% | 3% | 0.005–0.500 | 0.005–0.500 |
| Endosulfan beta | 3% | 1% | 3% | 1% | 2% | 5% | 0.005–0.500 | 0.005–0.500 |
| Endosulfan sulfate | 3% | 2% | 6% | 2% | 3% | 4% | 0.005–0.500 | 0.005–0.500 |
| Endrin | 4% | 1% | 6% | 1% | 3% | 5% | 0.005–0.500 | 0.005–0.500 |
| Endrin Aldehyde | 4% | 1% | 4% | 1% | 4% | 4% | 0.005–0.500 | 0.005–0.500 |
| Endrin-Ketone | 6% | 4% | 6% | 4% | 5% | 5% | 0.005–0.500 | 0.005–0.500 |
| EPN | 2% | 3% | 4% | 3% | 3% | 5% | 0.005–0.500 | 0.005–0.500 |
| Ethalfluralin | 3% | 3% | 5% | 3% | 4% | 4% | 0.005–0.500 | 0.005–0.500 |
| Ethion | 2% | 2% | 5% | 2% | 1% | 4% | 0.005–0.500 | 0.005–0.500 |
| Etofenprox | 3% | 1% | 5% | 1% | 1% | 4% | 0.005–0.500 | 0.005–0.500 |
| Fenarimol | 3% | 3% | 5% | 3% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| Fenchlorfos | 2% | 1% | 3% | 1% | 2% | 3% | 0.005–0.500 | 0.005–0.500 |
| Fenitrothion | 5% | 1% | 4% | 1% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| Fenpropathrin | 4% | 1% | 4% | 1% | 4% | 4% | 0.005–0.500 | 0.005–0.500 |
| Fenson | 2% | 2% | 4% | 2% | 2% | 3% | 0.005–0.500 | 0.005–0.500 |
| Fenthion | 4% | 2% | 3% | 2% | 1% | 3% | 0.005–0.500 | 0.005–0.500 |
| Fenvalerate | 2% | 4% | 6% | 4% | 2% | 5% | 0.005–0.500 | 0.005–0.500 |
| Fipronil | 5% | 1% | 5% | 1% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| Fluazifop-P-butyl | 2% | 2% | 5% | 2% | 1% | 4% | 0.005–0.500 | 0.005–0.500 |
| Fluchloralin | 4% | 2% | 8% | 2% | 4% | 3% | 0.005–0.500 | 0.005–0.500 |
| Fludioxonil | 1% | 1% | 3% | 1% | 4% | 4% | 0.005–0.500 | 0.005–0.500 |
| Fluquinconazole | 4% | 3% | 5% | 3% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| Fluridone | 4% | 3% | 4% | 3% | 5% | 5% | 0.005–0.500 | 0.005–0.500 |
| Flusilazole | 2% | 4% | 2% | 4% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |

