MACHEREY-NAGEL
Chromatography application note

MN application note 02/2020

Determination of pesticide residues in Cannabis sativa using an optimized QuEChERS method with high matrix reduction

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Abstract

This application note describes the determination of pesticide residues in Cannabis sativa using a QuEChERS method for most effective sample clean-up. Interfering substances (like e.g., lipids and pigments), which were also extracted with the organic layer, are almost completely removed with clean-up salt mixes with high amounts of GCB (graphitized carbon black) and CHROMABOND® C_{18} ec adsorbents. The organic extracts are finally analyzed by HPLC-MS/MS.

Introduction

While medical and recreational use of cannabis are legalized in more and more U.S. territories the markets for cannabis and cannabis-based products (e.g. concentrated oils, soda, candy and other edible forms) have grown year by year in North America and also in other countries[1]. A huge demand for marijuana has lead to professional cultivation forms of hemp to improve growth yields. The use of pesticides is a common tool for this monoculture plant production. Therefor an increasing interest in the determination of pesticide residues in marijuana is given.

New quality control methods have to be developed to ensure product safety and to reduce health risks by chronic exposure to pesticides. These methods have to be quick, easy, cheap, effective, rugged and safe like the QuEChERS extraction approach[2]. Interfering substances (like e.g., lipids and chlorophyll), which were also extracted with the organic layer, are nearly completely removed by using clean-up salt mixes with high amounts of GCB and of CHROMABOND® C_{18} ec adsorbents. On the other side, the composition of the clean-up salt mixes also has to ensure sufficient recovery rates for these pesticides. This work presents a QuEChERS method for the simultaneous analysis of more than 160 pesticides from Cannabis sativa. The organic extracts are finally analyzed by HPLC-MS/MS.

Figure 1: Marijuana (Cannabis sativa).

Dispersive solid phase extraction (dSPE)

Products from competitors

Competitor 1:

Supel™ QuE PSA/C_{18}/ENVI-Carb tube, 15 mL centrifuge tubes, 1200 mg $MgSO_4$, 400 mg Supleclean PSA, 400 mg Discovery DSC-18 und 400 mg ENVI-Carb

Competitor 2:

roQ™ QuEChERS dSPE kit, 15 mL centrifuge tubes, 1200 mg $MgSO_4$, 400 mg PSA, 400 mg C_{18} ec, 400 mg GCB

Competitor 3:

QuEChERS SPE Resprep Q352, 15 mL centrifuge tubes, 1200 mg $MgSO_4$, 400 mg PSA, 400 mg C_{18}, 400 mg Carbon

Extraction

- Weigh out 1 g of homogenized sample (milled in a grinder) into a 50 mL centrifuge tube
- Add 100 µL of standard solution (β = 1 µg/mL for each analyte in acetonitrile) for determining recovery rates
- Add 10 mL water and shake
- Add 10 mL 1 % acetic acid in acetonitrile and shake for 30 min
- Add the CHROMABOND® QuEChERS extraction mix I (REF 730970)
- Shake vigorously for 2 min and cool down the mixture in an ice bath
- Centrifuge the mixture at 4500 rpm, for 5 min at 4 °C

Clean-up

- Add 6 mL of acetonitrile supernatant to the CHROMABOND® QuEChERS clean-up mix XLVII (REF 730845)
- Shake vigorously for 60 s
- Centrifuge the mixture at 4500 rpm, for 5 min at 4 °C
- Take acetonitrile extract for injection

Subsequent analysis: HPLC-MS / MS

Chromatographic conditions

Column:	EC NUCLEOSHELL® Bluebird RP 18, 50 x 4.6 mm, 2.7 µm
Eluent A:	0.1 % formic acid in water
Eluent B:	0.1 % formic acid in acetonitrile
Gradient:	in 5 min from 5 % to 100 % B, hold for 1.0 min, in 0.1 min to 5 % B, hold 5 % B for 3.9 min

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Pesticide residues in cannabis with high matrix reduction

Flow rate: 0.7 mL/min
Temperature: 30 °C
Injection volume: 2 µL

MS conditions

AB Sciex QTRAP 5500
Acquisition mode: SRM
Interface: ESI
Polarity: positive
Curtain gas: 35 psig
Collision gas: medium
Ion spray voltage: 5000 V
Temperature: 450 °C
Ion source gas 1: 45 psig
Ion source gas 2: 45 psig
Detection window: 60 s

