Analysis of Trace Level Pesticides in Fruits and Vegetable by GC/MS/MS Using Agilent Ultra Inert Liners with Wool

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Introduction

Agilent Ultra Inert liner deactivation process significantly improves the efficiency and robustness of glass wool deactivation, allowing the use of Ultra Inert splitless liners with wool for the analysis of trace level pesticides in food matrices.

Ultra Inert liners with wool can provide many benefits including

- Superior surface inertness for the analysis of very active pesticides
- Homogeneous sample mixing and vaporization
- Protection to column and MS source from contamination and fast deterioration by trapping non-volatile matrix residue
- Prevent sample from hitting the bottom of the inlet before vaporization

Ultra Inert splitless liners with wool can be used under different injection modes

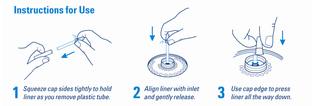
The suitability of Ultra Inert splitless liner with wool was demonstrated under various inlet injection mode using Multi Mode Inlet (MMI), including:

- Hot splitless (1 µL inj. volume)
- Cold splitless (1 µL inj. volume)
- Large Volume Injection (5 µL inj. volume)

The results show that there is no need to switch liner for different injection mode. The selection of injection mode depends on the purpose of analysis, such as required sensitivity, sample matrix, active analytes etc.

Other features of Agilent Ultra Inert Liners

- Pre-installed O-ring
- Touchless package
- Performance certificate for every individual liner



Experimental

Analysis of pesticides by GC/MS/MS

Instrument conditions

- Agilent 7890A/7000 GC/MS/MS system, equipped with Agilent 7693 Autosampler
- MMI Multi Mode inlet, refer to Table below for inlet conditions
- Inlet liner: Ultra Inert single taper splitless liner with wool (Agilent p/n 5190-2293)
- He, constant pressure
- HP-5MS UI, 15m x 0.25mm, 0.25µm (Agilent p/n 19091-431UI)
- Oven profile: 75 °C (2.57 min), 50 °C/min to 150 °C, 6°C/min to 200°C at, 16°C/min to 300°C (1min)
- Transfer line/Source/Quad (Q1 &Q2) @ 300°C/300°C/150°C
- Data acquisition: Multi Reaction Monitoring (MRM)

Testing standards

- 33 representative pesticides, 1 ng/mL to 100 ng/mL five points calibration standards, 10 ng/mL and 1 ng/mL QC

Matrix sample

- Three different fruits and vegetables matrix mixture: orange, pepper, strawberry, pear, flower and spinach
- Blank matrices sample were extracted following QuEChERS AOAC method, Pesticides standard were then post-spiked.
- Agilent BondElut QuEChERS AOAC extraction (p/n 5982-5755) and dispersive SPE kit for general fruits and vegetables (p/n 5982-5022) were used

	Hot Splitless (HSL)	Cold Splitless (CSL)	Large Volume Injection (LVI)
Inlet T	250°C	75°C for 0.02min, then 750°C/min to 350°C	75°C for 0.085min, then 750°C/min to 350°C
Purge flow to split vent	60 mL/min @ 1min	60 mL/min @ 1min	60 mL/min @ 2.57min
Injection Vol	1 µL	1 µL	5 µL
Injection speed	Fast	Fast	69 µL/min
Vent flow	--	--	100 mL/min
Vent pressure	--	--	2.5 psi until 0.085 min
Cryo	Off	On @ 75°C	On @ 75°C

Results and Discussion

Ultra Inert liners with wool provide superior inertness for assurance of accurate and reliable analysis of active pesticides

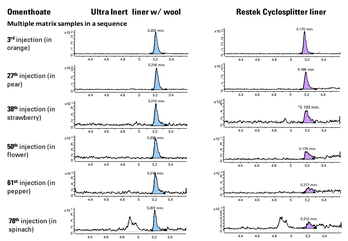
Even at the most stringent HSL condition, Ultra Inert liners with wool provide excellent repeatability for reliable quantitation of active pesticides in real matrix.

RSD of n = 10 injections of 10 ng/mL pesticides in matrix blank using Hot Splitless injection mode with Ultra Inert liner with wool

Matrices	Pear	Strawberry	Flower	Pepper	Orange	Spinach
Methamidophos	6.4	6.1	3.5	3.8	4.6	4.1
Acephate	4.6	14.6	5.7	6.0	8.6	9.3
Omenthoate	6.9	24.7	9.6	9.3	10.1	13.5
Dimenthoate	2.9	5.8	4.6	3.4	5.5	4.6
Lindane	1.8	1.8	2.3	2.0	3.5	7.0
Carbaryl	3.2	4.5	5.5	3.3	3.8	7.2
Dichlorfluanid	2.5	4.8	4.5	3.6	5.6	13.5
Tolyfluanid	2.3	7.7	4.9	4.2	4.0	14.5
Endrin	3.1	2.6	2.6	3.1	5.9	4.5
DDT	11.2	9.6	12.3	13.0	15.0	38.5
Endrin ketone	5.7	4.8	7.8	8.1	7.5	15.2
Iprodione	3.1	2.7	6.4	4.3	5.1	10.5
Phosmet	4.7	9.9	4.5	6.7	10.1	10.2
Deltamethrin	5.3	7.2	9.0	5.1	5.3	5.9

Thoroughly deactivated glass wool in the liner prevents non-volatile matrix getting into column, thus provides better peak shape and response consistency through runs, even for the very active pesticide like Omenthoate. Meanwhile, Ultra Inert liners with wool protect column and MS source, thus extend the whole system durability and increase the productivity.

