

Food safety

Confident analysis of ultra-trace pesticides residues in baby food using triple quadrupole GC-MS

Authors

Francisco José Díaz-Galiano¹,
Guillermo Garcia Gallego¹,
Giulia Riccardino², Adam Ladak³,
and Paul Silcock³

¹European Union Reference Laboratory for
Pesticide Residues in Fruit & Vegetables,
University of Almeria, Spain

²Thermo Fisher Scientific, Milan, IT

³Thermo Fisher Scientific,
Hemel Hempstead, UK

Keywords

Pesticides, baby food, gas
chromatography-mass spectrometry,
GC-MS, triple quadrupole,
TSQ 9610 mass spectrometer,
NeverVent Advanced Ionization
Ion source (AEI), TRACE 1610 GC,
programmable temperature vaporizing
injector, PTV, AI/AS 1610

Goal

The aim of this application note is to demonstrate the performance of the Thermo Scientific™ TSQ™ 9610 triple quadrupole mass spectrometer coupled to the Thermo Scientific™ TRACE™ 1610 GC equipped with programmable temperature vaporizing injector (PTV) for the determination of trace level pesticide residues in baby food.

Introduction

Pesticides are commonly used in agriculture to control various pests during cultivation, storage, and transportation.¹ The application of pesticides can result in residues at detectable concentrations in food. To ensure food safety for consumers and protect the environment, many organizations and countries around the world have established maximum residue limits (MRLs), which for the majority of pesticide-commodity combinations are set at the default level of 10 µg/kg.^{2,3} However, the European Union (EU) has established LOD MRLs between 3–8 µg/kg for specific pesticides prohibited in baby foods.⁴

The main challenge of pesticide analysis relates to the sensitivity required to meet strict regulatory limits. Moreover, analytical testing laboratories need to have multiclass, multiresidue methods that can be applied for the analysis of a large number of diverse pesticides in a high number of different sample types. These laboratories must also ensure high sample throughput, fast turnaround, and a low cost of analysis to offer a competitive service to their customers.

Gas chromatography coupled to triple quadrupole mass spectrometry (GC-MS/MS) ensures high sensitivity and selectivity for confident detection, identification, and quantitation of pesticide residues, while using faster, generic, small-scale sample extraction procedures such as QuEChERS (quick, easy, cheap effective, rugged, and safe). The QuEChERS procedure has become a popular approach for sample preparation in many laboratories because of improvement in productivity.⁵ The simplicity, low cost, speed, and wide analyte scope of QuEChERS acetonitrile extraction combined with dispersive solid phase extraction (dSPE) cleanup, has completely changed the pesticide residues analyst's approach to multi-residue analysis. This concept based on the extraction of a small test portion (2–15 g), with a low volume of solvent (10–15 mL) in a tube, has proved very successful. There is no need for homogenization in the solvent (shaking is sufficient). In addition, there is reduced waste and minimal requirements for equipment, glassware, reagents, and bench space.⁶

In this study the suitability of the TSQ 9610 triple quadrupole GC-MS/MS system was assessed for the analysis of >200 pesticides in baby food at trace concentrations in acetonitrile QuEChERS extracts. Overall method performance, including linearity, sensitivity, recovery, and precision, as well as system long-term robustness were evaluated.

Experimental

In the experiments described here, a TSQ 9610 triple quadrupole mass spectrometer equipped with a Thermo Scientific™ NeverVent™ Advanced Electron Ionization (AEI) ion source was coupled to a TRACE 1610 gas chromatograph equipped with a Thermo Scientific™ iConnect™ programmable temperature vaporizing (iConnect PTV) injector and a Thermo Scientific™ AI/AS 1610 liquid autosampler. The NeverVent technology allows for ion source cleaning, filament replacement, and column exchange without breaking instrument vacuum, therefore ensuring minimum downtime to the laboratory workflow. Chromatographic separation was achieved on a Thermo Scientific™ TraceGOLD™ TG-5SilMS capillary column 30 m × 0.25 mm × 0.25 μm (P/N 26096-1420). The phenyl groups incorporated in the polymer backbone ensure improved thermal stability and reduced susceptibility to oxidation resulting in low column bleed and outstanding inertness.

Additional GC-MS/MS and autosampler parameters as well as a complete list of the target compounds are detailed in Table 1 and Appendix 1, respectively.

Table 1. GC-MS/MS and autosampler experimental conditions for the analysis of pesticides

AI/AS 1610 Autosampler parameters	
Injection type	Standard
Sample mode	Standard
Fill strokes	10
Sample depth	Bottom
Injection mode	Fast
Pre-injection delay time (min)	0
Post-injection delay time (min)	0
Pre-injection wash cycles	1
Pre-injection solvent wash volume (μL)	6.0
Post-injection wash cycles	2
Pre-injection solvent wash volume (μL)	6.0
Sample wash cycles	1
Sample wash volume (μL)	1.0
Injection volume (μL)	1.0
TRACE 1610 GC parameters	
iConnect PTV parameters	
Injection temperature (°C)	70
Liner	PTV 6 baffle Siltek™ liner (P/N 453T2120)
Injection mode	Splitless
Injection time (min)	0.1
Transfer rate (°C/s)	5.0
Transfer temperature (°C)	300
Transfer time (min)	2.00
Cleaning rate (°C/s)	14.5
Cleaning temperature (°C)	320
Cleaning time (time)	5.00
Cleaning split flow (mL/min)	75
Post cycle temperature	Maintain
Split flow (mL/min)	50
Septum purge flow (mL/min)	5, constant
Carrier gas, flow (mL/min)	He, 1.2

Table 1 continued. GC-MS/MS and autosampler experimental conditions for the analysis of pesticides

TRACE 1610 GC parameters	
Oven temperature program	
Temperature (°C)	80
Hold time (min)	0.5
Rate (°C/min)	50
Temperature 2 (°C)	190
Rate (°C/min)	6
Temperature 3 (°C)	300
Hold time (min)	5
GC run time (min)	37.70
Column	
Trace GOLD TG-5SiIMS	30 m, 0.25 mm, 0.25 µm (P/N 26096-1420)
TSQ 9610 Mass Spectrometer parameters	
Transfer line temperature (°C)	250
Ion source type and temperature (°C)	NeverVent AEI, 320
Ionization type	EI
Emission current (µA)	50
Electron energy (eV)	50
Aquisition mode	timed-SRM
Tuning parameters	AEI SmartTune
Collision gas and pressure (psi)	Argon at 70

Data acquisition, processing, and reporting

Data was acquired, processed, and reported using the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.3. Integrated instrument control ensures full automation of the analytical workflow combined with an intuitive user interface for data analysis, processing, customizable reporting, and storage in compliance with the Federal Drug Administration Title 21 Code of Federal Regulations Part 11 (Title 21 CFR Part 11). The advanced reprocessing capability of Chromeleon CDS ensures immediate and easy data analysis, offering the possibility to easily flag and check the compliance of the results with the SANTE criteria⁷ as reported in Figure 2C.