## Appendix 2. Details of repeatability and linearity evaluation

### Part 3

| Pesticide | Repeatability (n = 5) | | | | | | Linear range [mg/kg] | |
|---|---|---|---|---|---|---|---|---|
| | 0.01 mg/kg | | | 0.05 mg/kg | | | | |
| | Baby food | Honey | Baby food (He) | Baby food | Honey | Baby food (He) | Baby food | Honey |
| Flutolanil | 2% | 1% | 5% | 1% | 1% | 3% | 0.005–0.500 | 0.005–0.500 |
| Flutriafol | 4% | 1% | 5% | 1% | 3% | 4% | 0.005–0.500 | 0.005–0.500 |
| Fluvalinate | 3% | 4% | 4% | 4% | 1% | 5% | 0.005–0.500 | 0.005–0.500 |
| Fonofos | 3% | 2% | 3% | 2% | 2% | 2% | 0.005–0.500 | 0.005–0.500 |
| Heptachlor | 3% | 3% | 6% | 3% | 4% | 3% | 0.005–0.500 | 0.005–0.500 |
| Hexachlorobenzene | 3% | 5% | 6% | 5% | 5% | 7% | 0.005–0.500 | 0.005–0.500 |
| Hexazinone | 1% | 1% | 4% | 1% | 4% | 5% | 0.005–0.200 | 0.005–0.500 |
| Iodofenfos | 1% | 1% | 3% | 1% | 5% | 4% | 0.005–0.500 | 0.005–0.500 |
| Iprodione | 4% | 3% | 3% | 3% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| Isazophos | 5% | 3% | 5% | 3% | 3% | 2% | 0.005–0.500 | 0.005–0.500 |
| Isodrin | 2% | 2% | 4% | 2% | 4% | 3% | 0.005–0.500 | 0.005–0.500 |
| Isopropalin | 3% | 1% | 3% | 1% | 3% | 4% | 0.005–0.500 | 0.005–0.500 |
| Lenacil | 5% | 1% | 4% | 1% | 3% | 5% | 0.005–0.500 | 0.005–0.500 |
| Leptophos | 1% | 2% | 4% | 2% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| Linuron | 5% | 2% | 8% | 2% | 3% | 5% | 0.005–0.500 | 0.005–0.500 |
| Malathion | 3% | 3% | 4% | 3% | 1% | 3% | 0.005–0.500 | 0.005–0.500 |
| Metalaxyl | 3% | 2% | 5% | 2% | 3% | 4% | 0.005–0.500 | 0.005–0.500 |
| Metazachlor | 3% | 2% | 5% | 2% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| Methacrifos | 3% | 4% | 3% | 4% | 3% | 5% | 0.005–0.500 | 0.005–0.500 |
| Methoxychlor | 9% | 8% | 5% | 8% | 6% | 7% | 0.005–0.500 | 0.005–0.500 |
| Metolachlor | 2% | 1% | 3% | 1% | 1% | 3% | 0.005–0.500 | 0.005–0.500 |
| Mevinphos | 3% | 4% | 4% | 4% | 3% | 4% | 0.005–0.500 | 0.005–0.500 |
| MGK-264 A | 4% | 2% | 2% | 2% | 1% | 3% | 0.005–0.500 | 0.005–0.500 |
| MGK-264 B | 3% | 1% | 3% | 1% | 1% | 4% | 0.005–0.500 | 0.005–0.500 |
| Mirex | 1% | 1% | 3% | 1% | 5% | 5% | 0.005–0.500 | 0.005–0.500 |
| Myclobutanil | 3% | 1% | 5% | 1% | 3% | 4% | 0.005–0.500 | 0.005–0.500 |
| N-(2,4-Dimethylphenyl) formamide | 5% | 1% | 3% | 1% | 5% | 3% | 0.005–0.500 | 0.005–0.500 |
| Nitralin | 2% | 4% | 7% | 4% | 2% | 2% | 0.005–0.500 | 0.005–0.500 |
| Nitrofen | 3% | 1% | 3% | 1% | 2% | 5% | 0.005–0.500 | 0.005–0.500 |
| Nonachlor-cis | 1% | 1% | 5% | 1% | 3% | 5% | 0.005–0.500 | 0.005–0.500 |
| Nonachlor-trans | 2% | 2% | 3% | 2% | 3% | 3% | 0.005–0.500 | 0.005–0.500 |
| Norflurazon | 2% | 1% | 3% | 1% | 3% | 2% | 0.005–0.500 | 0.005–0.500 |
| Ortho-phenylphenol | 3% | 3% | 5% | 3% | 3% | 3% | 0.005–0.500 | 0.005–0.500 |
| Oxadiazon | 1% | 2% | 5% | 2% | 2% | 3% | 0.005–0.500 | 0.005–0.500 |
| Oxyfluorfen | 1% | 2% | 5% | 2% | 2% | 5% | 0.005–0.500 | 0.005–0.500 |
| Paclobutrazol | 2% | 2% | 8% | 2% | 1% | 4% | 0.005–0.500 | 0.005–0.500 |
| Parathion (ethyl) | 5% | 3% | 2% | 3% | 3% | 4% | 0.005–0.500 | 0.005–0.500 |
| Parathion-methyl | 3% | 2% | 2% | 2% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| Pebulate | 3% | 5% | 6% | 5% | 6% | 9% | 0.005–0.500 | 0.005–0.500 |
| Penconazole | 2% | 1% | 4% | 1% | 3% | 3% | 0.005–0.500 | 0.005–0.500 |
| Pendimethalin | 2% | 1% | 6% | 1% | 3% | 4% | 0.005–0.500 | 0.005–0.500 |
| Pentachloroaniline | 2% | 4% | 4% | 4% | 3% | 2% | 0.005–0.500 | 0.005–0.500 |
| Pentachloroanisole | 2% | 4% | 4% | 4% | 4% | 5% | 0.005–0.500 | 0.005–0.500 |