MRM transitions

Analyte	RT [min]	Q_1 Mass [Da]	Q_3 Mass [Da]
Propamocarb.1	1.45	189.2	102.1
Propamocarb.2	1.46	189.2	74.0
Aminocarb.1	1.49	209.2	137.2
Aminocarb.2	1.49	209.2	152.2
Formetanate HCl.1	1.52	222.3	165.0
Formetanate HCl.2	1.52	222.3	120.1
Pymetrozine.1	1.56	218.1	105.0
Pymetrozine.2	1.56	218.1	78.0
Acephate.1	1.61	184.1	143.0
Acephate.2	1.62	184.1	49.0
Omethoate.1	1.83	214.1	183.0
Omethoate.2	1.84	214.1	125.1
Nitenpyram.1	1.88	271.1	224.9
Nitenpyram.2	1.88	271.1	126.1
Aldicarb sulfoxide.1	1.98	207.1	132.1
Aldicarb sulfoxide.2	1.98	207.1	89.1
Dinotefuran.1	2.03	203.0	129.0
Dinotefuran.2	2.03	203.0	157.0
Mexacarbate.1	2.08	223.1	166.1
Mexacarbate.2	2.08	223.1	151.1
Flonicamid.1	2.36	230.2	203.1
Flonicamid.2	2.36	230.2	174.0
Fuberidazole.1	2.41	185.1	157.1
Fuberidazole.2	2.41	185.1	65.0
Thiamethoxam.1	2.52	292.2	181.2
Thiamethoxam.2	2.52	292.2	211.0
Monocrotophos.1	2.56	224.1	127.1
Monocrotophos.2	2.56	224.1	98.1
Dicrotophos-1	2.70	238.1	112.1
Dicrotophos-2	2.70	238.1	193.0
Pirimicarb.1	2.74	239.2	72.1
Pirimicarb.2	2.75	239.2	182.0
Trichlorfon.1	2.89	257.0	109.0
Imidacloprid.1	2.90	256.2	175.0
Imidacloprid.2	2.90	256.2	209.0
Clothianidin.1	2.91	250.2	169.1
Clothianidin.2	2.91	250.2	132.1
Fenuron.1	2.95	165.1	46.0
Fenuron.2	2.95	165.1	72.0
Vamidothion.1	2.98	288.1	146.1
Vamidothion.2	2.98	288.1	118.1
3-Hydroxycarbofuran.1	3.00	238.2	181.0
3-Hydroxycarbofuran.2	3.00	238.2	163.1
Dimethoate.1	3.05	230.1	198.8
Dimethoate.2	3.05	230.1	125.0
Acetamiprid.1	3.14	223.1	126.1
Acetamiprid.2	3.14	223.1	99.0
Prometon.1	3.31	226.2	142.1
Prometon.2	3.31	226.2	86.0
Terbumeton.1	3.32	226.2	170.0
Secbumeton.2	3.32	226.2	100.0
Secbumeton.1	3.33	226.2	170.0
Mevinphos isomer 1.1	3.35	225.1	127.0
Mevinphos isomer 1.2	3.35	225.1	192.9
Butocarboxim.1	3.40	213.0	75.0
Butocarboxim.2	3.40	213.0	116.0
Imazalil.1	3.40	297.1	201.0
Imazalil.2	3.40	297.1	159.0
Aldicarb.1	3.44	208.1	116.0
Aldicarb.2	3.44	208.1	89.0
Tricyclazole.1	3.52	190.1	163.0
Tricyclazole.2	3.52	190.1	136.0
Mesotrione.1	3.56	340.1	228.0
Mesotrione.2	3.56	340.1	104.1
Carbetamide.1	3.62	237.1	192.1
Carbetamide.2	3.62	237.1	118.2
Ametryn.1	3.66	228.1	186.0
Ametryn.2	3.66	228.1	96.0
Fenpropimorph.1	3.70	304.3	147.0
Fenpropimorph.2	3.70	304.3	117.2
Methoprotryne.1	3.76	272.2	198.0
Methoprotryne.2	3.76	272.2	240.0
Thiophanate-methyl.1	3.77	343.2	151.0
Thiophanate-methyl.2	3.77	343.2	311.1
Metribuzin.1	3.78	215.2	187.0
Metribuzin.2	3.78	215.2	84.1
Spiroxamine isomer 1.1	3.79	298.2	144.2
Spiroxamine isomer 1.2	3.79	298.2	100.1
Spiroxamine isomer 2.1	3.79	298.2	144.2
Spiroxamine isomer 2.2	3.79	298.2	100.1
Carbofuran.1	3.81	222.0	165.0
Carbofuran.2	3.81	222.0	123.0
Sulfentrazone.1	3.85	387.0	307.0