Sample and matrix-matched standard preparation

Several baby food samples (blank and pre-spiked with some pesticides at 1 or 3 µg/kg) were extracted using the citrate-buffered QuEChERS protocol (Thermo Scientific™ QuEChERS EN 15662 Method Extraction Kit **P/N S1-10-EN-KIT**) according to the procedure described in Figure 1. Matrix-matched calibration standards were prepared by spiking the final extracts with a mixture of >200 pesticides and used to assess linearity, detection limits, and repeatability. The pre-spiked samples were used to assess recovery and quantitative performance. Some aliquots of the final extracts were spiked at 10 µg/kg and used to assess the long-term instrument robustness.

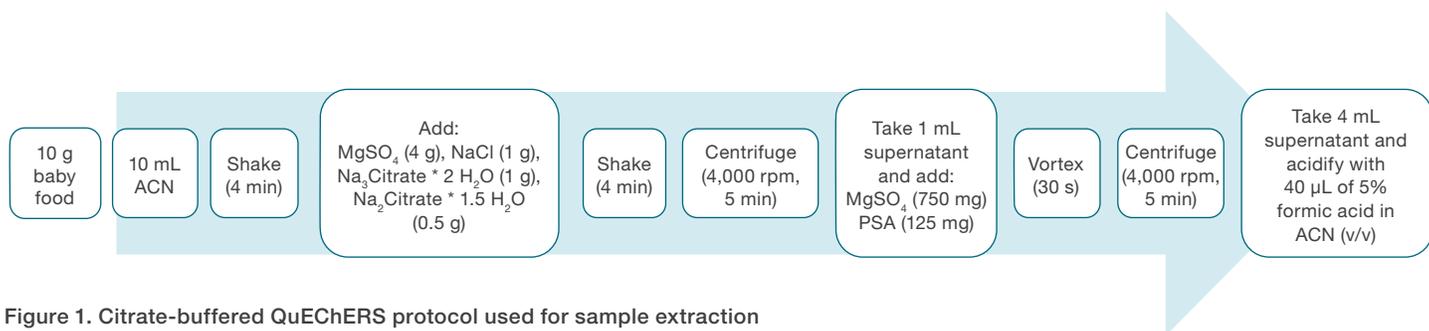


Figure 1. Citrate-buffered QuEChERS protocol used for sample extraction

Results and discussion

Chromatography

Food is a complex matrix; therefore, the capability to extract, detect, identify, and quantify ultra-trace level pesticides is key to ensure compliance with the maximum residue levels (MRLs) defined by the regulations. A timed-selected reaction monitoring (t-SRM) acquisition method allowed for simultaneous acquisition of multiple characteristic ions for each pesticide, maintaining high sensitivity combined with high selectivity to discriminate between the target compounds and the matrix thus ensuring a confident and selective identification of analytes. The identification of the target pesticides followed the criteria stated in the SANTE/12682/2019 guidance document⁶:

1. A minimum of two product ions are detected for each pesticide with peak S/N >3 (or, in case noise is absent, a signal should be present in at least five subsequent scans) and with the mass resolution for precursor ion isolation equal to or better than unit mass resolution.
2. Retention time tolerance of ± 0.1 minutes compared with standards in the same sequence.
3. Ion ratio within $\pm 30\%$ (relative) of the average of calibration standards from the same sequence.

As an example, the total ion chromatogram (TIC) acquired in EI, full-scan mode (m/z 50–500), and the t-SRM acquisition of an organically labeled baby food sample (32% potato, 15% carrot, 13% green bean, 10% tomato, 8% green peas, 3% celery, 2% olives, 3% onion, rice) pre-spiked at 3 $\mu\text{g}/\text{kg}$ are shown in Figure 2A, B. The use of the PTV injector allowed for efficient transfer of the analytes, reducing the risks of formation of breakdown products. Extracted ion chromatograms (XIC) for some pesticides pre-spiked in matrix (peach (23%), banana (23%), orange (10%), grape (4%), lemon, apple (31%)) at 1 $\mu\text{g}/\text{kg}$ are reported as an example in Figure 2. The high inertness of the sample path and the TraceGOLD column allowed for good chromatography with Gaussian peak shapes (peak asymmetry: As 1.0–1.5) even at a low analyte concentration of 1 $\mu\text{g}/\text{kg}$, ensuring easy peak integration and precise quantitative results despite the complexity of the matrix.

