An LC-MS/MS method for the rapid screening and quantitative analysis of 500 types of pesticide and metabolite residues with the ZenoTOF 7600 system

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ABSTRACT

Zeno trap technology significantly improves pesticide sensitivity, and electron activated dissociation (EAD) fragmentation technology improves the accuracy of qualitative pesticide analysis results. In this study, when the Zeno trap was on, the sensitivity increased by >10-fold for 95% of the pesticides, and by 5 to 10-fold for the remaining pesticides as compared to when the Zeno trap was off. The ZenoTOF 7600 system is equipped with an EAD cell that simultaneously captures precursor ions and free electrons. Precursors then form a free radical that dissociates, often generating more fragment ions and a more informative MS/MS, which helps to ensure precise quantitative and qualitative analysis for pesticide detection.

INTRODUCTION

Pesticides are used before and after harvest to protect crops from infestation by pests and plant diseases. A consequence of their prevalent use in the environment is the appearance of pesticide residues in treated crops and ultimately in human food supplies. Pesticide residues have become a major concern in the area of food safety, and a robust and sensitive screening method for a vast range of pesticides in food matrices is a pressing need. To meet this need, a method was developed for the analysis of 500 pesticides and their metabolites using the ZenoTOF 7600 system from SCIEX. The pesticides analyzed using the method were found to meet the requirements of food safety regulations in China, Europe and North America.

MATERIALS AND METHODS

Sample preparation:
All samples were extracted according to the standard QuEChERS method.

HPLC conditions:
Analytes were separated on a Phenomenex Luna Omega C18 column (1.6 µm, 2.1 × 100 mm) using an ExionLC AD system from SCIEX. Mobile phase solvents were (A) water and (B) methanol, both with 0.01% formic acid and 2 mM ammonium formate. Separation was performed at a flow rate of 300 µL/min with a column temperature of 40ºC. The gradient condition of mobile phase is shown in Table 1.

MS/MS conditions:
Pesticides were analyzed using the ZenoTOF 7600 system with time scheduled Zeno MRM^{HR} for optimal sensitivity using both collision induced dissociation (CID) and electron activated dissociation (EAD) fragmentation modes (Figure 1). All compounds were detected using 2 MRM transitions per compound to allow quantification and identification based on the ratio of quantifier and qualifier transitions as defined by regulation 2002/657/EC. Data processing was performed using SCIEX OS software.

Table 1. The gradient condition of mobile phase.

Time (min)	A%	B%
0	97	3
1	97	3
1.5	85	15
2.5	50	50
18	30	70
23	2	98
27	2	98
27.1	97	3
30	97	3

RESULTS

The use of the Zeno trap on the ZenoTOF 7600 system increases the duty cycle of the QTOF system in the orthogonal injection region to >90% of duty cycle, increasing the MS/MS sensitivity by 4-20 fold across the mass range. Further, since the selectivity afforded by accurate mass MS/MS analysis often results in little to no chemical or background noise, the gains in signal-to-noise approach the gains observed in raw signal (Figure 3). Sensitivity increased by more than 10 times for 95% and 5-10 times for 5% of the pesticides analyzed when the Zeno trap was on instead of off.

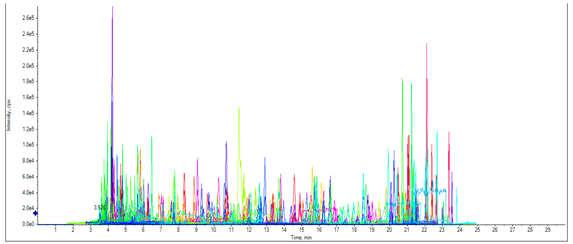

Figure 1. Detection of 500 types of pesticide and metabolite residues with the ZenoTOF 7600 system using time scheduled Zeno MRM^{HR} for best sensitivity and reproducibility.

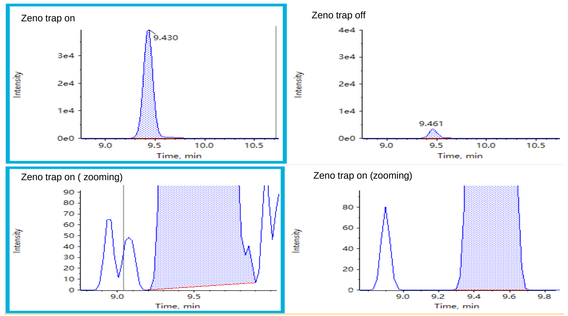

Figure 2. Detection of ametryn with the ZenoTOF 7600 system. When the Zeno trap was on, the sensitivity increased by 12.6 times, and the signal-to-noise increased by 13.7 times compared to when the Zeno trap was off.

