Multiresidue Analysis For Organophosphorus Pesticides in Fruits and Vegetables at Parts-per Billion Levels by Gas Chromatography with Pulsed Flame Photometric Detection

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- **The use of OP pesticides has led to frequent exposures in human populations through multiple routes.**
- **Studies have demonstrated that consumption of food items containing OP residues is the predominant pathway of OP pesticide exposures in children.**

The vulnerability of infants and children to OP toxicity warrants further research:

- **on the improved of assessment of dietary exposure**
- **on analytical methods capable of quantifying OP pesticide residues at low parts per billion (ppb) or even parts per trillion (ppt) levels.**

Studies on Dietary Exposure to OP Pesticides

Produce samples, were collected throughout a 12 month period, as part of two studies, were analyzed:

- **The Children's Pesticide Exposure Study (CPES) and**
- **The Longitudinal Dietary Pesticide Exposure Study (LDPES)**

A modified QuEChERS Method method was used for the rapid determination of OP pesticides at levels down to 1 ppb (µg/kg) using Pulsed Flame Photometric Detection.

Modified QuEChERS method: 15 grams/15.0-mL of MeCN

SHAKE

Add 6g $MgSO_4$ and 1g NaCl

Shake

CENTRIFUGE

Dispersive SPE:

9.0 mL MeCN extract

+ 3.0 mL toluene

Added to centrifuge tube containing:
PSA, GCB, & $MgSO_4$

vortex & centrifuge

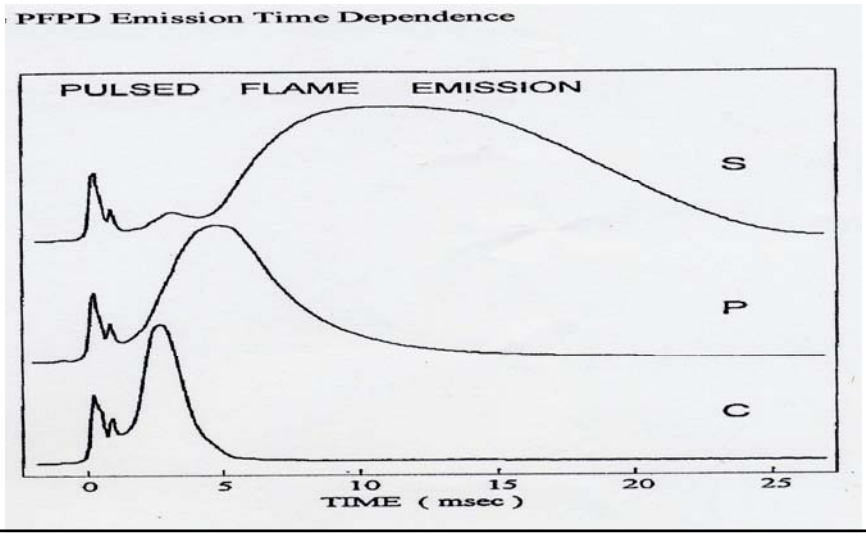
Wong et al. (2007) *J. Agric. Food Chem. 55, 1117-1128*

Take 8.0 mL extract
evaporate, to < 1.0 mL
Add internal standard
Adjust to 1.0 mL

Analysis using GC-Pulsed Flame Photometric Detector (PFPD)

- Chemiluminescence: HC, P, and S groups are excited in a flame.
- These excited groups emit light at different times after excitation by the flame.
- The PFPD can provide better sensitivity and selectivity for P groups than the FPD

PFPD



RECOVERY STUDIES

- 102 pesticides
- 1.0, 10 and 100 ppb
- Grape, orange, spinach, tomato
- Recoveries ranged from 63-125%, >80% achieved for most pesticides

Typical Recoveries

		%Recovery (% c.v.)		
Pesticide	Matrix	100 ppb	10 ppb	1 ppb
Acephate	tomato	94 (1)	85 (4)	86 (6)
Azinphos CH3	grape	106 (6)	100 (10)	104 (14)
Dimethoate	orange	97 (2)	94 (4)	102 (7)
Malathion	orange	104 (1)	102 (4)	100 (5)
Methamidophos	spinach	91 (4)	89 (9)	77 (12)
Omethoate	orange	91 (6)	100 (15)	85 (6)
Phosmet	spinach	96 (6)	97 (7)	103 (13)

Chromatography

- Retention times very stable, retention time of TPP was 26.320 ±0.002 min. over 20 hr. run.
- Retention times could be used for tentative identity of unknown peak.