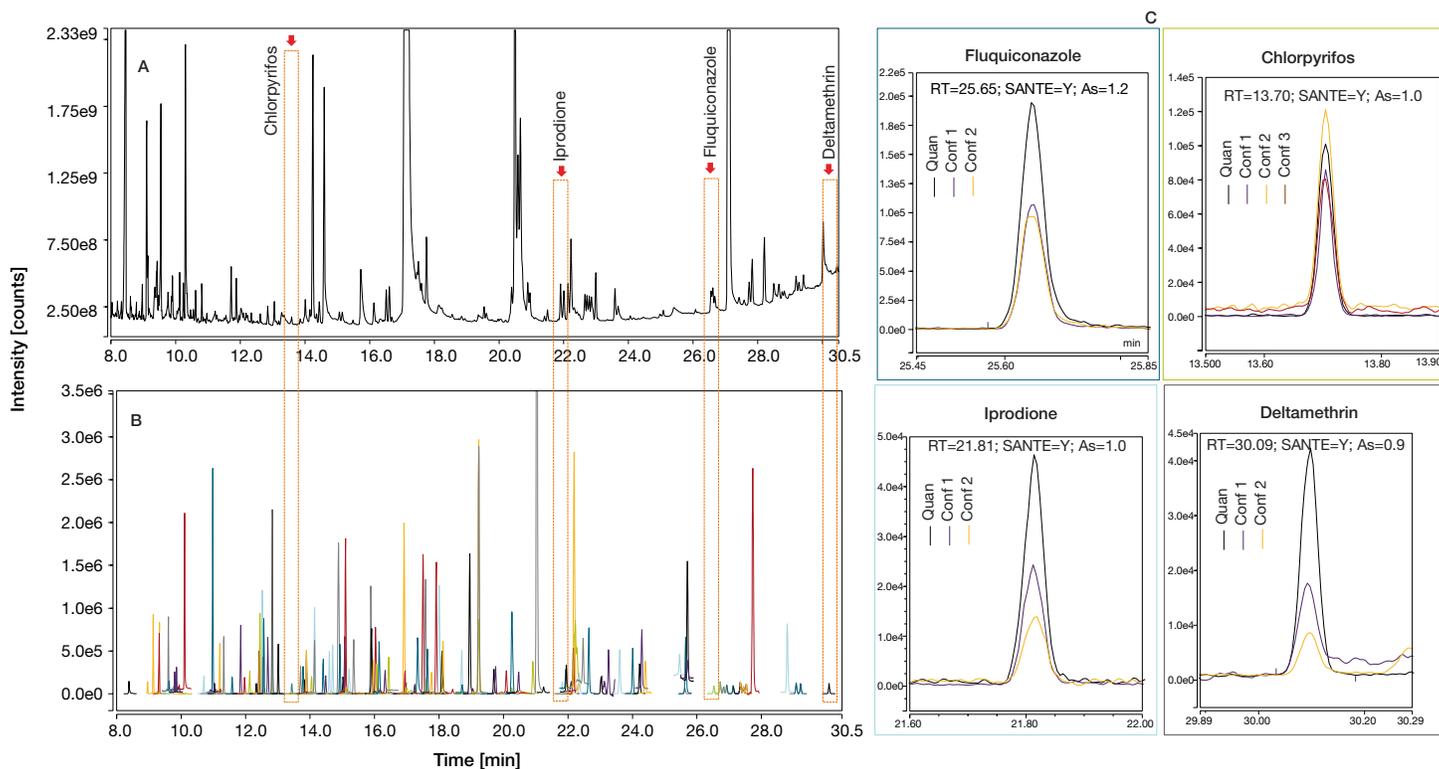


Figure 2. TIC (full scan: m/z 50–500, A-upper trace) and t-SRM acquisition (B-bottom trace) for organic food sample pre-spiked at 3 $\mu\text{g}/\text{kg}$. Some examples of pesticides (C) pre-spiked in matrix at 1 $\mu\text{g}/\text{kg}$. Compound identification as per SANTE guidance with compliance automatically flagged (SANTE=Y) and peak asymmetry (A_s) are annotated in the peak label.

Linearity, instrument detection limit (IDL), and limit of detection (LOD)

The TSQ 9610 mass spectrometer with the NeverVent AEI ion source is equipped with the Thermo Scientific™ XLXR™ detector, which is an electron multiplier that offers extended detector lifetime and dynamic range. To test the performance of the detector, matrix-matched calibration curves were prepared by spiking the QuEChERS extracts with pesticide mix ranging from 0.05 to 500 µg/kg. Each calibration level was injected in duplicate. All target analytes showed a linear trend with coefficients of determination (R^2) > 0.990 and residual values

(measured as %RSD of average response factors, AvCF %RSD) <20% as reported in Appendix 1, thus confirming a wider linear range can be easily achieved. All target compounds satisfied the SANTE criteria at the default MRL of 10 µg/kg and more than 95% were confirmed following the SANTE criteria at concentrations <1 µg/kg. Full range calibration curves (0.05–500 µg/kg) for dichlobenil, pentachlorobenzene, and pentachlorobenzonitrile, as well as zoomed detail (0.05–1.0 µg/kg) and the quantifier and qualifier ions at 0.05 µg/kg, are reported as an example in Figure 3.

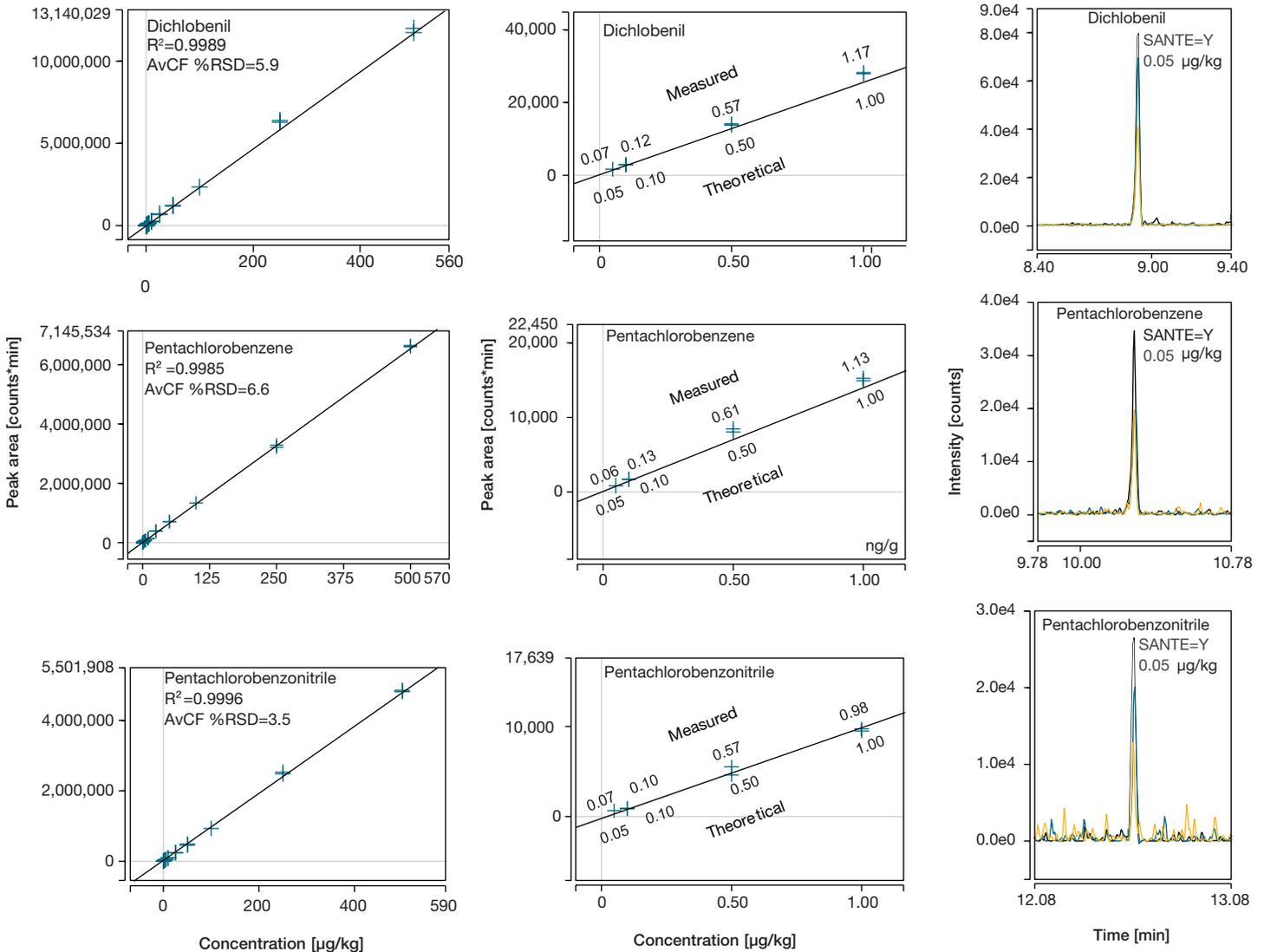


Figure 3. Example of matrix-matched calibration curves: full range (0.05–500 µg/kg) and zoomed detail (0.05–1.0 µg/kg) for dichlobenil, pentachlorobenzene, and pentachlorobenzonitrile, as well as quantifier and qualifier ions at 0.05 µg/kg, confirmed as per SANTE criteria. Each calibration level was injected in duplicate. Coefficient of determination (R^2) and AvCF %RSD are annotated.

