

Application of PSA and Carbon/PSA SPE Cartridges for Cleanup of Vegetables, Foods and Fruit Extracts

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Abstract

Primary-secondary amine (PSA) sorbent has been shown to be very effective in food residue cleanup, removing the greatest number of food matrix interferences (1-3). PSA alone or with graphite carbon, has been considered an important method in SPE for cleanup of pesticide residue analysis of fruits and vegetables.

The PSA and carbon/PSA SPE cartridges from several commercial sources have been characterized in terms of phase bleed, ion-exchange capacity, and their ability to remove matrices. Differences have been observed. Furthermore, although graphite carbon is very effective for removal of coloring substances, its combination with PSA dramatically reduces the capacity of PSA for removal of fatty acids. Therefore, the use of conventional carbon/PSA dual layer SPE should be limited to non-fatty foods or foods with low amounts of fatty substances.



Introduction

Cleanup of matrices is the first and most critical step for both broad-spectrum screening and accurate determination of pesticides and their metabolites in vegetables, meats, drinks and fruits. In most cases, solid-phase extraction (SPE) methods are used to clean up the extracts before a GC-MS analysis. The ideal SPE material(s) should remove the greatest number of food matrix interferences and offer high recoveries for a broad-spectrum of pesticides.

Glass beads, polymeric sorbents, florisil, alumina, silica, C18 and charcoal, although useful for particular classes of pesticides, were found to be inadequate for trapping diverse pesticides.



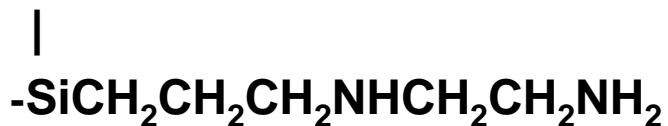
Introduction (continued)

The Luke method, using strong and weak anion-exchange SPE sorbents, requires the use of large amounts of chlorinated organic solvents, and is not able to clean samples with high amounts of fatty acids. ENVI-Carb/NH₂ dual layer SPE, although useful for extensive pesticide screening, were found to be also inadequate for removal of fatty acids (3).

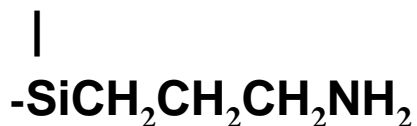
PSA has been found as the most effective sorbent for removal of various matrices and significantly reducing matrix-enhancement effect, followed by NH₂ SPE phase while SAX do little things (1-2). On the other hand, graphited carbon black (GCB) is very useful for removal of coloring substances (i.e. pigments). Therefore, PSA itself and GCB/PSA dual layer should be most effective for sample cleanup.

Chemical Structure of PSA, NH₂ and DEA

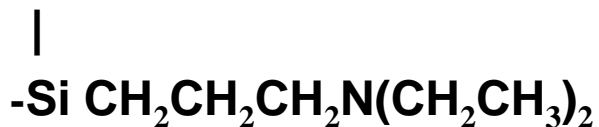
PSA: two pKa [10.1 and 10.9]



NH₂: one pKa at 9.8 (poor ability to remove fatty acids)



DEA: one pKa at 10.7 (poor ability to remove fatty acids)



Comparison of Ion-Exchange Capacity and PSA Bleed

Items	Vendor A	Vendor B	Vendor C	Supelclean™
Carbon (%)	6.5	7.2	8.4	8.4
Nitrogen (%)	2.8	3.2	3.16	3.3
Ion-Exchange Capacity (mmol/g)	0.65	0.92	0.72	1.05
PSA bleed (µg/g)	2.7– 5.8	0 - 5.4	2.4 – 7.2	0 – 3.7

Note:

- 1. Benzoic acid was used to produce the breakthrough curves for measurement of ion-exchange capacity.**
- 2. Salicylaldehyde was used as a probe to detect the PSA silane bleeding from SPE columns.**

Specification Range

Comparison between Vendor B and Supelclean PSA regarding product specification. Tighter specification ranges indicate the product may be more reproducible.