Chromatography

- Few interferences from sample matrix were noted.
- A chromatogram could be visually inspected and it could be rapidly determined if any of targeted pesticides were present.

•400 samples, were analyzed using GC-PFPD

•If chromatographic retention times of any peaks found matched retention time of any of the 102 targeted pesticides, peak identity was confirmed by:

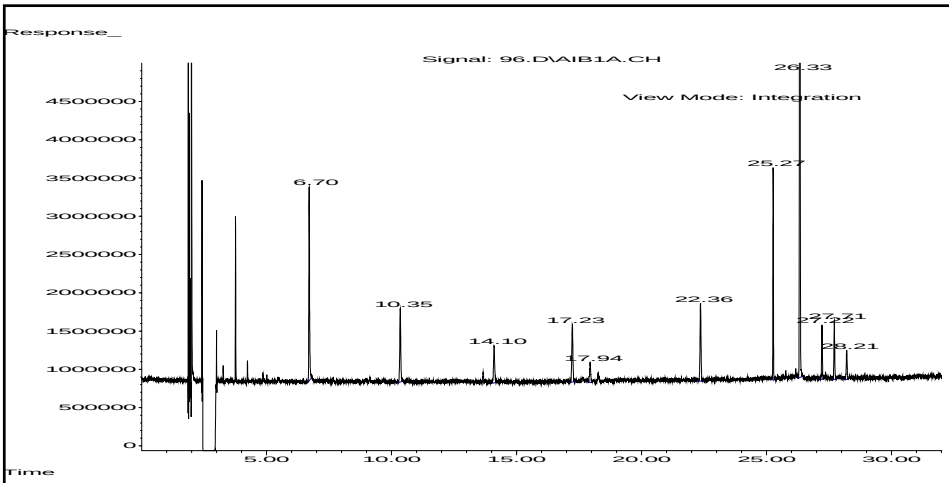
•GC/MSD

and/or

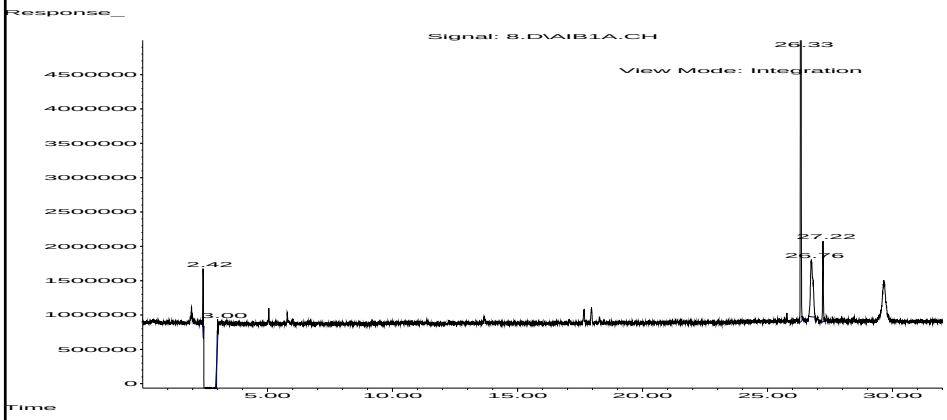
•GC/FPD, using a second column with a different polarity

OP Pesticides found in analysis of 400 fresh fruit and vegetable samples from the two studies