The instrument detection limit was determined for all the target compounds by spiking n=11 matrix extracts at 0.08, 0.8, 1.5, and 3.0 µg/kg. IDLs were calculated taking into account the one-tailed Student's t-test values for the corresponding n-1 degrees of freedom at 99% confidence, the concentration, and the absolute peak area %RSD (<15%) for each analyte. Calculated IDLs ranged from 6 to 650 fg on column (OC), corresponding to 0.006 to 0.65 µg/kg as reported in Figure 4.

Recovery and precision

Analytes recovery was assessed by spiking an organic baby food sample (potato (32%), carrot (15%), green bean (13%), tomato (10%), green peas (8%), celery (3%), olives (2%), onion (3%), rice) with some of the investigated pesticides at 3 µg/kg before extracting with QuEChERS. Calculated recoveries for the spiked compounds were between 70% and 120% with calculated precision ≤10% (Appendix 2). Calculated recoveries for some of the spiked compounds are reported as an example in Figure 5.

Robustness

Analytical testing laboratories need to process a high number of samples every day; therefore, it is critical that the instrument performs consistently. Mass calibration and resolution tuning are two of the most important aspects ensuring system performance. The Thermo Scientific™ SmartTune™ feature allows the user to check the tune status of the system with few mouse clicks in an easy and quick fashion.

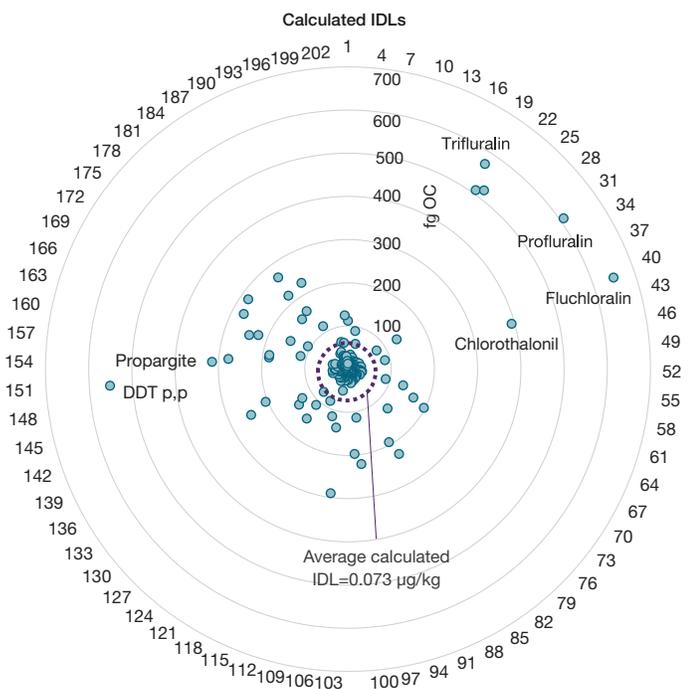


Figure 4. Calculated IDLs for all investigated pesticides. IDLs ranged from 6 to 650 fg OC corresponding to 0.006 to 0.65 µg/kg in the sample extract. The dotted grey circle marks the average calculated IDL of 0.073 µg/kg.

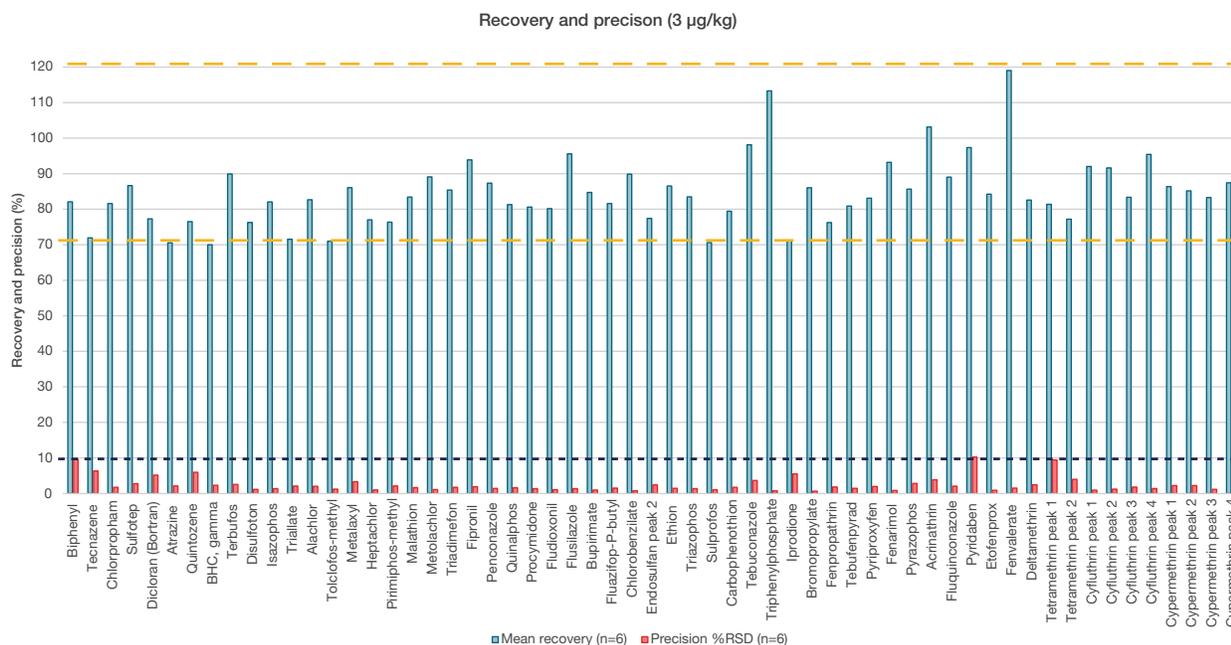


Figure 5. Calculated recoveries for a selection of the spiked compounds. Recoveries were between 70% and 120% with calculated precision ≤10%.

