Electronic Supplementary Material (ESI) for Analytical Methods.

Determination of underivatized chlormequat, fosetyl-aluminium and phosphonic acid residues in maize and soybean by LC-MS/MS

Hao Yang [a,b,c], Yue Geng* [a,b,c], Shu Lin [a,b,c], Lu Wang [a,b,c], Yi Peng [a,b,c], Yaping Xu [a,b,c], Jingran Zhang [d], and Xiaowei Liu [a,b,c]

Table S1 Summary information for the detection of chlormequat, fosetyl-aluminium and phosphonic acid residues

Target analyte/food matrix	Extraction	Clean up	Instrumental analysis	Analysis of time and organic solvents	LOQ (μg kg^{-1})	Recovery range (%)	Matrix effects (%)	Derivation time	spiked level
chlormequat, fosetyl-aluminium and phosphonic acid/maize and soybean (the present study)	2 g sample (57.2 μL acetic acid solution, 30 mL dichloromethane	Oasis HLB (Waters) SPE	LC-MS/MS	15 min, 0 mL	10	Chlormequat: 85.0 -106.4, fosetyl-aluminium: 81.7 - 109.5, phosphonic acid: 74.7 - 104.4	Chlormequat: -56.9 - -84.6 fosetyl-aluminium: -40.4 - -71.9 phosphonic acid: -52.1 - -72.7	NO	0.05, 0.1, 1 mg kg^{-1}
chlormequat/pears, potatoes [1]	5 g sample (3.5 mL acetonitrile)	SPE (25 mg PSA, 25 mg GCB and 125 mg $MgSO_4$)	HPLC-MS/MS	3.5 min, 0.805 mL (A: methanol, B: 20 mmol L^{-1} ammonium acetate containing 0.1% formic acid)	0.35	87.6 -105.8	16.1 (pear) 27.7 (potato)	NO	0.35, 35, 140 μg kg^{-1}
chlormequat/fresh fruit, fruit juices, vegetables, mushrooms, bread, baby foods, beer and coffee powder [2]	10 g sample (25 mL methanol: ammonium formate = 1: 4), 1 g coffee (10mL methanol: ammonium formate=1: 4)	C18 SPE (5 mL methanol, 5 mL (methanol: ammonium formate = 1: 4))	LC–MS/MS	4 min, 1.6 mL (A: acetonitrile B: methanol containing 50 mmol L^{-1} ammonium formate)	5 (apple and beer)	>78	Not reported	NO	beer and apple: 5 μg kg^{-1}

Target analyte/food matrix	Extraction	Clean up	Instrumental analysis	Analysis of time and organic solvents	LOQ (μg kg^{-1})	Recovery range (%)	Matrix effects (%)	Derivation time	spiked level
chlormequat/barley and wheat [3]	5 g sample (20 mL methanol: water = 1: 1)	PSA+C18 d-SPE	UHPLC-MS/MS	4 min, 1 mL (A: 60 mmol L^{-1} ammonium formate 40%, B: acetonitrile 60%)	20	barley: 93 -110 wheat: 70 -115	-92	NO	20, 40, 80, 200, 400, 1000 μg kg^{-1}
chlormequat/grain [4]	10 g sample (60 mL methanol: water: acetic acid = 75: 24: 1)	C18 SPE (5 mL methanol, 3 mL containing 50 mmol L^{-1} ammonium acetate methanol: water: acetic acid = 50: 49: 1)	LC-MS/MS	15 min, 3.75 mL (acetonitrile: methanol: water: acetic acid = 53: 21: 25: 1 containing 50 mmol L^{-1} ammonium acetate)	50	89 -99	Not reported	NO	0.05, 0.2, 1, 5 mg kg^{-1}
chlormequat/tomato or lemon, and chia seed, wheat, or sultana [5]	7 g sample (20 mL water: methanol: hydrochloric acid = 50: 25: 25)	NO	LC-MS/MS	16 min, 6.4 mL (A: formic acid containing 20 mmol L^{-1} ammonium formate, B: acetonitrile)	10	77 -120	67	NO	0.01, 0.1 mg kg^{-1}
chlormequat/ rice, wheat flour, pear, tomato and ketchup [6]	water and methanol (1: 1)	Strata-X-C SPE	LC-MS/MS	3.3 min, 0.198 mL acetonitrile, 0.792 mL 10 mmoL L^{-1} Ammonium acetate aqueous solution containing 0.1% formic acid	0.2	82 -102	rice: -8.2, wheat flour: -14.8, pear: -13.8, tomato: -14.5, ketchup: -11.6	NO	0.2, 5.0, 10 μg kg^{-1}