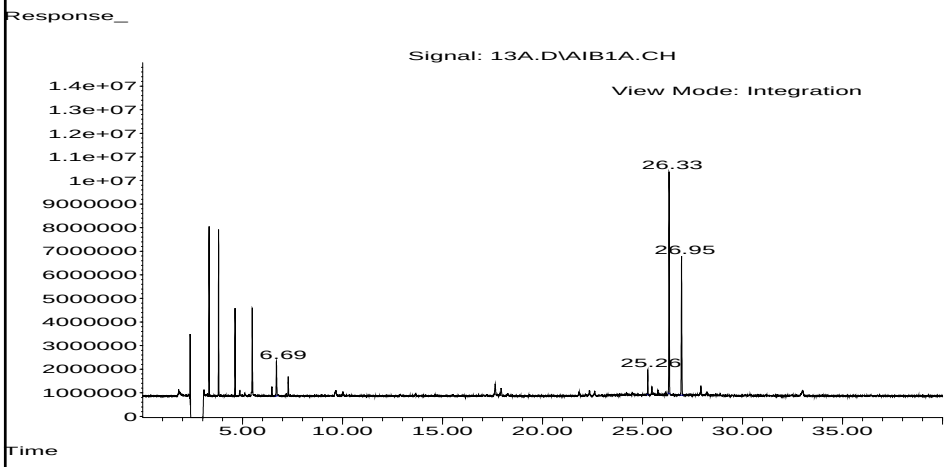
Pesticide	times found	amounts found
Acephate	10	<1.0 ppb – 95 ppb
Azinohos methyl	10	1 ppb – 111ppb
Chlorpyriphos methyl	1	330 ppb
Dichlorvos	1	4 ppb
Dimethoate	4	3 ppb – 12 ppb
Ethion	5	<1.0 ppb – 4 ppb
Malathion	8	4 ppb – 526 ppb
Malathion OA	1	21 ppb
Methamidophos	21	<1.0 ppb – 21 ppb
Omethoate	5	<1.0 ppb – 5 ppb
Phosmet	19	2 ppb – 387 ppb
Phorate sulfone	1	30 ppb
Phorate sulfoxide	1	110 ppb



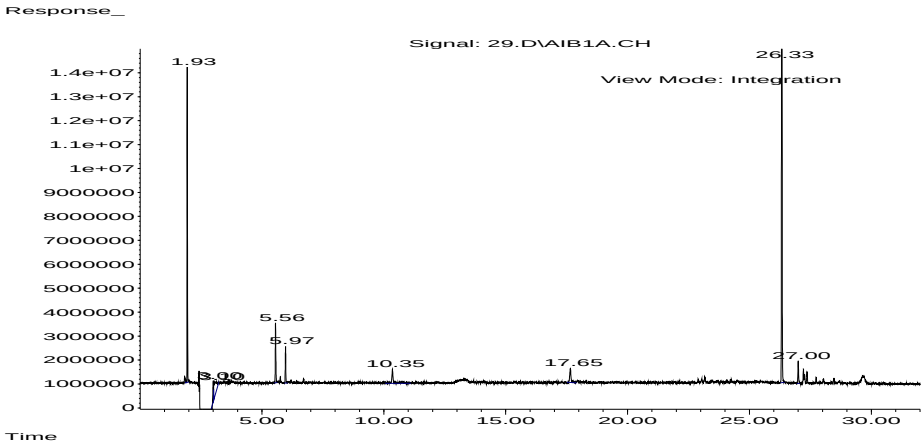
GC-PFPD Chromatogram of 0.01 µg/mL matrix standard (prepared in control grape extract). **Peak identities are: methamidophos (6.70);acephate (10.35); omethoate (14.10); commonly found matrix peak (17.94); chlorpyriphos (22.36); ethion (25.27); triphenyl phosphate (26.33); phosmet (27.22); phosalone (27.71) and azinphos methyl (28.21).**



GC-PFPD Chromatogram of peach sample containing incurred 3.0 ppb phosmet (Rt-27.22) and triphenyl phosphate internal standard (Rt-26.33).



GC-PFPD Chromatogram of pizza sauce sample containing 3 ppb incurred residue of methamidophos (Rt- 6.69) and triphenyl phosphate internal standard (Rt 26.33). Peak at 26.95 is a very commonly found matrix peak. Peak at 25.26 is false positive for ethion (did not match retention time of ethion on a second column using GC-FPD).



