Observations concerning…

☑ ***a compound*** ☑ ***a matrix*** ☑ ***a method*** ☐ ***other***

Analysis of Organotin-Pesticides by the QuEChERS Method - Impact of acidifying on the recoveries

Reported by: EURL-SRM

Version 1 (last update: 22.04.2013)

Brief description of problem/observation/solution:

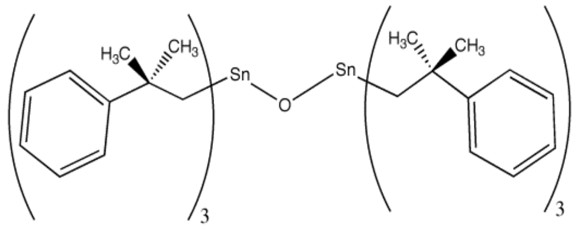
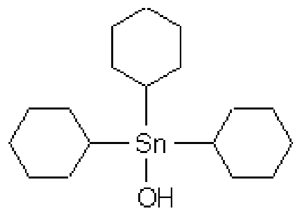
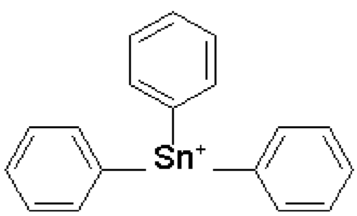
Using QuEChERS, organotin compounds tend to give low recoveries in various types of commodities with high pH commodities being affected the most. The losses are attributed to the tendency of these compounds to undergo interactions (e.g. with matrix-components and surfaces) via the free orbitals of the central tin atom. Such interactions can be intercepted by lowering the pH. Various versions of the QuEChERS method entailing different acidification approaches were tested. All showed a positive impact on the recoveries of fenbutatin oxide, cyhexatin and fentin.

Compound profiles:

Fenbutatin oxide (FBO) is widely used to control mites, aphids, thrips and whiteflies. Its application range is very broad including fruit trees (e.g. citrus, pome fruit, stone fruit), nut trees (e.g. walnut, pecans); fruiting vegetables (e.g. pepper, tomato, aubergine, cucumber, melons), tropical fruits (e.g. banana, mango, papaya, pineapple), berries (e.g. strawberry, raspberry, blueberry), grapes, leafy vegetables (e.g. spinach, lettuce), herbs (e.g. basil, parsley) and pulses (e.g. beans and peanuts). FBO is quite persistent in the environment and exhibits high toxicity to fish. It was originally excluded from Annex I but was then resubmitted for authorization and finally included in Annex I in 2011[1] but only for use in greenhouses. It is currently approved in BE, ES, NL, RO. Authorization in IT is in progress.
Cyhexatin and azocyclotin are both used as acaricides, e.g. in pome fruit, grapes, fruiting vegetables and berries. There are no authorizations in place within the EU. Residue findings are rare. In water azocyclotin spontaneously hydrolyzes to cyhexatin by a loss of 1,2,4-triazole. Both compounds are therefore covered by the same residue definition see Table below).
Fentin (triphenylstanilium cation, triphenyltin, TPT) is a biocide with fungicidal, moluscicidal and algicidal properties. In agriculture it is widely used to control fungal diseases of various crops such as potatoes (late and early blights), sugar beets and pecan trees (leaf spot diseases), beans and soy beans (anthracnose). It is also used to controls algae and snails in

[1] Commission Directive 2011/30/EU

rice fields and aquaculture. Due to its antifouling properties it has been widely incorporated in boats paintings to prevent growth of algae. Fentin has been subject of ecotoxicological concerns as it exhibits strong endocrine disruption properties and has thus not been included in Annex I of 91/414/EEC. As the three phenyl rings delocalize the positive charge fentin exhibits a much stronger ionic character that cyhexatin. Fentin is marketed in form of its chloride, hydroxide or acetate salts, which all quickly dissociate upon contact with water to release the triphenylstanilium cation (the analytically detected component). Strangely fentin hydroxide and fentin acetate have two separate MRL-residue definitions. In the case of food of animal origin they are however practically identical expressed as triphenyltin cation. Residue findings are rare.