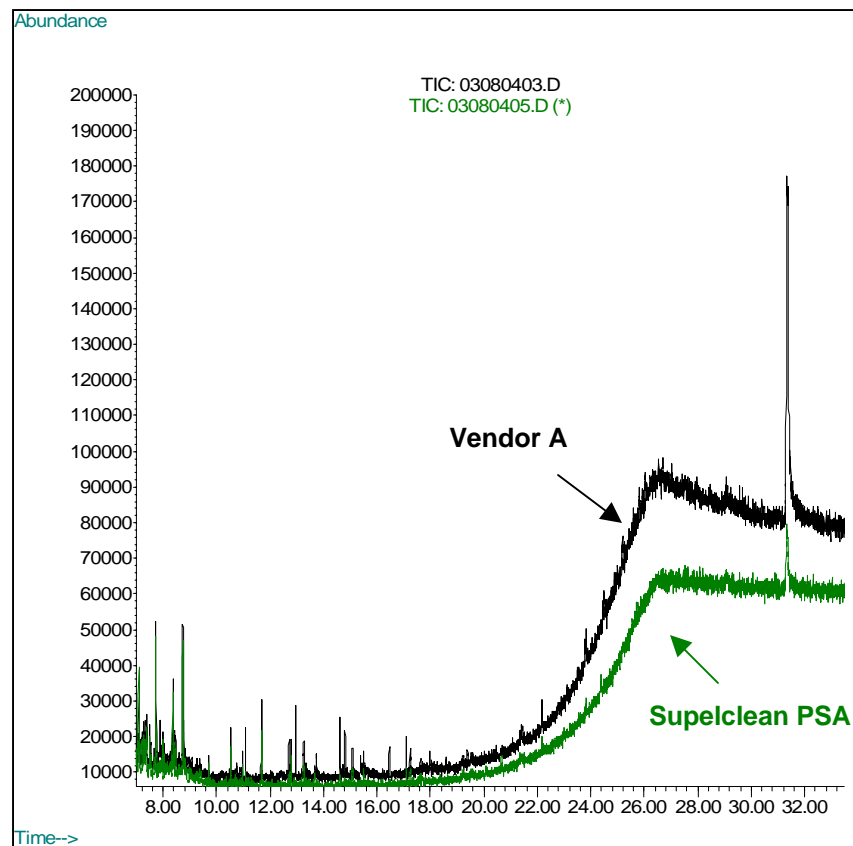
<u>Properties</u>	<u>Vendor B</u>	<u>Supelclean PSA</u>
Specific Surface		
Area (m²/g)	460 – 520	450 – 550
Carbon (%)	5.40 – 8.60	8.30 – 9.00
Nitrogen (%)	1.50 – 3.60	3.20 – 3.60
Bonded Coverage		
($\mu\text{mol}/\text{m}^2$)	1.96 – 3.82	2.30 – 2.50

Vendor Comparison: GC-MS Background of PSA SPE Cartridges

An ideal SPE cartridge should not bring additional impurities in the final elution. Supelclean PSA offers the cleanest background.

Experimental:

500mg/6CC PSA tube was conditioned with 5mL acetonitrile and then eluted with 14mL acetonitrile. The elution was collected and concentrated into 1.0mL for GC-MS total ion scanning.