Pesticide residues in cannabis with high matrix reduction

Analyte	RT [min]	Q_1 Mass [Da]	Q_3 Mass [Da]
Sulfentrazone.2	3.85	387.0	146.0
Tebuthiuron.1	3.87	229.2	172.1
Tebuthiuron.2	3.87	229.2	116.0
Carbaryl.1	3.98	202.1	145.2
Carbaryl.2	3.98	202.1	127.1
Prometryne.1	3.99	242.2	158.1
Prometryne.2	3.99	242.2	200.1
Carboxin.1	4.00	236.1	143.1
Carboxin.2	4.00	236.1	87.1
Pyrimethanil.1	4.02	200.2	107.0
Pyrimethanil.2	4.02	200.2	82.2
Terbutryn.1	4.02	242.2	186.0
Terbutryn.2	4.02	242.2	68.1
Ethiofencarb.1	4.03	226.2	107.1
Ethiofencarb.2	4.03	226.2	164.0
Monolinuron.1	4.05	215.1	126.1
Monolinuron.2	4.05	215.1	99.0
Fluometuron.1	4.08	233.0	72.0
Flutriafol.1	4.14	302.2	70.1
Flutriafol.2	4.14	302.2	123.0
Chlorotoluron.1	4.15	213.1	72.2
Chlorotoluron.2	4.15	213.1	46.0
Isoprocarb.1	4.16	194.1	95.1
Isoprocarb.2	4.16	194.1	137.0
Metobromuron.1	4.17	259.1	169.9
Metobromuron.2	4.18	259.1	148.2
Metalaxyl.1	4.21	280.2	220.3
Metalaxyl.2	4.21	280.2	192.0
Isoproturon.1	4.23	207.1	72.1
Isoproturon.2	4.23	207.1	46.1
Methabenzthiazuron.1	4.25	222.1	165.0
Methabenzthiazuron.2	4.25	222.1	150.0
Butoxycarboxim.1	4.26	223.1	106.0
Butoxycarboxim.2	4.26	223.1	166.0
Cycluron.1	4.29	199.2	89.0
Cycluron.2	4.29	199.2	89.1
Desmedipham.1	4.33	318.2	154.0
Desmedipham.2	4.33	318.2	182.0
Diuron.1	4.33	233.1	72.2
Diuron.2	4.33	235.2	72.1
Chlorantraniliprole.1	4.36	484.0	453.0
Chlorantraniliprole.2	4.36	484.0	285.8
Spinosad (Spinosyn A).1	4.36	732.5	142.2
Spinosad (Spinosyn A).2	4.36	732.5	98.1
Bupirimate.1	4.37	317.2	166.1
Bupirimate.2	4.37	317.2	108.0
Phenmedipham.1	4.37	301.2	168.0
Phenmedipham.2	4.37	301.2	107.9
Fenobucarb.1	4.44	208.0	95.0
Diethofencarb.1	4.45	268.1	226.1

