Poster Note PN-20

Determination of Pesticides in Foods using Dopant-optimized Gas Chromatography-Atmospheric Pressure Chemical Ionization Quadrupole-Time-of Flight Mass Spectrometry

Overview

A dopant optimized GC-APCI Q-TOF method for screening of pesticides in food matrix was developed. Dopant optimization studies found methanol as the optimal organic modifier using the Bruker GC-APCI II source. The developed technique utilizes facile dopant vapor introduction via nitrogen carrier gas and can be used to selectively enrich ionization for different classes of pesticides.

Introduction

Soft ionization modes in GC-hyphenation studies such as chemical ionization (CI), field ionization (FD), supersonic molecular beam (SMB), or atmospheric-pressure chemical ionization (APCI) allows the effective formation of pseudo-molecular ions from biomolecules. Soft-ionization techniques thus allows users to address a much wider scope for screening as well as improved identification confidence based on stable pseudo-molecular ion. GC-APCI generic source coupling is one of the more promising method as it is dually compatible with both GC and LC-hyphenated mass spectrometers. In this study, the optimization and development of a dopant-based APCI screening workflow using next-generation GC-APCI ion source on a QTOF platform for multi-target pesticide screening is presented.

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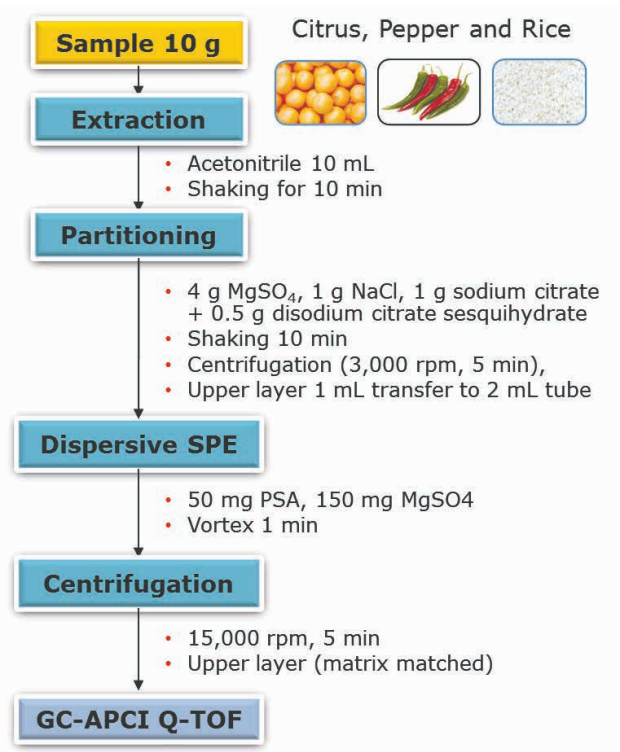
Keywords	Instrumentation and Software
Pesticides	Bruker 451 GC with compact Q-TOF
Dopant	TASQ 1.0
Soft ionization	
GC-APCI	
Compact Q-TOF	
GC-APCI II	
bbCID	
TASQ	

Methods

Instrument: Bruker Compact™ QTOF system
GC: Bruker 451 GC with 8400 Liquid Autosampler
GC Conditions:
GC Column: BP-5MS (30 m x 0.25 mm i.d, 0.25 m)
Injector Temperature: 260 °C
Oven Temperature Program:
90 °C (1min)→25 °C/min → 120 °C→6 °C/min to 300 °C (7.8min) Total run time: 40 min
Column flow: 1.5 mL/min with He
Injection: 2 L at 40 psi pulsed splitless for 1 min
Transfer line Temperature: 290 °C
MS Conditions:
Scan range: 50 -700 m/z at Positive mode
Scan mode: Full scan and bbCID at 6Hz (166 ms)
Corona current: 4000 nA
Neublizer Gas: 1.0 Bar with Dopant Solvent
Drying Gas: 2.0 L/min at 150 °C
Data Processing Software: TASQ 1.0