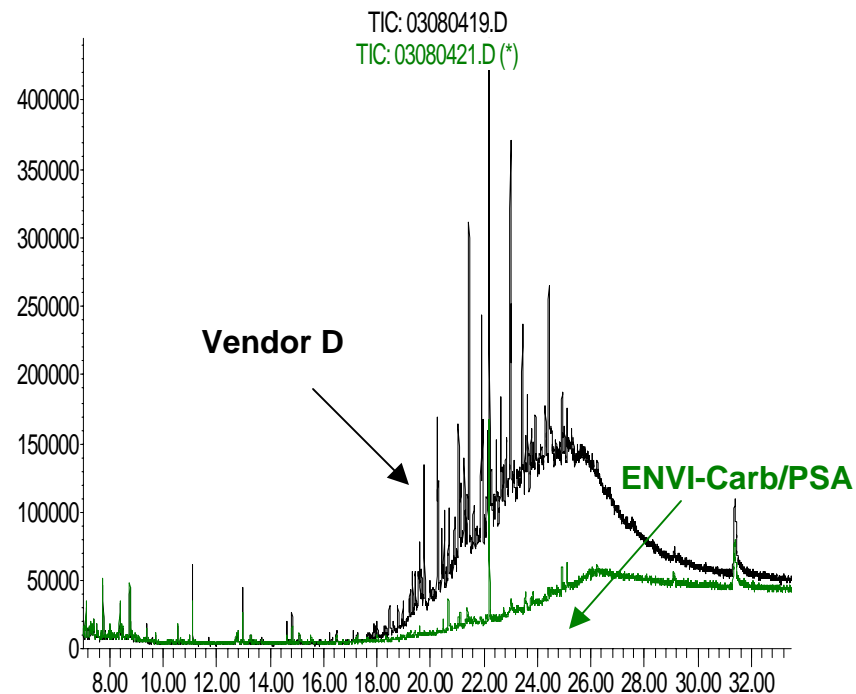
Vendor Comparison: GC-MS Background of Carbon/PSA Dual-Layer SPE Products

Experimental:

Carbon/PSA dual-layer SPE cartridges were conditioned with 5mL acetonitrile:toluene (3:1) and eluted with 20mL acetone:hexane (1:1).

Column: Equity-1, 30m x 0.25mm ID x 0.25 μ m (or an Equity-5, PTE-5 would work), Inj.: 200°C, Aux: 325°C oven: 50°C (5 min), 25°C/min to 125°C, 10°C/min to 300°C (8 min) Carrier: He, 0.9mL/min, constant flow mode injection: 1 μ L, splitless (splitter open at 1 min), Liner: 4mm ID, single taper, Scan Range: 45-450 amu, Tune: generated using ATUNE tuning macro

Abundance



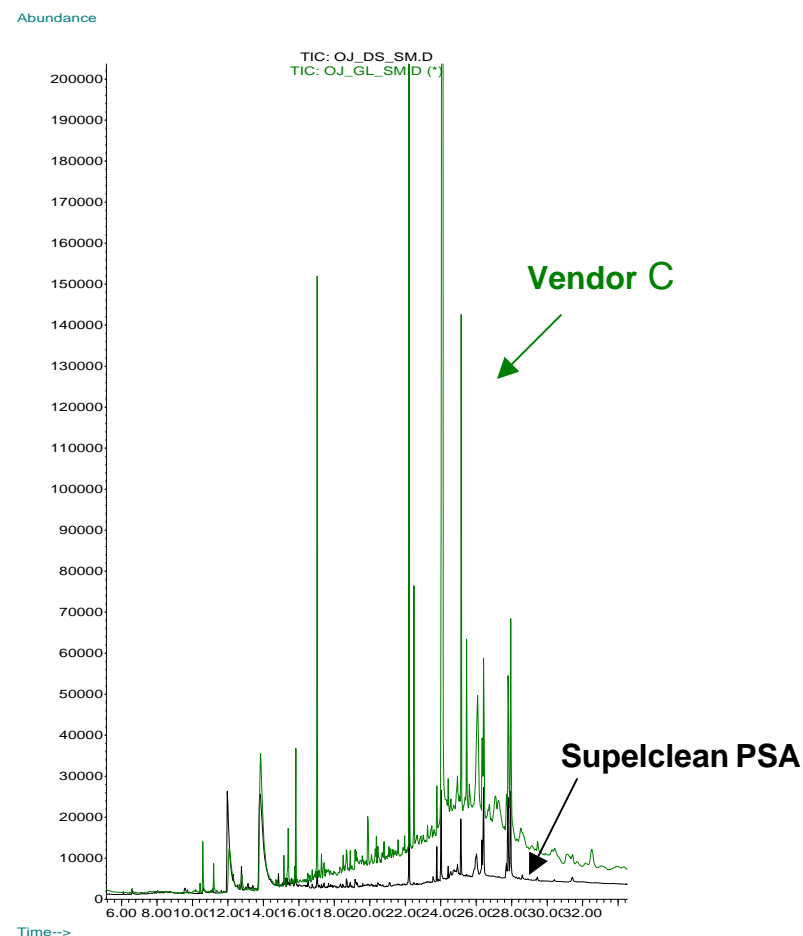
Milk Matrix Clean-Up Using Supelclean PSA