Analyte	RT [min]	Q_1 Mass [Da]	Q_3 Mass [Da]
Diethofencarb.2	4.45	268.1	124.0
Ethiprole.1	4.45	397.2	350.9
Ethiprole.2	4.45	397.2	255.0
Furalaxyl.1	4.47	302.2	242.0
Furalaxyl.2	4.47	302.2	95.1
Spinosad (Spinosyn D).1	4.48	746.4	142.3
Spinosad (Spinosyn D).2	4.47	746.4	98.0
Hydramethylnon.1	4.48	495.2	323.2
Hydramethylnon.2	4.48	495.2	151.1
Spinetoram.1	4.48	748.4	142.3
Spinetoram.2	4.48	748.4	98.0
Halofenozide.1	4.5	331.2	105.0
Halofenozide.2	4.5	331.0	275.0
Nuarimol.1	4.5	315.0	252.0
Nuarimol.2	4.5	315.0	81.0
Siduron.1	4.52	233.1	137.1
Siduron.2	4.51	233.1	94.1
Fenamidone.1	4.52	312.1	92.0
Fenamidone.2	4.52	312.1	236.1
Azoxystrobin.1	4.53	404.1	372.1
Azoxystrobin.2	4.53	404.1	344.0
Linuron.1	4.53	249.1	160.0
Linuron.2	4.53	249.1	182.1
Methiocarb.1	4.54	226.2	169.0
Methiocarb.2	4.54	226.2	121.2
Paclobutrazol.1	4.55	294.3	70.0
Paclobutrazol.2	4.55	294.3	125.0
Boscalid.1	4.56	343.0	307.0
Boscalid.2	4.56	343.0	140.0
Carfentrazone-ethyl.1	4.56	412.0	328.0
Carfentrazone-ethyl.2	4.56	412.0	356.0
Fenarimol.1	4.56	331.0	268.0
Fenarimol.2	4.56	331.0	81.0
Promecarb.1	4.57	208.1	151.0
Promecarb.2	4.57	208.1	109.2
Flutolanil.1	4.58	324.1	262.0
Flutolanil.2	4.58	324.1	241.9
Triadimenol.1	4.59	296.2	70.1
Triadimenol.2	4.59	296.2	227.1
Dimethomorph isomer 1.1	4.60	388.2	300.9
Dimethomorph isomer 1.2	4.60	388.2	164.9
Myclobutanil.1	4.61	289.1	70.0
Myclobutanil.2	4.61	289.1	125.0
Mepronil.1	4.62	270.2	119.1
Mepronil.2	4.62	270.2	227.9
Triadimefon.1	4.62	294.0	197.1
Triadimefon.2	4.62	294.0	225.0
Methoxyfenozide.1	4.65	369.2	149.1
Methoxyfenozide.2	4.65	369.2	313.2
Cyproconazole isomer 1.1	4.66	292.2	70.1

Pesticide residues in cannabis with high matrix reduction

Analyte	RT [min]	Q_1 Mass [Da]	Q_3 Mass [Da]
Cyproconazole isomer 1.2	4.66	292.2	125.1
Fenhexamid.1	4.68	302.0	97.0
Fenhexamid.2	4.68	302.0	55.0
Triticonazole.1	4.69	318.2	70.0
Triticonazole.2	4.69	318.2	125.0
Bifenazate.1	4.69	301.2	198.0
Bifenazate.2	4.69	301.2	170.0
Butafenacil.1	4.69	492.2	330.9
Butafenacil.2	4.69	492.2	348.9
Iprovalicarb isomer 1.1	4.70	321.2	119.2
Iprovalicarb isomer 1.2	4.70	321.2	203.1
Iprovalicarb isomer 2.1	4.70	321.2	119.2
Iprovalicarb isomer 2.2	4.70	321.2	203.1
Tetraconazole.1	4.70	372.2	158.9
Tetraconazole.2	4.70	372.2	70.1
Chloroxuron.1	4.71	291.1	72.1
Chloroxuron.2	4.72	291.1	218.1
Spirotetramat.1	4.71	374.2	330.2
Spirotetramat.2	4.71	374.2	302.2
Flufenacet.1	4.72	364.2	152.2
Flufenacet.2	4.72	364.2	193.9
Mefenacet.1	4.72	299.2	148.0
Mefenacet.2	4.72	299.2	120.2
Fluquinconazole.1	4.73	376.0	349.0
Fluquinconazole.2	4.73	376.0	307.0
Prochloraz.1	4.75	376.1	307.9
Prochloraz.2	4.75	376.1	70.1
Triflumizole.1	4.76	346.0	278.0
Triflumizole.2	4.76	346.0	73.0
Fluoxastrobin.1	4.76	459.1	427.0
Fluoxastrobin.2	4.76	459.1	188.1
Fenarimol.1	4.77	331.0	268.0
Fipronil.1	4.77	437.2	368.0
Fipronil.2	4.78	437.2	290.0
Etaconazole isomer 1.1	4.79	328.0	159.0
Etaconazole isomer 1.2	4.78	328.1	205.0
Fenbuconazole.1	4.80	337.1	125.1
Fenbuconazole.2	4.80	337.1	70.0
Cyazofamid.1	4.81	325.2	108.0
Cyazofamid.2	4.81	325.2	261.2
Epoxiconazole.1	4.81	330.1	121.1
Epoxiconazole.2	4.81	330.1	101.2
Mepanipyrim.1	4.81	224.1	77.0
Mepanipyrim.2	4.81	224.1	106.1
Flusilazole.1	4.83	316.2	247.0
Flusilazole.2	4.83	316.2	165.0
Tebufenozide.1	4.83	353.2	133.0
Tebufenozide.2	4.84	353.2	297.2
Flubendiamide.1	4.84	683.1	408.0
Flubendiamide.2	4.84	683.1	274.1