Sample Preparation



CG-APCI Q-TOF with Dopants systems

Figure 1: GC-APCI Q-TOF System

Table 1: Proton affinity of dopant solvents *

Dopant	Proton Affinity (kcal/mol)
Water	165
Acetonitrile	175
Methanol	182

* LC-MS for the Chromatographer © Crawford Scientific, 2001

Results

N_2 gas enriched with acetonitrile, methanol, and water organic mixtures were assessed for their compatibility as dopants for the new GC-APCI II ion source. Fig. 2 (a) demonstrates that methanol provided three (3) fold greater increase in ion response than datum non-enriched N_2 gas. Further optimization and overnight bake out showed that up to 10 fold greater response can be observed; as shown in Fig. 2 (b). We speculate that the observed increase in sensitivity is related to the proton affinity of the respective solvents. (Table 1.)

Fig. 3 shows high resolution extracted ion chromatogram (hrEIC) at 100 PPB and exemplar pesticides calibration curves showing good linearity down to 1 ppb levels (r2=0.99). Fig. 4 and Table 2 demonstrates dopant effect reproducibility at 1 PPB diazinon, across multiple injections. Fig. 5 shows capability to screen with complex background down to 1 PPB in citrus matrix. New capabilities afforded by the Bruker TASQ™ software allows automated high throughput screening and quantification studies of hundreds of injection in a few clicks.

Comparision between Chromatogram

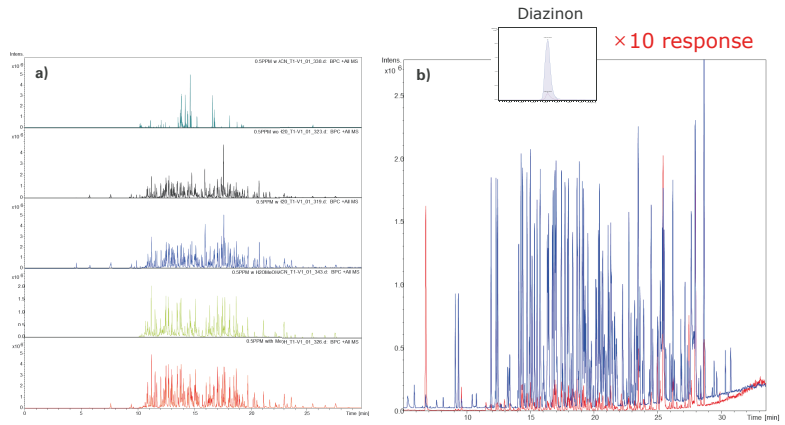


Figure 2: Comparision of Dopants effect for sensitivity

Chromatogram of 100 ppb Standard solution

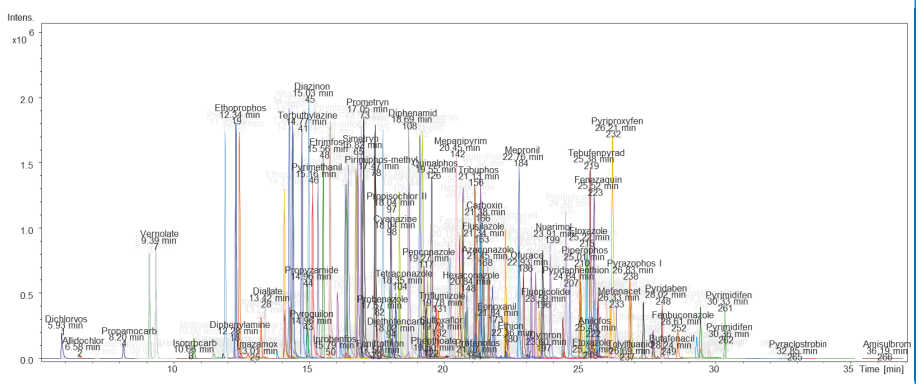


Figure 3: hrEIC (± 2mDa) chromatogram of 100 PPB Standard solution for all 418 pesticides and some calibration curves for 1 – 100 PPB