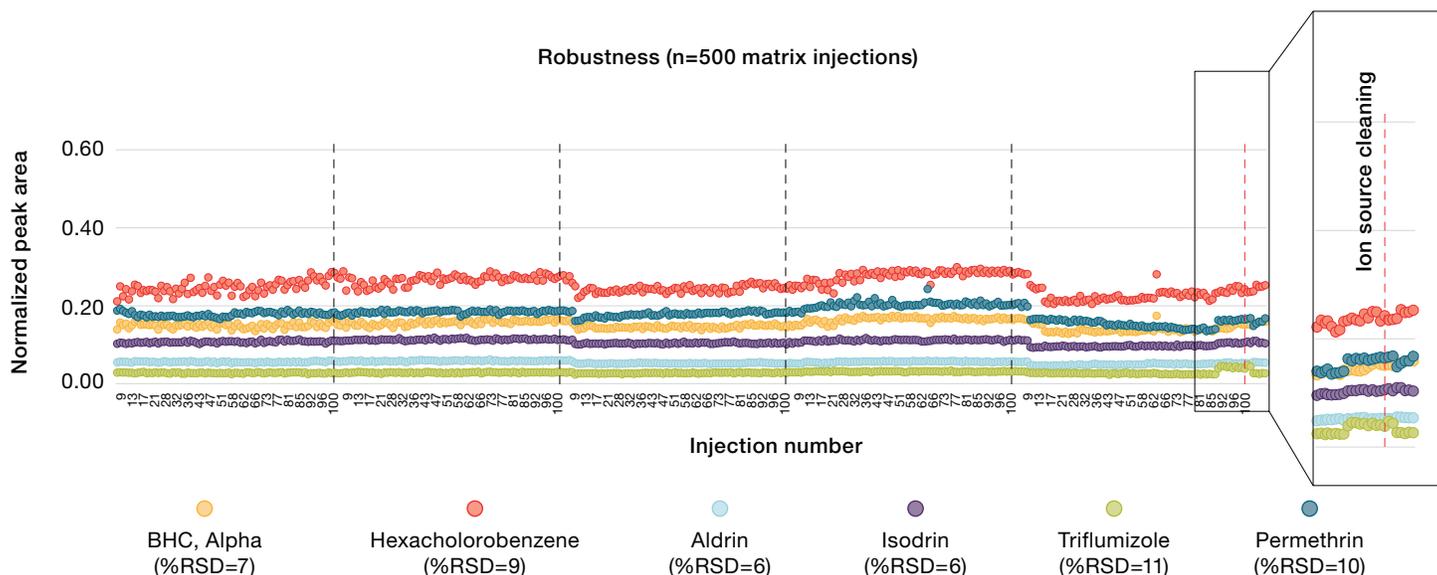


Figure 6. Normalized peak area response (analyte peak area / ISTD peak area) obtained for n=500 consecutive injections of matrix samples spiked at the default MRL (10 µg/kg). Every 100 injections (blue dotted lines), the PTV liner and septum were replaced, approximately 6 cm of the head of the column were trimmed, and the SmartTune feature was used to check the instrument status.

Instrument robustness for everyday analysis was evaluated over almost four weeks of continuous operation by repeatedly injecting various matrix extracts spiked at 10 µg/kg (total number of matrix injections = 500) in randomized order. A list of the matrices can be found in Appendix 3. A quality control standard (QC) was spiked at a concentration corresponding to 3 µg/kg and injected in duplicate every 12 samples to monitor the system stability. After every 100 injections, the PTV liner and septum were replaced, approximately 6 cm of the head of the column were trimmed, and the SmartTune feature was used to check the instrument status. SmartTune uses the MS parameters established during the initial tuning with a clean source and intelligently assesses the performance of the system, only re-tuning when MS performance has been compromised.

Even though the instrument was still performing well, an evaluation of how long ion source maintenance would take was performed. The ion source was cleaned after n=500 injections and the consistency of the data assessed after the cleaning. The NeverVent technology allowed the removal of the ion source without breaking the vacuum so that the instrument was producing useable data with a cleaned ion source in less than two hours, thus ensuring minimal instrument downtime. A spare ionization source would allow the replacement of the source be carried out in a minute, thus further minimizing downtime. Normalized peak area response (analyte peak area / ISTD peak area) as well as the ion ratios were stable at the default MRL (Figure 6).

Conclusions

The results obtained in these experiments demonstrate that the TSQ 9610 mass spectrometer equipped with a NeverVent AEI ion source in combination with the TRACE 1610 GC and the AI/AS 1610 liquid autosampler delivers excellent analytical performance for multi-residue analysis of pesticides in baby food samples.

- Wide linear response and accurate quantitative performance for the investigated pesticides was obtained with a coefficient of determination of $R^2 > 0.99$ and AvCF %RSDs < 20 in spiked matrix over a concentration range of 0.05 to 500 µg/kg.
- High recovery (70–120%) and precision (RSD $\leq 10\%$) were demonstrated for pre-spiked QuEChERS extracts of at 3 µg/kg.
- Low instrument detection limits ranging from 6 to 650 fg on column corresponding to 0.006 to 0.65 µg/kg were achieved. The average calculated IDL for all compounds was 0.073 µg/kg.
- The enhanced robustness and reliability of the AI/AS 1610 liquid autosampler combined with the efficient transfer of the analyte through the PTV injector, the inertness of the flow path, and the stability of the NeverVent AEI ion source allowed for n=500 injections of acetonitrile QuEChERS extracts over four weeks continuous operations with minimal maintenance, keeping compliance with SANTE guidelines.

References

1. Fussell R. J. An overview of regulation and control of pesticide residues in food, Thermo Fisher Scientific, White Paper 71711, <http://tools.thermofisher.com/content/sfs/brochures/WP-71711-Regulatory-Pesticide-Residue-WP71711-EN.pdf>
2. European Commission, Guidelines - Maximum Residue levels, https://ec.europa.eu/food/plants/pesticides/maximum-residue-levels_en
3. Commission Directive 2006/125/EC of 5 December 2006 on processed cereal-based foods and baby foods for infants and young children, <https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX%3A32006L0125>
4. Payá, P.; Anastassiades, M.; Mack, D.; Sigalova, I.; Tasdelen, B.; Olivia, J.; Barba, A. Analysis of pesticide residues using the Quick Easy Cheap Effective Rugged and Safe (QuEChERS) pesticide multiresidue method in combination with gas and liquid chromatography and tandem mass spectrometric detection. *Analytical and Bioanalytical Chemistry*. **2007**, *389*(6), 1697–1714 (Note: basis of Official CEN method EN15662). <http://link.springer.com/article/10.1007%2Fs00216-007-1610-7> (accessed Apr 20, 2016)
5. Fussell R. J. Analytical challenges for pesticide residue analysis in food: sample preparation, processing, extraction and cleanup, Thermo Fisher Scientific, White Paper 72048, <https://tools.thermofisher.com/content/sfs/brochures/WP-72048-MS-Sample-Preparation-WP72048-EN.pdf>
6. SANTE/12682/2019, Analytical quality control and method validation procedures for pesticide residues analysis in food and feed. Implemented 01/01/2020. https://ec.europa.eu/food/system/files/2020-01/pesticides_mrl_guidelines_wrkdoc_2019-12682.pdf

Appendix 1

Table A1. List of target analytes, calibration ranges, residual values (measured as %RSD of average response factors, AvCF %RSD), calculated coefficient of determination (R^2), instrument detection limits (IDLs), and limits of detection (LOD)

