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Pesticide Analysis in Fruit/Vegetable Juice by LC/MS/MS and GC/MS

BRUKER

Screening & Quantitation of 250 Pesticides in Fruit/Vegetable Juice using the eXtreme|FV® by LC/MS/MS

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Abstract

A study was conducted using the Bruker EVOQ for the analysis of 250 pesticides in apple, orange, cranberry, white grape and vegetable juices using only one method in store-bought juice and simple sample preparation using the Thomson eXtreme|FV®s in a dilute-and-shoot approach without sample enrichment. LC-MS/MS operated in Multiple Reaction Monitoring (MRM) mode with dual scan Electrospray Ionization (ESI) is widely used for polar, semi-volatile, and thermally labile pesticides in food testing. The Bruker EVOQ Elite LC-Triple Quadrupole System provides fast positive/negative switching, allows for simultaneous determination of hundreds of positive and negative co-eluting compounds numbering in the hundreds. Simple sample preparation is explored using Thomson eXtreme|FV®s for sample clean-up instead of lengthy alternatives like SPE or centrifugation followed by liquid-liquid extraction.

Equipment

- EVOQ Elite Triple Quadrupole Mass Spectrometer
- Bruker UHPLC
- CTC Autosampler
- Source: HESI
- Spray Voltage Positive: 4000V
- Spray Voltage Negative: 4000V
- Column: YMC-Pack ODS-AQ 3µm
- Column Temperature: 40˚C
- Injection Volume: 30µL
- Mobile Phase:
  - Mobile Phase A: 5mM Ammonium Fluoride in Water
  - Mobile Phase B: Methanol
    - Gradient:

Time	%A	%B	Flow (µL/min)
0.00	90	10	400
0.20	90	10	400
2.00	30	70	400
10.0	0	100	400
15.0	0	100	400
15.1	90	10	500
18.0	90	10	400

Sample Preparation

1. Pipette 50µL of store-bought apple juice and 450µL of solvent (10% Methanol/90% Water) directly into the outer shell of Thomson eXtreme|FV®, 0.2µm PVDF.
2. Partially depress the eXtreme|FV® plunger and vortex.
3. Depress the completely and load onto the autosampler.

Results

Table 1. Store bought fruit juice test results.

Fruit Juice=>	Apple Juice	Orange Juice	Cranberry Juice	White Grape Juice	Vegetable Juice
Pesticide	µg/L (ppb)				
Azoxystrobin	ND	ND	0.32	ND	0.48
Boscalid	ND	ND	0.16	ND	ND
Carbaryl	ND	0.39	1.47	ND	ND
Carbofuran	ND	0.14	ND	ND	ND
Dimethoate	ND	0.30	ND	ND	ND
Imidacloprid	ND	ND	0.60	ND	0.20
Mandipropamid	ND	ND	0.59	ND	ND
Metalaxyl	ND	ND	0.21	ND	ND
Methoxyfenozide	ND	ND	ND	ND	0.84
Tebuconazole	ND	ND	0.32	ND	ND
Thiabendazole	1.8	ND	ND	ND	ND

Fig 1. Chromatogram of a 0.01ppb standard solution containing the compounds listed in Table 1 This is equivalent to 0.1ppb in juice.

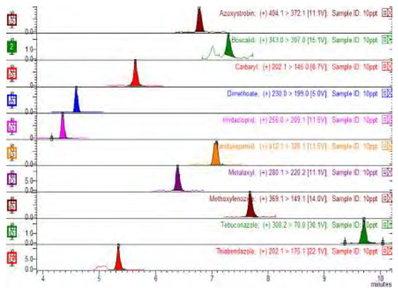
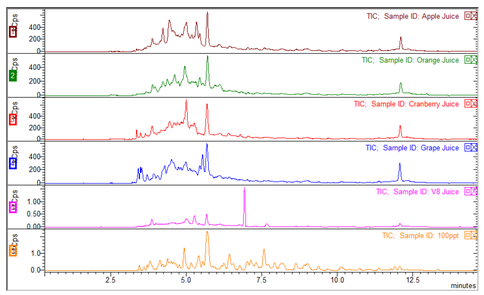


Fig 2. Total Ion Chromatograms for all juices



Conclusion

- The calibration on triplicate injections showed excellent linearity and response factor RSD over 3 orders, range using the Thomson eXtreme|FV® for sample preparation.
- Good linearity, sensitivity and response factor, RSD for positive and negative co-eluting pesticides.
- Pesticides were detected in store-bought apple, orange, cranberry and vegetable juices.

Comparison of eXtreme|FV® vs SPE for Improved Pesticide Recovery in Orange Juice by GC/MS

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Abstract

Pesticide residues are toxic when found in sufficient quantities in food. This is of particular importance for orange juice because it is consumed in large quantities. In order to reduce the risk to consumers, sensitive, rapid, and cost effective analytical methods are required. The pesticides in orange juice testing shown below compares recoveries for samples prepared using SPE versus Thomson eXtreme|FV®.