Analyte	RT [min]	Q_1 Mass [Da]	Q_3 Mass [Da]
Diclobutrazol.1	4.87	328.0	70.0
Diclobutrazol.2	4.87	328.2	59.1
Fenoxycarb.1	4.87	302.3	88.0
Fenoxycarb.2	4.87	302.3	116.1
Mandipropamid.1	4.89	412.0	346.0
Mandipropamid.2	4.89	412.0	366.0
Neburon.1	4.89	275.1	88.0
Neburon.2	4.89	275.1	114.0
Tebuconazole.1	4.89	308.2	70.1
Tebuconazole.2	4.89	308.2	125.0
Picoxystrobin.1	4.90	368.2	145.1
Picoxystrobin.2	4.90	368.2	204.9
Bromucanozole isomer 1.1	4.91	378.1	70.0
Bromucanozole isomer 1.2	4.91	378.1	159.0
Dimoxystrobin.1	4.91	327.1	205.0
Dimoxystrobin.2	4.91	327.1	116.0
Penconazole.1	4.92	284.2	70.0
Penconazole.2	4.92	284.2	158.9
Hexaconazole.1	4.97	331.0	105.0
Hexaconazole.2	4.97	314.2	159.0
Propiconazole isomer 1.1	4.97	342.1	159.0
Propiconazole isomer 1.2	4.97	342.1	69.0
Zoxamide.1	4.97	336.1	186.9
Zoxamide.2	4.97	336.1	158.9
Prothioconazole.1	4.99	344.0	189.0
Prothioconazole.2	5.00	344.0	125.0
Metconazole.1	4.99	320.2	70.1
Metconazole.2	4.99	320.2	125.1
Triflumuron.1	4.99	359.2	156.2
Triflumuron.2	4.99	359.2	139.1
Amitraz.1	5.00	294.2	148.3
Amitraz.2	5.00	294.2	91.2
Benalaxyl.1	5.00	326.3	148.2
Benalaxyl.2	5.00	326.3	294.2
Bitertanol.1	5.02	338.0	70.0
Bitertanol.2	5.02	338.0	99.0
Pyraclostrobin.1	5.05	388.2	194.0
Pyraclostrobin.2	5.05	388.2	163.0
Diniconazole.1	5.10	326.3	159.0
Diniconazole.2	5.09	326.3	70.0
Thiobencarb.1	5.10	258.3	125.0
Thiobencarb.2	5.10	258.3	89.1
Difenoconazole isomer 1.1	5.13	408.2	253.1
Difenoconazole isomer 1.2	5.13	406.0	251.0
Benzoximate.1	5.14	364.2	198.9
Benzoximate.2	5.14	364.2	105.0
Trifloxystrobin.1	5.15	409.0	186.0
Trifloxystrobin.2	5.15	409.0	145.0
Buprofezin.1	5.16	306.2	201.0
Buprofezin.2	5.16	306.2	116.1

Pesticide residues in cannabis with high matrix reduction

Analyte	RT [min]	Q_1 Mass [Da]	Q_3 Mass [Da]
Clethodim isomer 1.1	5.19	360.3	164.0
Clethodim isomer 1.2	5.19	360.3	268.1
Tebufenpyrad.1	5.26	334.2	145.0
Tebufenpyrad.2	5.26	334.2	117.1
Furathiocarb.1	5.27	383.2	195.1
Furathiocarb.2	5.27	383.2	252.0
Piperonyl butoxide.1	5.34	356.2	177.1
Piperonyl butoxide.2	5.34	356.2	119.2
Temephos.1	5.35	467.1	419.0
Temephos.2	5.35	467.1	404.9
Pyriproxyfen.1	5.39	322.1	96.0
Pyriproxyfen.2	5.39	322.1	184.9
Hexythiazox.1	5.40	353.2	228.0
Hexythiazox.2	5.40	353.2	168.1
Quinoxyfen.1	5.40	308.1	196.9
Quinoxyfen.2	5.40	308.1	161.9
Propargite.1	5.43	368.2	231.2
Propargite.2	5.43	368.2	175.1
Etoxazole.1	5.45	360.3	141.1
Etoxazole.2	5.45	360.3	57.0
Chlorfluazuron.1	5.48	540.0	383.0
Chlorfluazuron.2	5.49	540.0	158.0
Eprinomectin.1	5.52	914.5	185.9
Eprinomectin.2	5.52	914.5	154.0
Fenpyroximate.1	5.57	422.2	366.2
Fenpyroximate.2	5.57	422.2	134.9
Pyridaben.1	5.59	365.2	308.9
Pyridaben.2	5.59	365.2	147.2
Fenazaquin.1	5.67	307.0	161.0
Fenazaquin.2	5.67	307.0	147.0
Moxidectin.1	5.7	640.4	528.5
Moxidectin.2	5.7	640.4	498.5