GC-PFPD Chromatogram of spinach sample containing 0.4 ppb incurred residue of acephate (Rt- 10.35) and triphenyl phosphate internal standard (Rt 26.33). Peak at 17.65 is a very commonly found matrix peak.

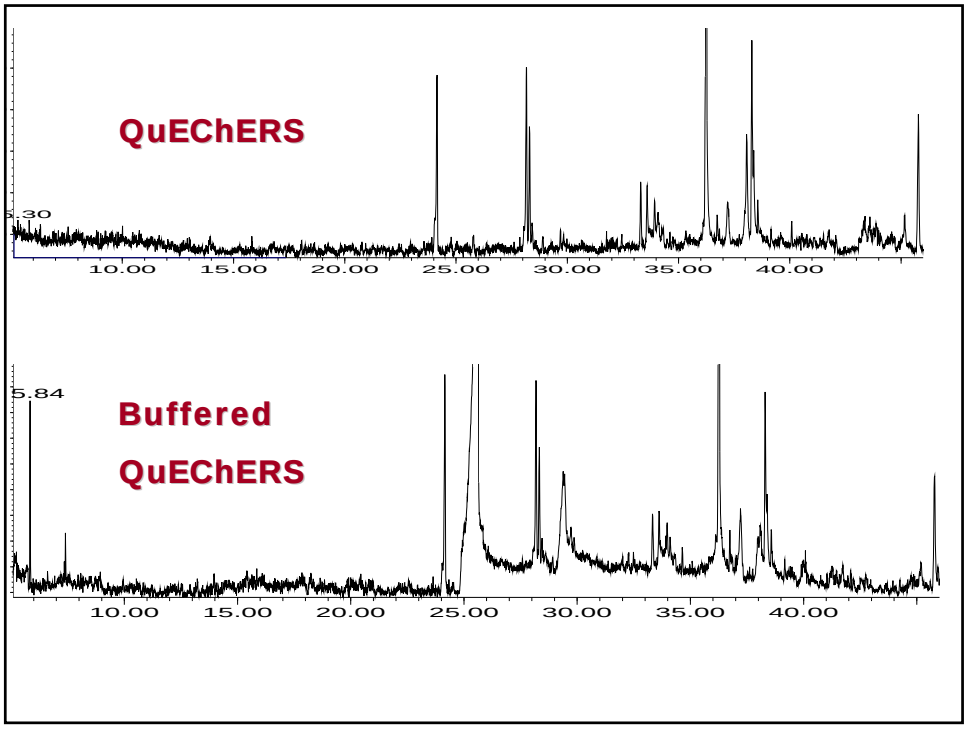
Conclusions

- The modified QuEChERS method provided an excellent cleanup, resulting in sub-ppb detection levels for some pesticides.
- High sample throughput, extraction and cleanup of 24-48 samples per day, was possible.
- With the PFPD there was very little interference from sample matrix peaks, and possible pesticide peaks could be rapidly identified.
- Significant savings in both time and cost of analysis can be achieved; solvent usage and hazardous waste production were reduced by ca. 90% when compared to traditional methods.

Additional advantages of the GCB/PSA SPE cleanup:

QuEChERS
(better cleanup)
- **Acetonitrile extraction**
- **NaCl/$MgSO_4$ salt-out**

Buffered QuEChERS
(base sensitive pesticides)
- **1% HOAc/Acetonitrile extraction**
- **NaOAc/$MgSO_4$ salt-out**



QuEChERS MeCN/Toluene & GCB/PSA

	Recovery	CV
LETTUCE		
chlorothalonil	74.2%	7%
chlorpyriphos	91.0%	3%
tolyfluanid	90.5%	3%
SPINACH		
chlorothalonil	70.8%	10%
chlorpyriphos	90.9%	7%
tolyfluanid	78.3%	10%

TOLUENE: stabilizes base sensitive organochlorine pesticides, allowing the use of original (non-buffered) QuEChERS, which results in better cleanup.

QUESTIONS?

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