Target analyte/food matrix	Extraction	Clean up	Instrumental analysis	Analysis of time and organic solvents	LOQ (μg kg^{-1})	Recovery range (%)	Matrix effects (%)	Derivation time	spiked level
fosetyl/apple [7]	sulfuric acid (1%)	NO	GC	30.5 min	1000	71.3 -119.9	Not reported	>30min	1.0, 5.0, 10.0 mg kg^{-1}
fosetyl/commercial pesticide formulations (wettable powder containing 50% mass) [8]	water	NO	HPLC	11 min, 0.5206 mL acetonitrile, 0.002739 mL formic acid	0.1	96.7 -100.6	Not reported	NO	100, 250, 500 mg kg^{-1}
fosetyl/cabbage [9]	20 mL acetonitrile	100 mg $MgSO_4$ and 100 mg PSA	LC-MS/MS	10 min, 2.5 mL (A: acetonitrile, B: 0.05% formic acid)	10	82 -107	ethyl phosphonic acid: 80, phosphorous acid: 103	NO	0.01, 0.1, 0.5 mg kg^{-1}
fosetyl/tomato, apple, lemon, sultana, avocado and wheat [10]	10 g sample (10 mL methanol containing 1% formic acid)	NO	IC-MS/MS	25 min (acetonitrile: 1.397 mL)	10	76 -113	Apple: -1, wheat: -80, sultana: -75, tomato: -42, lemon: -76, avocado: -19	NO	0.01, 0.1 mg kg^{-1}
fosetyl aluminum/grape [11]	5 g sample 16 mL (50 mmol L^{-1} acetic acid, 10 mmol L^{-1} Na_2EDTA: methanol = 3: 1)	Oasis HLB SPE	LC-MS-MS	17 min (formic acid: 6.5 mL ammonium formate: 0.6549 μL)	100	87 -111	7 -13	NO	0.1, 0.5, 2 mg kg^{-1}

References

1 J. Gao, J. Wang, M. Zuo, L. Ma, Y. Cui, T. Yang and M. Ding, RSC advances, 2015, 5, 5895-5903.
2 X. Esparza, E. Moyano and M. T. Galceran, Journal of Chromatography A, 2009, 1216, 4402-4406.
3 J. Z. Francesquett, T. M. Rizzetti, T. J. Cadaval, O. D. Prestes, M. B. Adaime and R. Zanella, J Chromatogr A, 2019, 1592, 101-111.
4 M. Vahl, A. Graven and R. K. Juhler, Fresenius' journal of analytical chemistry, 1998, 361, 817-820.
5 A. Bauer, J. Luetjohann, S. Rohn, J. Kuballa and E. Jantzen, Food analytical methods, 2018, 11, 2237-2243.
6 L. Lu, X. Luo, Y. Wang and J. Hao, Journal of Instrumental Analysis, 2011, 30, 321-325.
7 L. Sun, Z. Chi, X. Liu and X. Yu, Agrochemicals, 2009, 48, 747-748+759.
8 H. Karasali, K. M. Kasiotis and K. Machera, Chemical papers, 2014, 68, 725-731.
9 B. Han, Y. He, B. Lin, H. Huang, L. Chen and L. Xu, Chinese Journal of Pesticide Science, 2017, 19, 403-408.
10 A. Bauer, J. Luetjohann, S. Rohn, J. Kuballa and E. Jantzen, Journal of Agricultural and Food Chemistry, 2018, 66, 346-350.
11 N. Chamkasem, J Agric Food Chem, 2017, 65, 7535-7541.