Extracted Ion Chromatograms (EIC) of 1ppb Diazinon

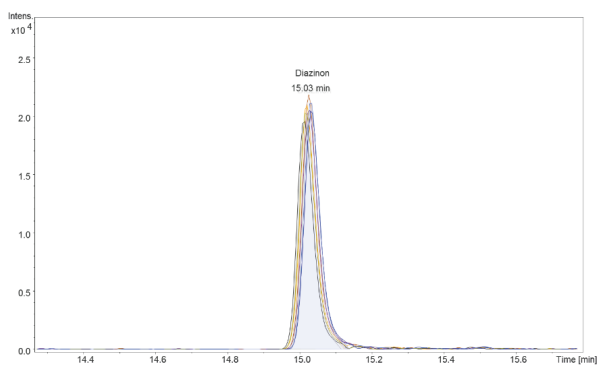


Figure 4: 1 PPB Diazinon (n=7)

Table 2: Reproduciblity of 1 PPB Diazinon

Analysis	Area	RT [min]	Concentration	Accuracy [%]
S_STD_1PPB_1_01_927	65712.70	15.03	0.98	97.88
S_STD_1PPB_1_01_928	67330.98	15.02	1.00	99.66
S_STD_1PPB_1_01_929	64728.11	15.01	0.97	96.80
S_STD_1PPB_1_01_930	65459.79	15.02	0.98	97.60
S_STD_1PPB_1_01_931	65672.31	15.03	0.98	97.83
S_STD_1PPB_1_01_932	68610.07	15.03	1.01	101.07
S_STD_1PPB_1_01_933	68993.38	15.03	1.01	101.49
Mean	66643.91	15.02	0.99	98.90
SD	1670.40	0.01	0.02	1.84
%RSD	2.51	0.05	1.86	1.86

Chromatogram of 1 ppb in citrus matrix

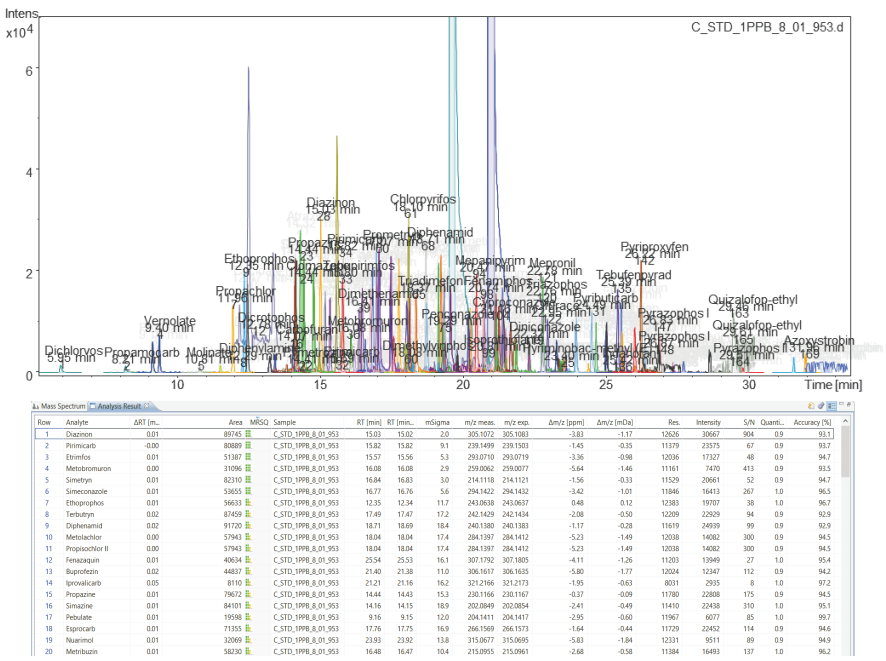


Figure 5: hrEIC (± 2mDa) chromatogram of 1 PPB in citrus matrix

Conclusion

A method for screening of pesticides in food matrix using dopant optimized GC-APCI II source with Q-TOF is developed.

- Methanol was shown best sensitivity and have the greatest effect before (3x increase) and after overnight bake-out (10x increase).
- >270 pesticides could be simultaneously detected from 418 pesticides standard mixture in citrus matrix.
- Only a small amount of methanol was consumed throughout the analysis of hundreds of samples.
- Citrus, Pepper and Rice matrix was tested and easily screened and quantified with TASQ Software.

Further extended optimization would be undertaken to maximize the detection of pesticides at lower concentration.

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