Table 1: MRM transitions and retention times of pesticides. (.1 = first transition, .2 = second transition; Q_1 = Qualifier 1, Q_3 = Qualifier 3)

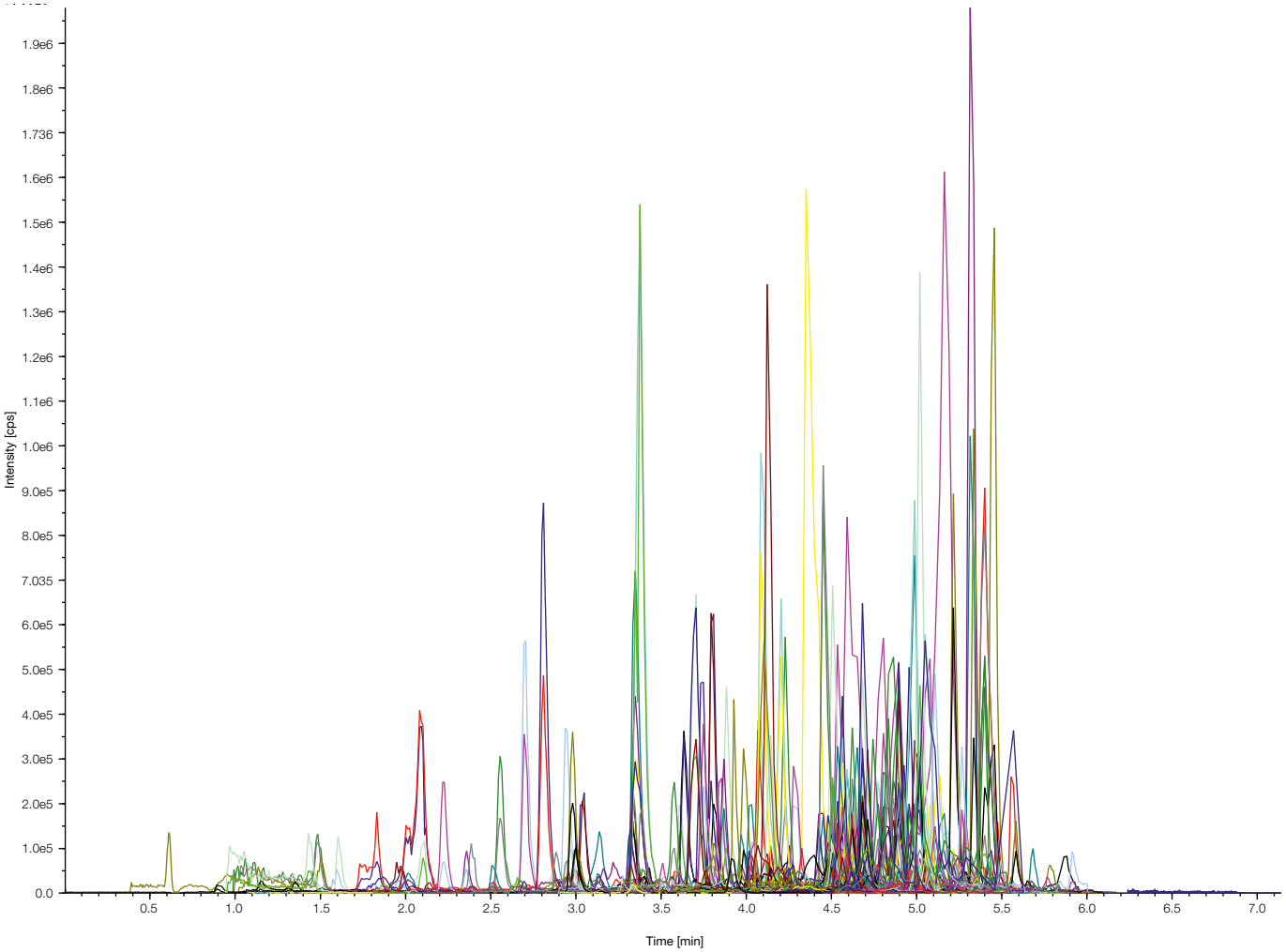

Figure 2: Separation of pesticides on NUCLEOSHELL® Bluebird RP 18 column (QuEChERS extract of Cannabis sativa spiked with β = 100 µg/g).

