Fosetyl and Phosphonic acid –
Residue Situation and some Interesting Facts

Kathi Hacker, Anne Benkenstein, Eric Eichhorn, Diana Kolberg, Cristin Wildgrube, Ellen Scherbaum and Michelangelo Anastassiades

E-Mail: Kathi.Hacker@cvuas.bwl.de

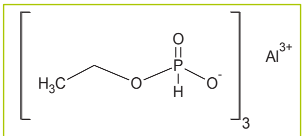
cvua STUTTGART

European Commission

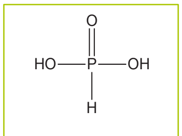
EURL-SRM

Introduction

Residues of phosphonic acid in crops can occur as a result of the application of plant protection products (PPPs) containing phosphonic acid itself or via the application of fosetyl-Al, which degrades to phosphonic acid. To reflect this, the current residue definition of fosetyl-Al is defined in the EU as follows: "sum of fosetyl, phosphonic acid and their salts, expressed as fosetyl".



Fosetyl-Al



Phosphonic acid

From January 2014 to December 2015 a total of 4265 samples of different commodity types of plant origin were separately analyzed for residues of fosetyl and phosphonic acid. Analysis was accomplished by the QuPPe-Method involving extraction by acidified methanol, filtration, dilution and LC-MS/MS in the ESI negative mode using the Hypercarb column.

Results and Summary

Overall, 36% of all the analyzed samples contained residues of fosetyl and/or phosphonic acid above the LOQ, with phosphonic acid being ca. 40x more frequently detected than fosetyl. Conventionally grown products contained phosphonic acid at levels exceeding the LOQ more frequently than products labelled as organic (39% vs. 17%) – see tables of the main findings in conventional and organic products.

Table I Phosphonic acid and fosetyl findings in CONVENTIONAL products

Commodity conventional production	Number of samples	No. of samples containing phosphonic acid	No. of samples containing fosetyl	No. of samples exceeding the MRL	Minimum and maximum contents of phosphonic acid and fosetyl [mg/kg]
Babyfood on fruitbasis	12	7 (58%)		4	0.051 – 0.59
Berry fruits	572	377 (66%)	11 (grapes)	2 (blackberries)	0.014 – 60.9 0.007 – 0.23
Pome fruits	202	141 (70%)			0.01 - 6.0
Stone fruits	260	92 (35%)		5 (3x nectarines, cherries, avocados)	0.021 - 51.7
Citrus fruits	194	138 (71%)	1 (lemons)		0.025 - 13.4 0.011
Exotic fruits	297	113 (38%)		3 (2x kiwis, mangos)	0.044 – 17.2
Fruiting vegetables	647	182 (28%)	5 (2x tomatos, cucumbers, zucchinis, melons)		0.033 – 15.4 0.018 – 0.086
Leafy vegatables	712	181 (25%)	7 (4x rucola, pak-choy, 2x lettuce)	3 (2x basil, cabbages, rucola, spinach)	0.058 – 153.0 0.016 – 0.28
Stem vegetables	226	49 (22%)		1 (stem cabbage)	0.050 – 13.0
Root vegetables	176	28 (16%)		3 (2x root celery, parsnip)	0.063 – 5.8
Potatoes	55	13 (24%)			0.035 – 21.9
Dry pulses and cereals	68	20 (29%)		3 (3x rice)	0.034 – 9.9
Fungi	144	37 (26%)			0,087 - 8,5
Wine	31	24 (77%)	4		0,16 - 12,1 0,025 – 0,040
Fruit juice	31	30 (97%)	8 (grape juice)		0,026 – 4,0 0,016 – 0,066

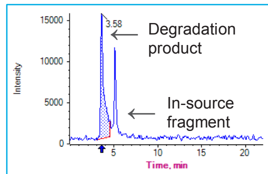
Despite the clear classification of phosphonic acid as a synthetic pesticide, the frequency of findings in organic products is still remarkably high. The highest levels of phosphonic acid were detected in leafy vegetables (highest value: >150 mg/kg), grapes, berries and pears. The highest frequency of fosetyl findings were encountered in rucola (highest value: < 0.3 mg/kg) and grapes (also grape products). We suspect that fosetyl is formed as an artefact during production or storage of wine.

Analytical method

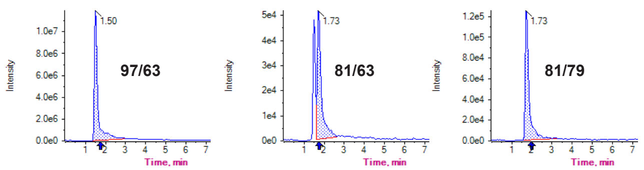
Phosphonic acid and fosetyl are extracted by the QuPPe method. While phosphonic acid is measured by the PerChloPhos method (No. 1.4), fosetyl is analysed via method 1.3 Glyphosate & Co..

When analyzing for phosphonic acid and fosetyl there are some important aspects to keep in mind:

- We recommend the separated measurement due to formation of phosphonic acid from fosetyl both in solution and through in-source fragmentation. This can be easily seen by measuring fosetyl-D_5 solution. The chomatogram on the right shows two peaks at the mass trace of phosphonic acid.
- Many samples naturally contain high concentrations of phosphoric acid, which is co-extracted during the sample preparation process. The chromatographic separation of phosphonic acid from phosphoric acids is often compromised resulting in a suppression of the phosphonic acid signal and in some cases even leads to false negative results. In addition, the qualifier mass-trace of phosphonic acid (m/z 81/63) is interfered by phosphoric acid, due to in-source fragmentation of the latter.



Phosphonic acid 81/79



unique to Phosphoric acid — common to Phosphoric and Phosphonic acid — unique to Phosphonic acid

Although m/z 81/63 is a very minor transition of phosphoric acid its interference on phosphonic acid can be very significant due to the typically high levels of phosphoric acid in samples. By diluting the sample extracts, the chromatographic separation considerably improves allowing proper peak integration next to the high levels of Phosphoric acid. Fortunately phosphonic acid has additionally a mass-transition (m/z 81/79), which is only negligibly interfered, thus allowing proper identification and accurate quantification. The elution time and peak shape of the ILIS ($^{18}O_3$-phosphonic acid) can also be used to distinguish phosphonic from phosphoric acid.

Table II Phosphonic acid findings in ORGANIC products

Commodity organic production	Number of samples	No. of samples containing phosphonic acid*	No. of samples exceeding the MRL	Minimum and maximum contents [mg/kg]
Babyfood on fruitbasis	29	14 (48%)	8	0.01 - 0.56
Berry fruits	64	20 (31%)		0.014 – 2.4
Pome fruits	31	6 (19%)		0.035 – 6.8
Stone fruits	23	5 (22%)	1 (cherries)	0.077 – 1.7
Citrus fruits	36	10 (28%)		0.058 – 2.0
Exotic fruits	20	6 30%)	1 (bananas)	0.033 – 3.7
Fruiting veg.	110	17 (15%)		0.035 – 18.6
Leafy veg.	99	3 (3%)		0.40 – 30.1
Stem veg.	39	4 (10%)	1 (fennel)	0.033 – 7.7
Dry pulses and cereals	38	10 (26%)		0.054 – 0.42

** No fosetyl was detected in samples of organic production*

Reference

Quick Method for the Analysis of numerous Highly Polar Pesticides in Foods of Plant Origin via LC-MS/MS involving Simultaneous Extraction with Methanol (QuPPe-Method), Version 9.1, May 2016

EPRW 2016

Baden-Württemberg