Equipment

Agilent Technologies GC/MS, 7000 Triple Quad System
Agilent 7890A GC System
Agilent 7693 Autosampler.

Sample Preparation

1. Spike 10 mL of commercially available High Pulp Orange Juice with 1 mL of 1 ppm pesticide standard mix containing 87 pesticides in a 40 mL vial.
2. Add one pack (approximately 6 g) of Restek Extraction Salts (Restek catalog # 26236) to the spiked orange juice.
3. Extract the spike orange juice with 4 x 25 mL portions of methylene chloride.
4. Concentrate to dryness using a Turbovap II concentrator.
5. Dissolve the residue in approximately 10 mL of acetonitrile.
6. Vortex and sonicate the re-suspended residue with frequent swirling.
7. Split the re-suspended residue into two 5 mL portions.
8. Dilute each 5 mL portion with acetonitrile to 10 mL using a volumetric flask.
9. Label one flask “for SPE” and the other “for Thomson eXtreme|FV®”.

Filter Vial Cleanup Prior to Analysis - Thomson eXtreme|FV®

1. Add 400µL of the re-suspended residue from the flask labeled “for Thomson eXtreme|FV®” to the shell of one Thomson eXtreme|FV® 0.45µm,
2. Insert plunger completely.

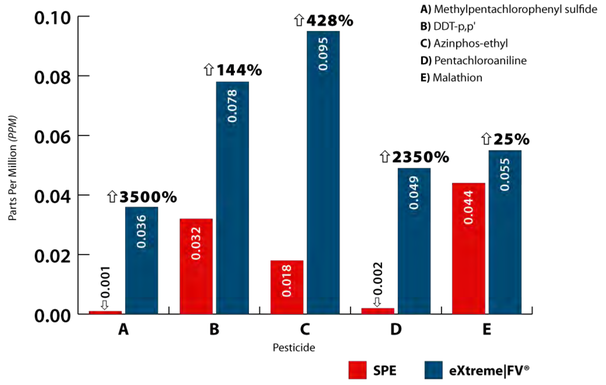
SPE Cleanup Prior to Analysis - 6 mL Combo SPE Cartridge

1. Wash one 6 mL Combo SPE Cartridge (packed with 200 mg CarboPrep 200 and 400mg PSA) with acetonitrile.
2. Add the 10mL portion of the re-suspended residue from the flask labeled “for SPE” to the SPE cartridge.
3. Elute the sample from the cartridge with 50mL of acetonitrile.
4. Concentrate the eluted sample to 10mL using a Turbovap II concentrator.
5. Filter sample with a syringe and syringe filter, PTFE 0.45µm and elute into autosampler vial

Results

Compound NAME	SPE+ Syringe FILTER Average ppm	EXTREME| FV Average ppm
Azinphos-ethyl	0.018	0.095
Azinphos-methyl	0.023	0.115
Bromophos-ethylBHC-beta	0.025	0.057
BromopropylateBHC-delta	0.063	0.076
Cyfluthrin	0.082	0.113
Cypermethrin	0.082	0.117
Cypermethrin III	0.058	0.104
Cypermethrin IV	0.070	0.097
DDT-o,p'DDD-p,p'Cypermethrin III (Beta)	0.035	0.065
DDT-p,p'DDE-o,p'Cypermethrin IV	0.032	0.078
Deltamethrin DDE-p,p'DCPA	0.053	0.102
Diazinon DDT-o,p'DDD-o,p'Cyhalothrin (lambda)	0.028	0.035
Dicofol DDT-p,p'DDD-p,p'Cypermethrin I (Zeta)	0.033	0.028
Dieldrin Deltamethrin DDE-o,p'Cypermethrin II	0.041	0.052
DimethoateDiazinonDDE-p,p'Cypermethrin III (Beta)	0.061	0.077
Endosulfan I (alpha isomer)	0.041	0.076
Fenvalerate I	0.076	0.106
Fenvalerate	0.055	0.073
Fluvalinate-tau II	0.058	0.084
Methylpentachlorophenyl sulfide Malathion Heptachlor endo-epoxide	0.001	0.036
Octachlorodipropyl ether (S421)Methidathion Hexachlorobenzene	0.021	0.047
Pentachloroaniline Parathion Mirex Hexachlorobenzene	0.002	0.049
Permethrin I	0.068	0.097
Phosalone Pentachloroanisole Parathion Methidathion	0.005	0.089
Phosmet Permethrin I	0.031	0.104
Prothiofos Pirimiphos	0.033	0.060

Comparison of Pesticide Recoveries



Conclusion

- The Thomson eXtreme 0.45µm, PTFE Filter Vials yielded 26% higher recoveries on average when tested with 87 different common pesticides .
- In the case of Hexachlorobenzene, no pesticide was detected in the sample prepared by SPE and 0.019 ppm was detected in the sample prepared with the eXtreme| FV.
- The results show Thomson eXtreme|FV® offer a viable alternative with higher recovery and less preparation time compared to SPE for the preparation of juices, and specifically orange juice samples prior to pesticide analysis .
- Conforms to USP 561