The acquisition speed of the ZenoTOF 7600 system is very high (>100 Hz), which helps ensure enough data points are collected across the chromatographic peak for each pesticide peak. This, combined with the time scheduling of Zeno MRM^{HR} acquisition (Figure 3), enables very high data quality and improves reproducibility. A calibration curve, which ranged from 0.002 to 200 ng/mL with regression coefficients >0.99, was generated for the quantification of target chemicals (Figure 4).

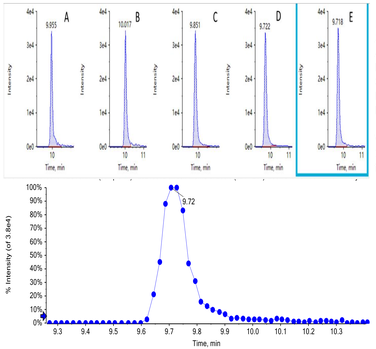

Figure 3. Detection of albendazole with the ZenoTOF 7600 system.
A - number of MRM^{HR} transitions is 80
B - number of MRM^{HR} transitions is 200
C - number of MRM^{HR} transitions is 400
D - number of MRM^{HR} transitions is 600
E - number of MRM^{HR} transitions is 1,000

When the number of MRM^{HR} transitions is 1,000, 15 data points were collected across the chromatographic peak (below).

Index	Sample Name	Sample T...	Component Name	Component Type	Component Group Name	Actual Concentr...	Calculated Concentrat...	Accuracy
1055	2ppt	Standard	mandipropamid...	Quantifiers	mandipropamid	2.00	1.759	87.95
2587	20ppt	Standard	mandipropamid...	Quantifiers	mandipropamid	20.00	14.566	72.83
3319	200ppt	Standard	mandipropamid...	Quantifiers	mandipropamid	200.00	205.448	102.72
4091	1ppb	Standard	mandipropamid...	Quantifiers	mandipropamid	1000.00	1000.756	100.08
4783	2ppb	Standard	mandipropamid...	Quantifiers	mandipropamid	2000.00	2245.265	112.26
5515	10ppb	Standard	mandipropamid...	Quantifiers	mandipropamid	10000.00	11260.075	112.60
6247	20ppb	Standard	mandipropamid...	Quantifiers	mandipropamid	20000.00	22735.044	113.68
6979	200ppb	Standard	mandipropamid...	Quantifiers	mandipropamid	200000.00	195759.006	97.88

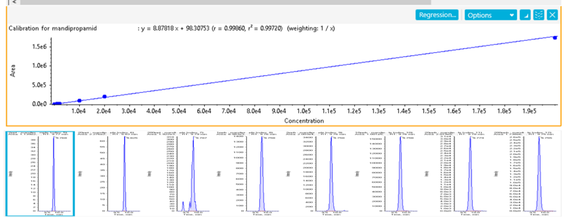

Figure 4. Detection of mandipropamid with the ZenoTOF 7600 system. Concentration range tested was from 0.002 to 200 ng/mL with regression coefficients >0.99).

Tandem mass spectrometry typically uses CID to produce ion fragments for quantitative and qualitative identification. However, some pesticides produce only one fragment with CID, which is insufficient for MRM quantitative analysis or structural qualitative identification. The ZenoTOF 7600 system is equipped with an EAD cell that simultaneously captures precursor ions and free electrons. Precursors then form a free radical that dissociates, often generating more fragment ions and a more informative MS/MS, which helps to ensure precise quantitative and qualitative analysis for pesticide detection (Figure 5). A library search using EAD fragmentation identified the correct pesticide while a search using CID fragmentation did not.

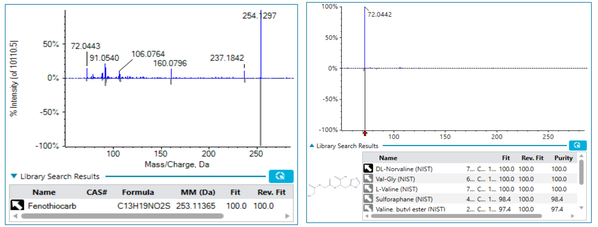

Figure 5. Library search result of fenothiocarb with ZenoTOF 7600 system using EAD cell (left) and CID cell (right).

CONCLUSIONS

A fast, robust, and reliable method for the detection 500 types of pesticide and metabolite residues was developed and validated. Zeno trap technology significantly improves pesticide sensitivity, and EAD fragmentation technology improves the accuracy of pesticide qualitative results.

REFERENCES

1. Qualitative flexibility combined with quantitative power. SCIEX application note, RUO-MKT-02-13053-A.
2. Highly sensitive quantification and selective identification of pesticides in food with Zeno MRM^{HR}. SCIEX application note RUO-MKT-02-13902-B.

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