Number	Pesticide	Calibration range ($\mu\text{g}/\text{kg}$)	AvCF %RSD	R^2	IDL (fg OC)	LOD ($\mu\text{g}/\text{kg}$)
1	Allidochlor	0.5–500	7.5	0.9987	112	0.112
2	Dichlobenil	0.05–500	8.0	0.9985	6	0.006
3	Biphenyl	0.05–500	14.7	0.9949	16	0.016
4	Mevinphos	0.05–500	9.6	0.9979	11	0.011
5	3,4–Dichloroaniline	0.05–500	6.7	0.9990	13	0.013
6	Etridiazole (Terrazole)	0.05–500	11.7	0.9970	34	0.034
7	Pebulate	0.5–500	7.4	0.9987	90	0.09
8	N–(2,4–Dimethylphenyl)formamide	0.05–500	10.6	0.9966	15	0.015
9	Methacrifos	0.05–500	5.9	0.9991	23	0.023
10	Tetrahydrophthalimide (THPI)	0.5–500	9.3	0.9978	61	0.061
11	Chloroneb	0.05–500	6.9	0.9989	15	0.015
12	Ortho–phenylphenol	0.05–500	6.7	0.9989	29	0.029
13	Pentachlorobenzene	0.05–500	7.1	0.9988	10	0.01
14	Tecnazene	0.05–500	7.4	0.9988	15	0.015
15	Propachlor	0.05–500	3.9	0.9996	16	0.016
16	Diphenylamine	0.05–500	4.8	0.9995	13	0.013
17	2,3,5,6–Tetrachloroaniline	0.05–500	5.1	0.9994	22	0.022
18	Cycloate	0.05–500	4.2	0.9995	13	0.013
19	Chlorpropham	0.05–500	7.5	0.9986	18	0.018
20	Trifluralin	1.0–500	13.1	0.9963	571	0.571
21	Ethalfuralin	1.0–500	14.6	0.9954	509	0.509
22	Benfluralin	1.0–500	14.6	0.9954	520	0.52
23	Sulfotep	0.05–500	4.0	0.9996	17	0.017
24	Phorate	0.05–500	5.6	0.9993	22	0.022
25	BHC, Alpha	0.05–500	4.3	0.9995	11	0.011

Table A1 continued. List of target analytes, calibration ranges, residual values (measured as %RSD of average response factors, AvCF %RSD), calculated coefficient of determination (R^2), instrument detection limits (IDLs), and limits of detection (LOD)

Number	Pesticide	Calibration range ($\mu\text{g}/\text{kg}$)	AvCF %RSD	R^2	IDL (fg OC)	LOD ($\mu\text{g}/\text{kg}$)
26	Hexachlorobenzene	0.05–500	5.4	0.9993	9	0.009
27	Pentachloroanisole	0.05–500	4.7	0.9995	11	0.011
28	Dicloran (Bortran)	0.05–500	8.8	0.9983	25	0.025
29	Atrazine	0.05–500	4.9	0.9994	25	0.025
30	BHC, Beta	0.05–500	3.5	0.9997	19	0.019
31	Clomazone	0.05–500	5.4	0.9993	17	0.017
32	Profluralin	1–500	14.7	0.9954	609	0.609
33	Quintozene	0.5–500	8.4	0.9982	79	0.079
34	Pentachlorobenzonitrile	0.05–500	13.4	0.9959	132	0.132
35	BHC, gamma	0.05–500	4.7	0.9995	21	0.021
36	Terbutylazine	0.05–500	4.6	0.9995	29	0.029
37	Terbufos	0.05–500	8.5	0.9984	17	0.017
38	Propyzamide	0.05–500	4.5	0.9995	9	0.009
39	Diazinon	0.05–500	4.9	0.9995	20	0.02
40	Fonofos	0.05–500	4.6	0.9995	14	0.014
41	Fluchloralin	1–500	16.8	0.9934	650	0.65
42	Pyrimethanil	0.05–500	7.6	0.9987	16	0.016
43	Chlorothalonil	1–500	14.9	0.9952	393	0.393
44	Terbacil	0.5–500	5.3	0.9993	88	0.088
45	Disulfoton	0.05–500	4.2	0.9996	24	0.024
46	Isazophos	0.05–500	4.9	0.9994	31	0.031
47	Tefluthrin	0.05–500	3.7	0.9997	10	0.01
48	BHC, delta	0.05–500	4.2	0.9996	14	0.014
49	Triallate	0.05–500	3.6	0.9997	8	0.008
50	Pentachloroaniline	0.05–500	4.6	0.9995	16	0.016
51	Endosulfan ether	0.05–500	4.4	0.9995	18	0.018
52	Dimethachlor	0.05–500	5.5	0.9993	10	0.01
53	Propanil	0.05–500	5.1	0.9994	17	0.017
54	Acetochlor	0.05–500	4.8	0.9995	27	0.027
55	Chlorpyrifos–methyl	0.05–500	4.2	0.9996	29	0.029
56	Vinclozolin	0.05–500	4.7	0.9995	26	0.026
57	Parathion–methyl	0.05–500	14.4	0.9956	33	0.033
58	Tolclofos–methyl	0.05–500	3.8	0.9996	20	0.02
59	Alachlor	0.05–500	3.3	0.9997	32	0.032
60	Propisochlor	0.5–500	3.7	0.9996	90	0.09
61	Metalaxyl	0.5–500	3.3	0.9997	133	0.133
62	Fenclorfos	0.05–500	3.1	0.9998	14	0.014
63	Heptachlor	0.05–500	3.0	0.9998	13	0.013
64	Pirimiphos–methyl	0.05–500	1.6	0.9999	17	0.017
65	Prodiamine	0.5–500	12.9	0.9960	165	0.165
66	Fenitrothion	0.05–500	14.7	0.9955	30	0.03
67	Linuron	0.5–500	5.1	0.9993	197	0.197
68	Pentachlorothioanisole	0.05–500	5.1	0.9994	14	0.014
69	Dichlofluanid	0.05–500	5.2	0.9994	24	0.024
70	Malathion	0.05–500	2.8	0.9998	14	0.014

Table A1 continued. List of target analytes, calibration ranges, residual values (measured as %RSD of average response factors, AvCF %RSD), calculated coefficient of determination (R^2), instrument detection limits (IDLs), and limits of detection (LOD)