Experimental:

Fresh milk (20mL with 2% fat) was extracted with 50mL acetonitrile by Canadian Pest Management Regulatory Agency (PMRA) method.

A 500mg/6cc PSA cartridge was conditioned with 5mL acetonitrile. Then 5mL of the acetonitrile extract from the milk was loaded on the cartridge and eluted with 14mL acetonitrile.

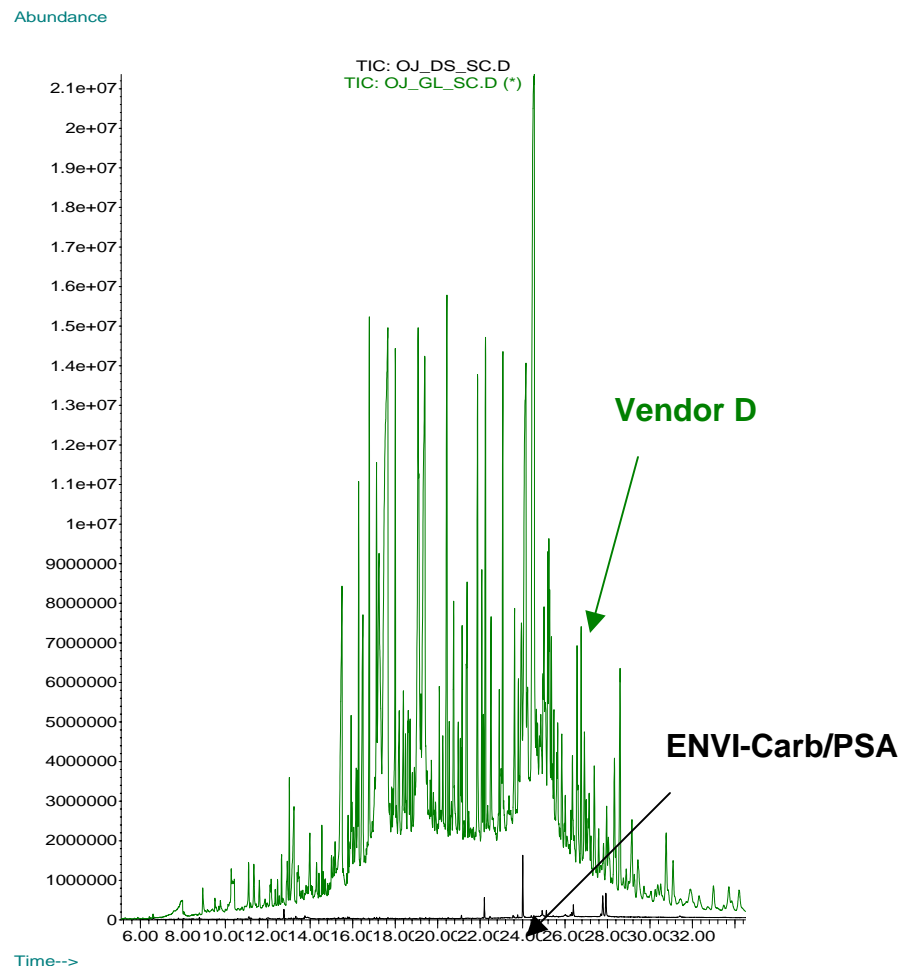
The elution was concentrated and reconstituted into 1.0mL acetone for GC-MS screening.