## Appendix 2. Details of repeatability and linearity evaluation

### Part 4

| Pesticide | Repeatability (n = 5) | | | | | | Linear range [mg/kg] | |
|---|---|---|---|---|---|---|---|---|
| | 0.01 mg/kg | | | 0.05 mg/kg | | | | |
| | Baby food | Honey | Baby food (He) | Baby food | Honey | Baby food (He) | Baby food | Honey |
| Pentachlorobenzene | 6% | 8% | 8% | 8% | 7% | 7% | 0.005–0.500 | 0.005–0.500 |
| Pentachlorobenzonitrile | 4% | 4% | 5% | 4% | 4% | 2% | 0.005–0.500 | 0.005–0.500 |
| Pentachlorothioanisole | 2% | 4% | 4% | 4% | 4% | 3% | 0.005–0.500 | 0.005–0.500 |
| Permethrin | 7% | 2% | 3% | 2% | 3% | 4% | 0.005–0.500 | 0.005–0.500 |
| Perthane (Ethylan) | 1% | 1% | 5% | 1% | 3% | 4% | 0.005–0.500 | 0.005–0.500 |
| Phenothrin | 5% | 1% | 5% | 1% | 2% | 3% | 0.005–0.500 | 0.005–0.500 |
| Phorate | 4% | 3% | 5% | 3% | 2% | 2% | 0.005–0.500 | 0.005–0.500 |
| Phosalone | 3% | 4% | 5% | 4% | 1% | 5% | 0.005–0.500 | 0.005–0.500 |
| Phosmet | 4% | 5% | 6% | 5% | 2% | 5% | 0.005–0.500 | 0.005–0.500 |
| Piperonyl butoxide | 1% | 2% | 5% | 2% | 3% | 4% | 0.005–0.500 | 0.005–0.500 |
| Pirimiphos-ethyl | 2% | 1% | 4% | 1% | 2% | 3% | 0.005–0.500 | 0.005–0.500 |
| Pirimiphos-methyl | 4% | 2% | 4% | 2% | 1% | 2% | 0.005–0.500 | 0.005–0.500 |
| Pretilachlor | 4% | 1% | 3% | 1% | 4% | 4% | 0.005–0.500 | 0.005–0.200 |
| Prochloraz | 5% | 3% | 8% | 3% | 5% | 3% | 0.005–0.500 | 0.005–0.500 |
| Procymidone | 6% | 2% | 5% | 2% | 1% | 4% | 0.005–0.500 | 0.005–0.500 |
| Prodiamine | 1% | 3% | 6% | 3% | 2% | 5% | 0.005–0.500 | 0.005–0.500 |
| Profenofos | 5% | 2% | 7% | 2% | 5% | 5% | 0.005–0.500 | 0.005–0.200 |
| Profluralin | 3% | 1% | 8% | 1% | 4% | 4% | 0.005–0.500 | 0.005–0.500 |
| Propanil | 2% | 1% | 4% | 1% | 3% | 3% | 0.005–0.500 | 0.005–0.500 |
| Propargite | 5% | 2% | 6% | 2% | 3% | 4% | 0.005–0.500 | 0.005–0.500 |
| Propisochlor | 3% | 2% | 4% | 2% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| Propyzamide | 3% | 2% | 5% | 2% | 3% | 3% | 0.005–0.500 | 0.005–0.500 |
| Prothiofos | 3% | 1% | 4% | 1% | 1% | 4% | 0.005–0.500 | 0.005–0.500 |
| Pyraclofos | 2% | 3% | 5% | 3% | 4% | 5% | 0.005–0.500 | 0.005–0.500 |
| Pyrazophos | 7% | 1% | 5% | 1% | 1% | 5% | 0.005–0.200 | 0.005–0.500 |
| Pyridaben | 5% | 4% | 5% | 4% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| Pyridaphenthion | 1% | 3% | 4% | 3% | 1% | 5% | 0.005–0.500 | 0.005–0.500 |
| Pyrimethanil | 3% | 3% | 2% | 3% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| Pyriproxyfen | 3% | 1% | 5% | 1% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| Quinalphos | 4% | 1% | 4% | 1% | 1% | 4% | 0.005–0.500 | 0.005–0.500 |
| Quintozene | 5% | 3% | 5% | 3% | 2% | 5% | 0.005–0.500 | 0.005–0.500 |
| Sulfotep | 5% | 3% | 2% | 3% | 2% | 2% | 0.005–0.500 | 0.005–0.500 |
| Sulprofos | 2% | 1% | 4% | 1% | 1% | 4% | 0.005–0.500 | 0.005–0.500 |
| Tebuconazole | 2% | 2% | 6% | 2% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| Tebufenpyrad | 2% | 2% | 5% | 2% | 3% | 4% | 0.005–0.500 | 0.005–0.500 |
| Tecnazene | 3% | 4% | 4% | 4% | 4% | 3% | 0.005–0.500 | 0.005–0.500 |
| Tefluthrin | 2% | 3% | 3% | 3% | 3% | 2% | 0.005–0.500 | 0.005–0.500 |
| Terbacil | 4% | 1% | 5% | 1% | 1% | 4% | 0.005–0.500 | 0.005–0.500 |
| Terbufos | 4% | 3% | 3% | 3% | 1% | 2% | 0.005–0.500 | 0.005–0.500 |
| Terbuthylazine | 4% | 2% | 3% | 2% | 2% | 2% | 0.005–0.500 | 0.005–0.500 |
| Tetrachlorvinphos | 3% | 3% | 5% | 3% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |
| Tetradifon | 3% | 1% | 4% | 1% | 2% | 3% | 0.005–0.500 | 0.005–0.500 |
| Tetrahydrophthalimide (THPI) | 6% | 2% | 3% | 2% | 2% | 4% | 0.005–0.500 | 0.005–0.500 |