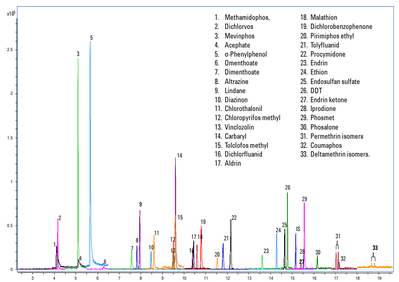
Omenthoate peak shape and responses deterioration comparison across runs in a sequence of multi-matrix samples spiked with 10 ng/mL pesticides



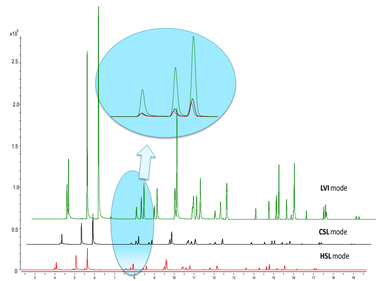
Ultra Inert splitless liners with wool are suitable for different injection modes from HSL, CSL to LVI

Ultra Inert splitless liners with wool can be used for different injection mode with MMI inlet, from Hot Splitless (HSL) to Cold Splitless (CSL), to Large Volume Injection (LVI). With optimal LVI GC/MS/MS method, the system sensitivity can be improved significantly, thus meet trace level detection requirement.

Chromatogram of **1 ng/mL** of pesticides standard with LVI (5µL) GC/MS/MS method using Ultra Inert liner with wool.



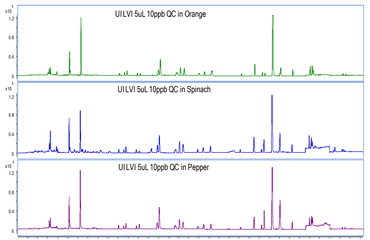
Comparison of HSL, CSL and LVI injection mode using Ultra Inert liners with wool. 10 ng/mL pesticides standard.



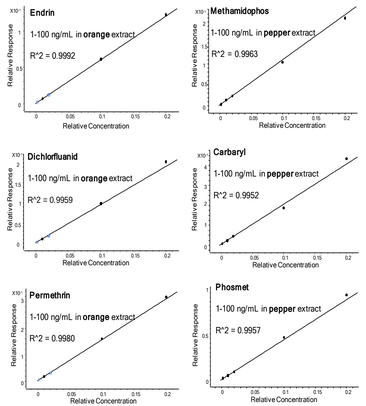
Results and Discussion

Pesticides Analysis in Fruit and Vegetable Matrices

The optimized LVI method was applied for the pesticides analysis in real matrices, including orange, pepper and spinach. With improved system sensitivity, the limit of quantitation (LOQ) by GC/MS/MS can be lowered to 1 ng/mL in real matrix for most of common pesticides.



Satisfactory linearity (R^2 > 0.99) for the calibration of 1-100 ng/mL of target pesticides in matrix extracts was achieved using LVI method.



The system performance repeatability (%RSD) comparison for three different injection modes.

% RSD	HSL	CSL	LVI	
	10 ng/mL in pepper (n =10)	10 ng/mL in pepper (n = 10)	10 ng/mL in pepper (n = 6)	1 ng/mL in pepper (n = 6)
Methamidophos	3.8	4.8	9.2	6.6
Acephate	6.0	8.6	23.7	45.1
Omenthoate	9.3	13.9	34.3	41.7
Dimenthoate	3.4	4.6	8.8	20.9
Lindane	2.0	1.4	1.2	7.7
Carbaryl	3.3	1.2	2.3	6.0
Dichlorfluanid	3.6	2.2	4.4	14.3
Endrin	3.1	0.9	1.3	7.5
DDT	13.0	8.0	4.2	5.1
Endrin ketone	8.1	2.2	2.4	5.5
Iprodione	4.3	4.7	13.4	13.0
Phosmet	6.7	17.0	12.6	23.6
Deltamethrin	5.1	3.5	3.7	9.4

Conclusions

Ultra Inert liners with wool provide the following benefits for trace level pesticides analysis applications in matrices.

- Excellent inertness for the analysis of active compounds
- Flexible feasibility for different injection mode with MMI inlet, including hot splitless, cold splitless and large volume injection.
- The optimal 5µL LVI GC/MS/MS method provides significant improvement on the system sensitivity (1 ng/mL in matrix LOQ), acceptable calibration curve linearity across 1 – 100 ng/mL , and comparable repeatability to those of HSL and CSL 1µL methods.
- When using LVI method, sample matrix has more impacts on the liner durability, especially for active pesticides, due to much more sample matrix being introduced to the system. More frequent liner switch is necessary to maintain the performance, and to protect column and MS source.