Pesticide residues in cannabis with high matrix reduction

Matrix reduction

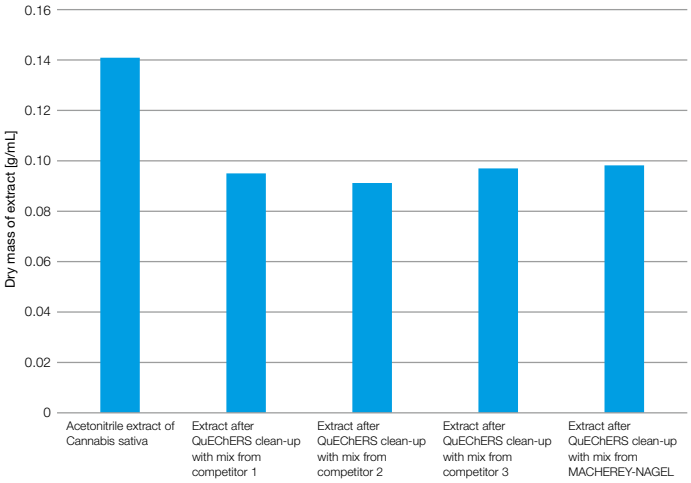

Figure 3: Comparison of drying residue of extracts before and after using clean-up.

Figure 4: Visible matrix reduction: cannabis extract, competitor 1, competitor 2, competitor 3, MACHEREY-NAGEL (from left to right).

Recovery rates

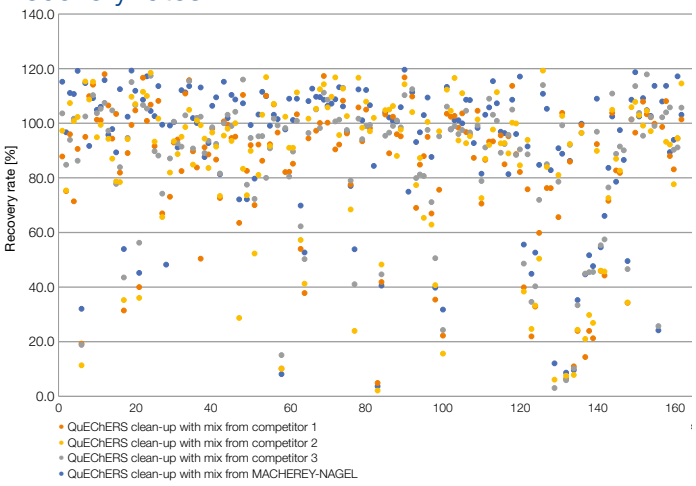

Figure 5: Comparison of recovery rates between MACHEREY-NAGEL and different competitors.

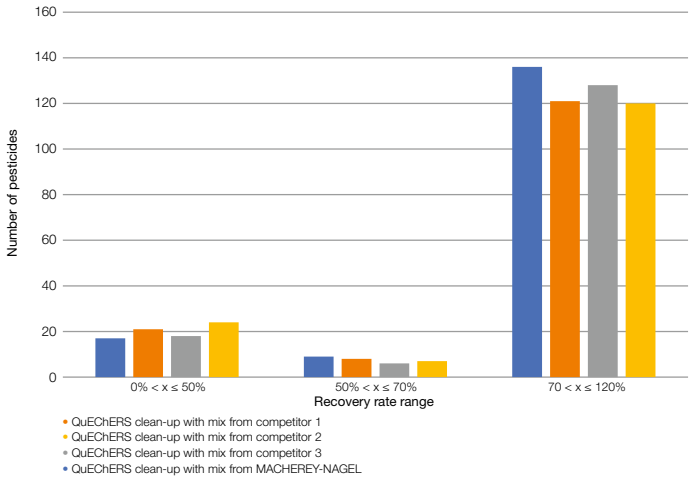

Figure 6: Comparison of distribution of recovery rates between MACHEREY-NAGEL and different competitors.