Extraction and Cleanup of Florida Orange Juice Using Supelclean ENVI-Carb/PSA

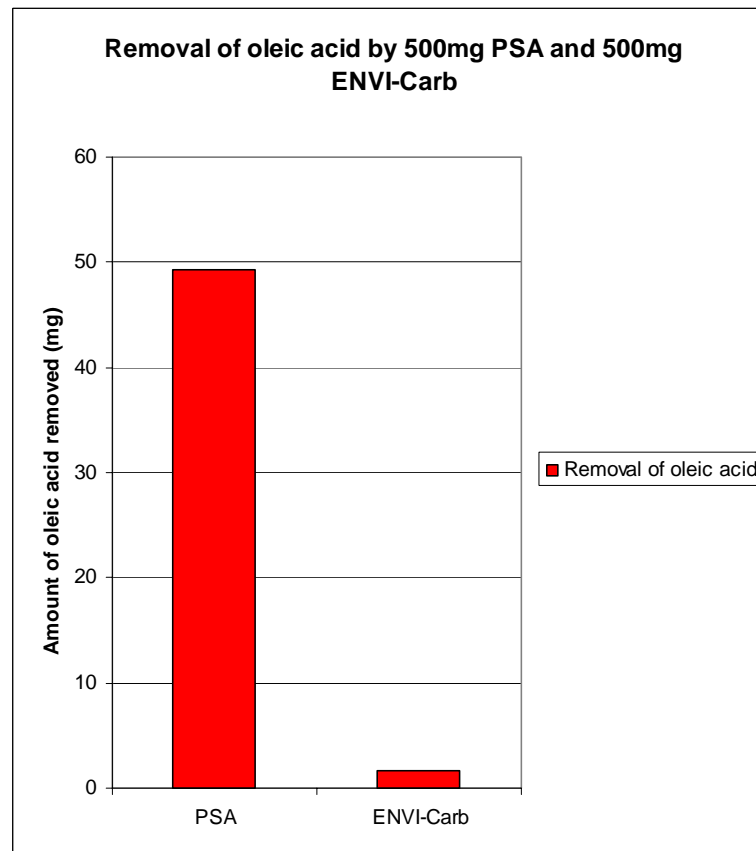
Experimental:

50mL of the orange juice was extracted with 100mL acetonitrile by PMRA method. Carbon/PSA cartridges were first conditioned with 5mL acetonitrile:toluene (3:1). Then 10mL acetonitrile extract was loaded, followed by 20mL acetone:hexane elution (1:1). The elution was concentrated and re-constituted into 1.0mL acetone for GC-MS analysis



PSA Plays a Vital Role for Removal of Fatty Acids

1. Using acetonitrile:toluene (3:1) as elution solvent, PSA (500mg) removes 49.37mg oleic acid when the same amount of ENVI-Carb removes only 1.6mg oleic acid.
2. PSA also plays a vital role for removal of some other matrices that induces matrix enhanced effect.