Number	Pesticide	Calibration range ($\mu\text{g}/\text{kg}$)	AvCF %RSD	R^2	IDL (fg OC)	LOD ($\mu\text{g}/\text{kg}$)
71	Metolachlor	0.05–500	4.3	0.9996	7	0.007
72	Chlorpyrifos–ethyl	0.05–500	3.2	0.9998	14	0.014
73	Fenthion	0.05–500	3.0	0.9998	22	0.022
74	Chlorthal–dimethyl (Dacthal)	0.05–500	2.5	0.9999	21	0.021
75	Aldrin	0.05–500	5.9	0.9991	25	0.025
76	Anthraquinone	0.05–500	6.2	0.9991	10	0.01
77	Parathion (ethyl)	0.5–500	12.4	0.9966	129	0.129
78	Triadimefon	0.05–500	3.9	0.9996	22	0.022
79	Dichlorobenzophenone, 4, 4	0.05–500	3.4	0.9997	9	0.009
80	Fenson	0.05–500	2.6	0.9998	8	0.008
81	Pirimiphos–ethyl	0.05–500	2.5	0.9998	15	0.015
82	Diphenamid	0.05–500	2.6	0.9998	27	0.027
83	Bromophos–methyl (Bromophos)	0.05–500	3.3	0.9997	16	0.016
84	MGK–264 A	0.05–500	3.5	0.9997	19	0.019
85	Isopropalin	0.5–500	9.5	0.9980	229	0.229
86	Pendimethalin	0.5–500	10.1	0.9976	194	0.194
87	Cyprodinil	0.05–500	2.4	0.9999	18	0.018
88	Isodrin	0.05–500	4.3	0.9995	18	0.018
89	Metazachlor	0.05–500	6.0	0.9992	9	0.009
90	MGK–264 B	0.05–500	5.0	0.9992	29	0.029
91	Fipronil	0.05–500	4.4	0.9996	24	0.024
92	Penconazole	0.05–500	2.7	0.9998	20	0.02
93	Chlozolate	0.05–500	2.6	0.9998	22	0.022
94	Tolyfluanid	0.05–500	6.3	0.9991	30	0.03
95	Chlorfenvinphos	0.05–500	5.4	0.9993	24	0.024
96	Bromfenvinphos–methyl	0.05–500	10.5	0.9976	33	0.033
97	Quinalphos	0.5–500	5.7	0.9991	114	0.114
98	Triadimenol	0.5–500	10.8	0.9965	222	0.222
99	Procymidone	0.05–500	4.1	0.9996	19	0.019
100	Triflumizole	0.5–500	3.1	0.9997	197	0.197
101	Allethrin (Bioallethrin)	0.05–500	8.6	0.9983	21	0.021
102	Bromophos–ethyl	0.05–500	2.5	0.9999	25	0.025
103	Chlorbenside	0.05–500	3.1	0.9998	9	0.009
104	Chlordane alpha–cis	0.05–500	4.7	0.9995	14	0.014
105	DDE o,p	0.05–500	3.4	0.9997	6	0.006
106	Tetrachlorvinphos	0.05–500	8.8	0.9983	26	0.026
107	Paclobutrazol	0.5–500	8.2	0.9985	290	0.29
108	Chlordane gamma–trans	0.05–500	2.9	0.9998	14	0.014
109	Endosulfan peak 1	0.5–500	3.7	0.9997	138	0.138
110	Flutriafol	0.5–500	4.0	0.9996	51	0.051
111	Nonachlor–trans	0.05–500	3.0	0.9998	28	0.028
112	Bromfenvinphos	0.05–500	2.1	0.9999	14	0.014
113	Fenamiphos	0.5–500	3.7	0.9997	115	0.115
114	Flutolanil	0.05–500	5.8	0.9992	19	0.019
115	Iodofenfos	0.05–500	3.2	0.9997	21	0.021

Table A1 continued. List of target analytes, calibration ranges, residual values (measured as %RSD of average response factors, AvCF %RSD), calculated coefficient of determination (R^2), instrument detection limits (IDLs), and limits of detection (LOD)

Number	Pesticide	Calibration range ($\mu\text{g}/\text{kg}$)	AvCF %RSD	R^2	IDL (fg OC)	LOD ($\mu\text{g}/\text{kg}$)
116	Chlorfenson	0.05–500	4.2	0.9996	11	0.011
117	Fludioxonil	0.05–500	4.3	0.9995	10	0.01
118	Prothiofos	0.05–500	2.9	0.9998	22	0.022
119	Pretilachlor	0.5–500	5.2	0.9992	84	0.084
120	Profenofos	0.5–500	3.2	0.9997	32	0.032
121	DDE p,p	0.05–500	5.0	0.9994	8	0.008
122	Oxadiazon	0.05–500	6.0	0.9991	8	0.008
123	Myclobutanil	0.05–500	4.1	0.9996	25	0.025
124	Flusilazole	0.05–500	4.0	0.9996	20	0.02
125	Dieldrin	0.5–500	3.7	0.9996	149	0.149
126	Oxyfluorfen	0.5–500	9.5	0.9978	111	0.111
127	DDD o,p	0.05–500	6.1	0.9990	17	0.017
128	Bupirimate	0.05–500	3.8	0.9997	17	0.017
129	Chlorfenapyr	0.5–500	5.0	0.9993	77	0.077
130	Nitrofen	0.05–500	6.5	0.9990	27	0.027
131	Fluazifop–P–butyl	0.05–500	3.2	0.9998	15	0.015
132	Perthane (Ethylan)	0.05–500	2.3	0.9999	11	0.011
133	Endrin	0.5–500	1.6	0.9999	140	0.14
134	Chlorobenzilate	0.05–500	2.7	0.9998	7	0.007
135	Endosulfan peak 2	0.5–500	5.5	0.9991	125	0.125
136	Nonachlor–cis	0.05–500	3.3	0.9997	25	0.025
137	DDD p,p	0.05–500	9.1	0.9983	25	0.025
138	Ethion	0.05–500	3.8	0.9997	14	0.014
139	DDT o,p	0.5–500	9.8	0.9979	248	0.248
140	Chlorthiophos	0.05–500	3.1	0.9998	9	0.009
141	Endrin Aldehyde	0.5–500	9.3	0.9978	205	0.205
142	Triazophos	0.05–500	5.2	0.9994	12	0.012
143	Sulprofos	0.05–500	2.9	0.9998	16	0.016
144	Carfentrazone–ethyl	0.05–500	2.4	0.9999	20	0.02
145	Carbophenothion	0.05–500	3.3	0.9997	36	0.036
146	4,4'–Methoxychlor olefin	0.05–500	2.0	0.9999	12	0.012
147	Norflurazon	0.05–500	6.5	0.9990	18	0.018
148	Edifenphos	0.05–500	10.2	0.9977	18	0.018
149	Endosulfan sulfate	0.05–500	3.4	0.9997	9	0.009
150	Lenacil	0.05–500	4.3	0.9995	36	0.036
151	DDT p,p	1–500	19.7	0.9925	552	0.552
152	Hexazinone	0.05–500	2.5	0.9999	16	0.016
153	2,4'–Methoxychlor	0.05–500	9.1	0.9982	31	0.031
154	Tebuconazole	0.05–500	5.7	0.9992	29	0.029
155	Propargite	1–500	6.3	0.9985	315	0.315
156	Nitralin	1–500	17.3	0.9913	278	0.278
157	Piperonyl butoxide	0.05–500	4.6	0.9995	11	0.011
158	Resmethrin peak 1	0.5–500	5.3	0.9991	185	0.185
159	Resmethrin peak 2	0.5–500	5.3	0.9991	185	0.185

Table A1 continued. List of target analytes, calibration ranges, residual values (measured as %RSD of average response factors, AvCF %RSD), calculated coefficient of determination (R²), instrument detection limits (IDLs), and limits of detection (LOD)