Parameter	Value	Notes	
FENBUTATIN OXIDE			Fenbutatin oxide 
Pka	-		
LogP (pKow)	5,15	(25°C; pH 5.8)	
Water solubility	0.0152 mg/L	(20°C; pH 5)	
Hydrolytic behavior	Quite stable		
Residue definition EU	Fenbutatin Oxide		
Approved in…	BE, ES, NL, RO and IT in progess		
CYHEXATIN			Cyhexatin 
Pka	-		
LogP (pKow)	4.84		
Water solubility	0,014 mg/L	(25°C)	
Hydrolytic behavior	Quite stable	Azocyclotin hydrolyses to cyhexatin	
Residue definition EU	Azocyclotin and Cyhexatin (sum of azocyclotin and cyhexatin expressed as cyhexatin)		
Approved in…	Not approved with the EU		
FENTIN			Fentin 
Pka	-		
LogP (pKow)	3,43	for fentin hydroxide	
Water solubility	1 mg/L	(pH 7, 20°C), for fentin hydroxide	
Hydrolytic behavior	Quite stable	The salts dissociate to the cation	
Residue definition EU	**Plant Origin:** 1) Fentin Hydroxide; 2) Fentin Acetate **Animal Origin:** 1) Fentin hydroxide expressed as triphenyltin cation, 2) Fentin acetate expressed as triphenyltin cation,		
Approved in…	Not approved with the EU		

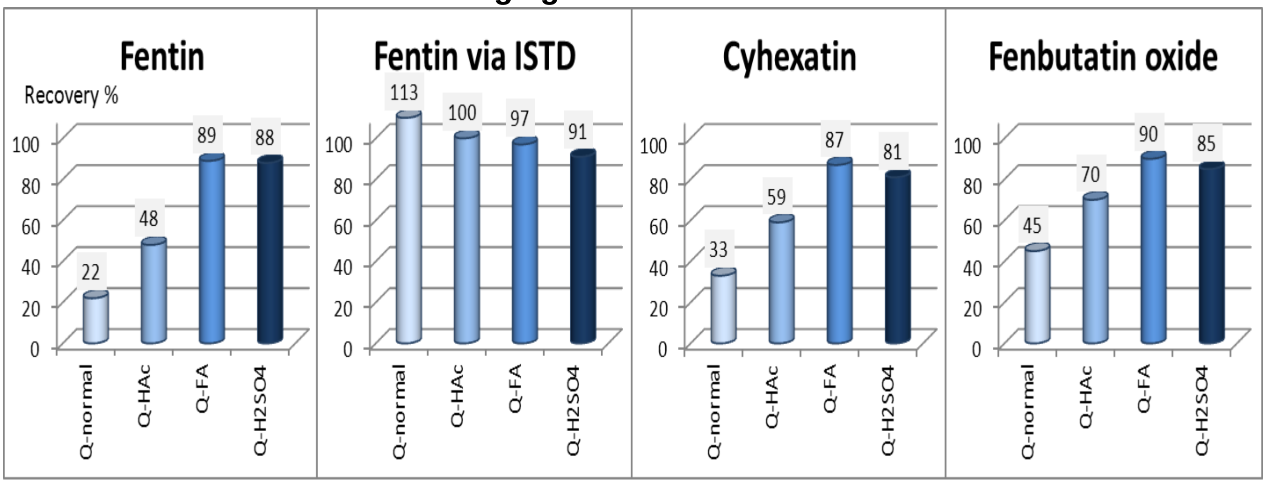
Experiments conducted and observations:

In order to explore the impact of pH on organotin compounds recoveries we have conducted recovery experiments on Lentils, Potatoes and Oranges using the QuEChERS procedure in 4 different versions as follows:

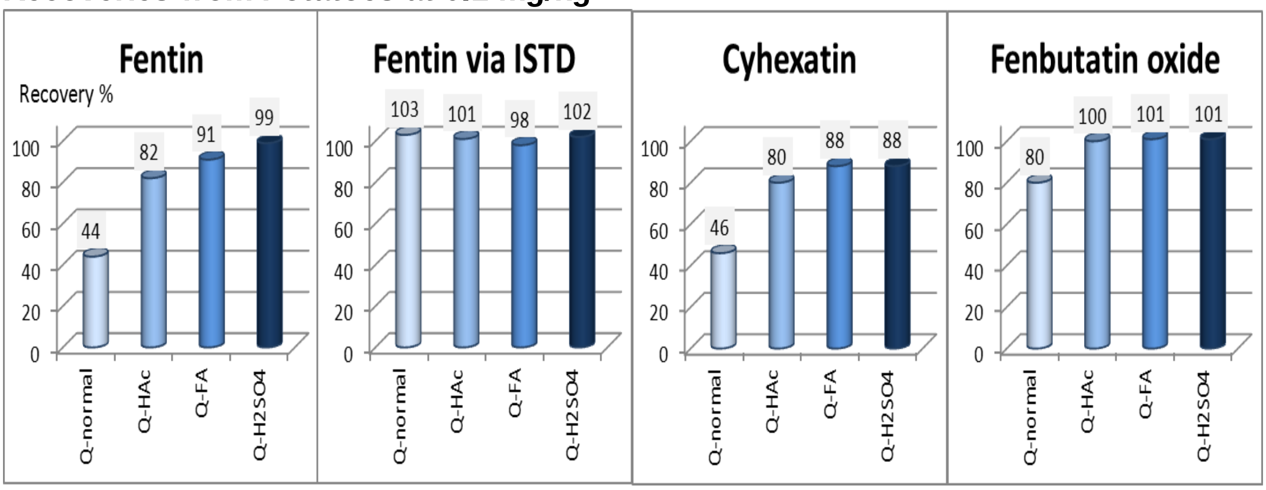
1) EN-15662[2],
2) As EN-15662 but replace citrate salts by 400µL acetic acid (HAc)
3) As EN-15662 but replace citrate salts by 100µL formic acid (FA)
4) As EN-15662 but replace citrate salts by 100µL sulfuric acid conc. (H_2SO_4)

All experiments were conducted in duplicate without d-SPE cleanup (Note: previous experiments have shown that dSPE does not lead to any losses of organotin compounds). Chlorpyriphos D10 was used as ISTD. Fentin D15 was additionally used for fentin. The results of these experiments are shown below:

Recoveries from Lentils at 0.1 mg/kg

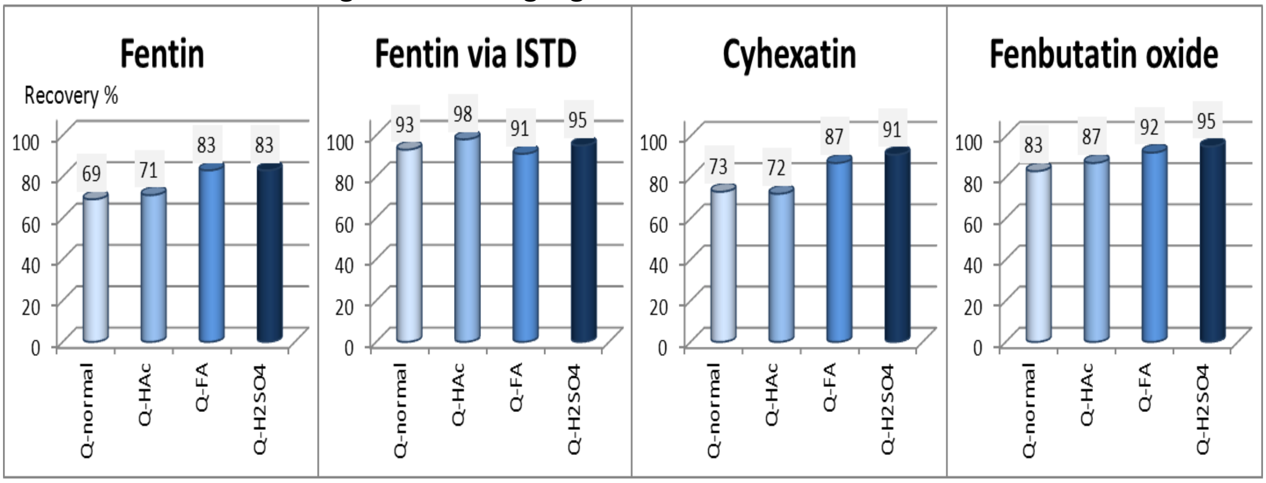


Recoveries from Potatoes at 0.1 mg/kg



[2] Detailed instructions on the QuEChERS method are given in the CEN method EN 15662 (citrate buffered), see also brief description under www.quechers.de .

Recoveries from Oranges at 0.1 mg/kg



Materials:

Fenbutatin oxide (purity 99,5%), purchased from Dr. Ehrenstorfer (Cat #: C 13450000)
Cyhexatin (purity 99,0%), purchased from Dr. Ehrenstorfer (Cat #: C 11870000)
Fentin hydroxide (purity 99,0%), purchased from Dr. Ehrenstorfer (Cat #: C 13602000)
Triphenyl-D15-tin chloride (purity 98,0%), purchased from CDN-isotopes (Cat#: D-5565)
Chlorpyriphos D10 (purity 97,0%), purchased from Dr. Ehrenstorfer (Cat #: C 11600100)

Instrumentation details (exemplary chromatogram, see Annex)**:**

<table>
<tr><th colspan="2">LC-MS/MS method:</th></tr>
<tr><td>LC</td><td>Waters UPLC</td></tr>
<tr><td>MS/MS</td><td>ABSCIEX API 4000, run in ESI positive mode</td></tr>
<tr><td>MRMs Cyhexatin</td><td>365/201, 365/283, 365/203</td></tr>
<tr><td>MRMs Fentin</td><td>347/116, 347/193, 347/118, 351/120</td></tr>
<tr><td>MRMs Fentin D15</td><td>366/120</td></tr>
<tr><td>MRMs Fenbutatin oxide</td><td>517/195, 517/349, 517/461</td></tr>
<tr><td>ISTD Chlorpyriphos D10</td><td>360/199</td></tr>
<tr><td>Column</td><td>Zorbax 3,5 µm; Eclipse XDB-C18; 2,1x 50 mm</td></tr>
<tr><td>Pre-column</td><td>C18 ODS 4mm x 2mm ID (Phenomenex AJO-4286)</td></tr>
<tr><td>Mobile Phase</td><td>A: 5 mmol NH4formate in purified water + 1% FA
B: 5 mmol NH4formate in Methanol + 1% FA</td></tr>
<tr><td>Gradient</td><td>
<table>
<tr><th>Time
min</th><th>Mobile Phase A
%</th><th>Mobile Phase B
%</th></tr>
<tr><td>0</td><td>60</td><td>40</td></tr>
<tr><td>2</td><td>0</td><td>100</td></tr>
<tr><td>8</td><td>0</td><td>100</td></tr>
<tr><td>8.1</td><td>60</td><td>40</td></tr>
<tr><td>13</td><td>60</td><td>40</td></tr>
</table>
</td></tr>
<tr><td>Flow</td><td>0.4 mL min^{-1}</td></tr>
<tr><td>Injection volume</td><td>2 µL</td></tr>
<tr><td>Column temperature</td><td>40°C</td></tr>
</table>

Discussion and conclusions:

It is obvious that acidification improves the recoveries of organotin pesticides using QuEChERS. Formic and sulfuric acid exhibit a stronger effect than acetic acid. Fenbutatin oxide shows good recoveries by the citrate buffered QuEChERS method except for lentils. Fentin and cyhexatin are clearly more affected both showing too low recoveries in lentils and potatoes. In oranges recoveries were acceptable for all compounds even with the unmodified QuEChERS method. In the case of fentin the use of isotope labeled ISTDs satisfactorily corrected recoveries with any version of the method.

Annex:

Exemplary chromatograms of organotin pesticides at 0.001 mg/mL