## Appendix 2. Details of repeatability and linearity evaluation

### Part 5

| Pesticide | Repeatability (n = 5) | | | | | | Linear range [mg/kg] | |
|---|---|---|---|---|---|---|---|---|
| | 0.01 mg/kg | | | 0.05 mg/kg | | | | |
| | Baby food | Honey | Baby food (He) | Baby food | Honey | Baby food (He) | Baby food | Honey |
| Tolclofos-methyl | 3% | 1% | 2% | 1% | 2% | 2% | 0.005–0.500 | 0.005–0.500 |
| Triadimefon | 3% | 0% | 3% | 0% | 1% | 3% | 0.005–0.500 | 0.005–0.500 |
| Triadimenol | 3% | 3% | 5% | 3% | 3% | 3% | 0.005–0.500 | 0.005–0.500 |
| Triallate | 2% | 2% | 4% | 2% | 2% | 3% | 0.005–0.500 | 0.005–0.500 |
| Triazophos | 3% | 3% | 5% | 3% | 2% | 4% | 0.005–0.200 | 0.005–0.500 |
| Tricyclazole | 4% | 1% | 5% | 1% | 3% | 5% | 0.005–0.200 | 0.005–0.500 |
| Triflumizole | 2% | 2% | 3% | 2% | 2% | 3% | 0.005–0.500 | 0.005–0.500 |
| Trifluralin | 3% | 3% | 4% | 3% | 4% | 5% | 0.005–0.500 | 0.005–0.500 |
| Vinclozolin | 1% | 4% | 4% | 4% | 4% | 3% | 0.005–0.500 | 0.005–0.500 |

Learn more at **thermofisher.com/helium-saver**