Number	Pesticide	Calibration range (µg/kg)	AvCF %RSD	R ²	IDL (fg OC)	LOD (µg/kg)
160	Pyridaphenthion	0.05–500	7.3	0.9988	20	0.02
161	Iprodione	0.05–500	2.7	0.9998	25	0.025
162	Endrin–Ketone	0.5–500	8.4	0.9983	114	0.114
163	Tetramethrin peak 1	0.05–500	3.4	0.9997	37	0.037
164	Phosmet	0.5–500	14.4	0.9946	242	0.242
165	EPN	0.5–500	7.8	0.9982	222	0.222
166	Bifenthrin	0.05–500	3.1	0.9997	32	0.032
167	Bromopropylate	0.05–500	2.7	0.9998	9	0.009
168	Tetramethrin peak 2	0.5–500	3.4	0.9997	148	0.148
169	Methoxychlor	1–500	19.9	0.9920	273	0.273
170	Fenpropathrin	0.5–500	2.7	0.9998	107	0.107
171	Tebufenpyrad	0.05–500	2.1	0.9999	8	0.008
172	Tetradifon	0.05–500	3.9	0.9996	18	0.018
173	Phenothrin	0.5–500	4.0	0.9996	282	0.282
174	Phosalone	0.05–500	6.9	0.9988	18	0.018
175	Leptophos	0.05–500	9.2	0.9981	16	0.016
176	Pyriproxyfen	0.05–500	5.1	0.9994	6	0.006
177	Mirex	0.05–500	3.3	0.9997	6	0.006
178	Cyhalothrin I (lambda)	0.05–500	4.0	0.9996	12	0.012
179	Fenarimol	0.05–500	2.9	0.9998	12	0.012
180	Pyrazophos	0.5–500	4.5	0.9994	157	0.157
181	Acrinathrin	0.05–500	6.7	0.9989	18	0.018
182	Azinphos–ethyl	0.5–500	10.4	0.9973	219	0.219
183	Pyraclufos	0.5–500	9.0	0.9980	267	0.267
184	Permethrin peak 1	0.5–500	3.4	0.9997	165	0.165
185	Coumaphos	0.05–500	5.0	0.9994	15	0.015
186	Fluquinconazole	0.05–500	3.5	0.9997	9	0.009
187	Permethrin peak 2	0.5–500	4.6	0.9994	115	0.115
188	Prochloraz	0.5–500	4.1	0.9995	227	0.227
189	Pyridaben	0.78–100	5.2	0.9993	40	0.04
190	Cyfluthrin peak 1	0.05–500	4.7	0.9994	22	0.022
191	Cyfluthrin peak 2	0.05–500	5.2	0.9993	23	0.023
192	Cyfluthrin peak 3	0.5–500	5.8	0.9991	43	0.043
193	Cyfluthrin peak 4	0.05–500	5.8	0.9991	33	0.033
194	Cypermethrin peak 1	0.05–500	3.1	0.9998	29	0.029
195	Cypermethrin peak 2	0.05–500	5.7	0.9992	24	0.024
196	Cypermethrin peak 3	0.5–500	7.2	0.9987	65	0.065
197	Cypermethrin peak 4	0.05–500	7.4	0.9986	30	0.03
198	Etofenprox	0.05–500	3.0	0.9998	8	0.008
199	Fluridone	0.05–500	5.4	0.9993	62	0.062
200	Fenvalerate	0.05–500	4.9	0.9994	30	0.03
201	Fluvalinate peak 1	0.05–500	6.1	0.9991	19	0.019
202	Fluvalinate peak 2	0.5–500	3.1	0.9998	125	0.125
203	Deltamethrin	0.05–500	3.8	0.9997	13	0.013

Appendix 2

Table A2. Calculated recoveries for a bio baby food sample spiked with pesticides at 3 µg/kg prior to QuEChERS extraction

Name	Recovery (% n=7)	Precision (RSD% n=6)
Biphenyl	82	10
Pebulate	80	8
Tecnazene	72	6
Diphenylamine	75	2
Chlorpropham	82	2
Sulfotep	87	3
Dicloran (Bortran)	77	5
Atrazine	71	2
Quintozene	77	6
BHC, gamma	70	2
Terbufos	90	3
Propyzamide	80	1
Diazinon	88	2
Fonofos	81	2
Pyrimethanil	79	3
Disulfoton	76	1
Isazophos	82	1
Triallate	72	2
Chlorpyrifos-methyl	72	3
Vinclozolin	80	1
Alachlor	71	1
Tolclofos-methyl	83	2
Metalaxyl	86	3
Heptachlor	77	1
Pirimiphos-methyl	76	2
Fenitrothion	85	6
Malathion	83	2
Metolachlor	89	1
Chlorpyrifos-ethyl	80	1
Chlorthal-dimethyl (Dacthal)	76	1
Triadimefon	85	2
Cyprodinil	75	2
Fipronil	94	2
Penconazole	87	1
Chlorfenvinphos	85	1
Quinalphos	81	2
Procymidone	81	1
Flutriafol	91	2
Flutolanil	82	1
Fludioxonil	80	1
Myclobutanil	90	1
Flusilazole	96	1
Bupirimate	85	1
Fluazifop-P-butyl	82	2
Endrin	71	2
Chlorobenzilate	90	1

Table A2 continued. Calculated recoveries for a bio baby food sample spiked with pesticides at 3 µg/kg prior to QuEChERS extraction

Name	Recovery (% n=7)	Precision (RSD% n=6)
Ethion	87	1
Triazophos	84	1
Sulprofos	71	1
Carbophenothion	79	2
Tebuconazole	98	4
Iprodione	71	6
Tetramethrin peak 1	81	10
Bromopropylate	86	1
Tetramethrin peak 2	77	4
Fenpropathrin	76	2
Tebufenpyrad	81	1
Pyriproxyfen	83	2
Fenarimol	93	1
Pyrazophos	86	3
Acrinathrin	103	4
Fluquinconazole	89	2
Pyridaben	97	10
Cyfluthrin peak 1	92	1
Cyfluthrin peak 2	92	1
Cyfluthrin peak 3	83	2
Cyfluthrin peak 4	95	1
Cypermethrin peak 1	86	2
Cypermethrin peak 2	85	2
Cypermethrin peak 3	83	1
Cypermethrin peak 4	87	3
Etofenprox	84	1
Fenvalerate	119	2
Deltamethrin	83	2

Appendix 3

Table A3. List of QuEChERS extracts spiked at 10 µg/kg that have been injected repeatedly in randomized order to evaluate system robustness

Matrix	Composition
1	Peach (23%), banana (23%), orange (10%), grape (4%), lemon, apple (31%)
2	Pineapple (23%), apple (23%), banana (23%), orange (15%), grape (2%), rice flour
3	Apple, banana (37%), grape, lemon, strawberry (23%)
4	Pumpkin (45%), banana (43%), carrot (10%), lemon
5	Pear (41%), apple (34%), banana (25%), lemon
6	Potato (32%), carrot (15%), green bean (13%), tomato (10%), green peas (8%), celery (3%), olives (2%), onion (3%), rice

Learn more at thermofisher.com/TSQ9610