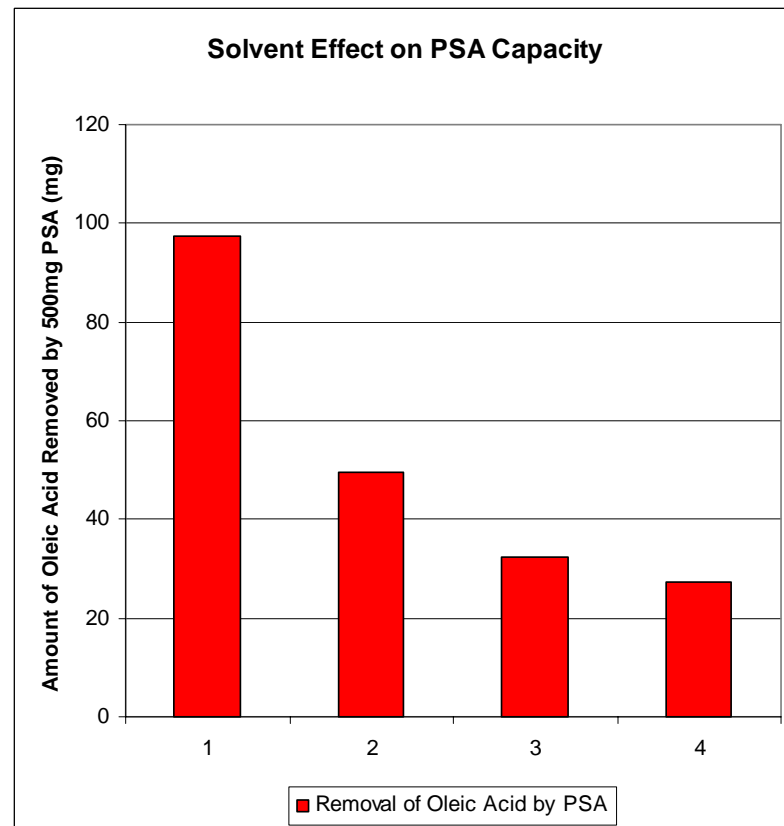


Solvent Effect on PSA Capacity for Removal of Fatty Acids

Experimental:

500mg/6cc Supelclean PSA

1. Conditioned and eluted with acetonitrile:97.4mg oleic acid was removed.
2. Conditioned and eluted with acetonitrile:toluene (3:1): 49.4mg oleic acid was removed.
3. Conditioned and eluted with acetone:hexane (1:1): 32.2mg oleic acid was removed.
4. Preconditioned by acetonitrile:toluene:acetic acid (74:25:1), then conditioned and eluted by acetonitrile:toluene (3:1): 27.2mg oleic acid was removed.





Comparison Between PSA SPE and Carbon/PSA Dual-Layer SPE

PSA:

- 1. Mild generic protocol (using only acetonitrile)**
- 2. Removal of larger amount of fatty acids, particularly suitable for samples with large amount of fatty acids, and without a requirement for removal of pigments (i.e., milk)**
- 3. No side-effect from graphite carbon for pesticides**

ENVI-Carb/PSA:

- 1. Toluene has to be added into acetonitrile for elution in order to eliminate the interactions between graphite carbon and aromatic pesticides. But such a step weakens the capacity of PSA for removal of fatty acids and other matrices.**
- 2. Particularly suitable for samples with a requirement for removal of coloring substances, although coloring substances do not induce matrix-enhancement effect in GC and GC-MS analyses.**

Recoveries Between ENVI-Carb/PSA and the Competitors for Cleanup of Milk

Compound	Pesticide Recovery from ENVI-Carb/PSA (%)	Pesticide Recovery from Competitor (%)
Metamidophos	86	82
Dichlorvos	83	75
Acephate	83	64
Trifluralin	91	80
Diazinon	99	83
Chlorothalonil	59	33
Dimethipin	99	77
Vinclozoline	107	72
Methyl parathion	100	88
Methyl primophos	107	91
Triadimenol-1	104	148
DDE	104	93
Cypermethrin-3	103	132
Difenoconazole-1	114	132
Difenoconazole-2	107	160
Imibenconazole	104	142



Conclusions

- 1. PSA alone or combined with graphite carbon is very useful for cleanup of food matrices.**
- 2. Both suppliers and users should pay attention to the lot-to-lot reproducibility, especially GC-MS background from the cartridges and their ability to remove matrices.**
- 3. When acetone:hexane and acetonitrile:toluene are used as the elution solvents, the capacity of PSA toward to fatty acids will be compromised.**
- 4. Conventional carbon/PSA dual layer should be only used to clean foods with low amount of fatty substances. PSA alone may be the better choice for cleanup of fatty foods.**



Acknowledgement

We thank Ms. Katherine Stenerson and Mr. Chuck Germek of Supelco for GC-MS analyses.



References

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2. F.J. Schenck, S.J. Lehotay and V. Vega, *J. Sep. Sci.* 25 (2002) 883-890.
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