	QuEChERS clean-up mix from MACHEREY-NAGEL	QuEChERS clean-up mix from competitor 1	QuEChERS clean-up mix from competitor 2	QuEChERS clean-up mix from competitor 3
Analyte	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]
3-Hydroxycarbofuran	115.2 ± 7.8	87.8 ± 11.2	97.3 ± 5.8	103.6 ± 6.1
Acephate	96.7 ± 13.9	75.2 ± 13.1	75.4 ± 10.0	84.8 ± 21.8
Acetamiprid	111.1 ± 7.7	96.0 ± 3.6	107.4 ± 7.5	93.9 ± 6.5
Aldicarb sulfoxide	110.7 ± 8.3	71.4 ± 14.2	100.8 ± 14.1	101.7 ± 11.5
Aldicarb	119.2 ± 7.5	90.6 ± 6.9	102.3 ± 12.4	86.3 ± 9.1
Ametryn	32.1 ± 8.2	19.3 ± 5.3	11.3 ± 11.3	18.8 ± 15.5
Aminocarb	114.7 ± 10.0	95.0 ± 8.6	115.3 ± 14.8	102.5 ± 11.6
Amitraz	91.7 ± 11.2	109.9 ± 10.1	108.7 ± 14.1	out of specification*
Azoxystrobin	109.2 ± 9.8	114.1 ± 6.1	115.2 ± 6.2	110.3 ± 6.6
Benalaxyl	104.9 ± 10.7	101.3 ± 7.5	94.9 ± 7.2	103.7 ± 12.8
Benzoximate	106.0 ± 15.1	101.1 ± 10.1	99.4 ± 13.6	105.3 ± 15.7
Bifenazate	115.8 ± 11.6	118.0 ± 12.8	out of specification*	107.5 ± 13.5
Bitertanol	95.8 ± 18.4	106.5 ± 4.7	94.3 ± 10.2	97.3 ± 7.0
Boscalid	97.9 ± 15.0	94.4 ± 17.7	87.0 ± 17.8	104.7 ± 15.4
Bromucanozole isomer 1	89.3 ± 22.5	103.4 ± 3.2	78.7 ± 8.7	77.8 ± 20.9
Bromucanozole isomer 2	112.5 ± 22.3	81.9 ± 19.0	78.5 ± 13.9	83.9 ± 13.0

Pesticide residues in cannabis with high matrix reduction

	QuEChERS clean-up mix from MACHEREY-NAGEL	QuEChERS clean-up mix from competitor 1	QuEChERS clean-up mix from competitor 2	QuEChERS clean-up mix from competitor 3
Analyte	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]
Bupirimate	53.9 ± 6.3	31.4 ± 17.7	35.2 ± 2.6	43.5 ± 8.9
Buprofezin	102.4 ± 10.3	89.1 ± 11.1	94.2 ± 5.4	94.7 ± 7.4
Butafenacil	119.3 ± 9.2	99.4 ± 13.5	109.7 ± 2.6	115.1 ± 7.1
Butocarboxim	111.9 ± 5.7	104.7 ± 15.0	107.0 ± 8.1	106.7 ± 8.1
Butoxycarboxim	45.2 ± 15.1	40.0 ± 22.7	36.0 ± 10.4	56.2 ± 9.9
Carbaryl	108.6 ± 10.5	116.7 ± 17.2	111.5 ± 12.9	106.7 ± 10.9
Carbetamide	117.2 ± 5.4	100.9 ± 7.0	110.0 ± 5.2	105.4 ± 10.4
Carbofuran	104.5 ± 8.8	106.8 ± 11.1	118.5 ± 11.1	117.4 ± 6.0
Carboxin	102.6 ± 1.6	91.6 ± 3.4	93.3 ± 4.8	89.8 ± 8.4
Carfentrazone-ethyl	113.6 ± 11.2	108.2 ± 10.9	101.7 ± 3.2	88.2 ± 7.5
Chlorantraniliprole	99.5 ± 12.9	67.0 ± 13.7	65.6 ± 8.9	74.2 ± 13.9
Chlorfluazuron	48.2 ± 15.7	out of specification*	out of specification*	out of specification*
Chlorotoluron	99.2 ± 6.5	73.1 ± 8.1	81.9 ± 6.8	87.1 ± 3.1
Chloroxuron	100.4 ± 7.6	93.0 ± 7.2	93.4 ± 3.2	100.6 ± 12.8
Clethodim isomer 1	91.2 ± 19.0	94.0 ± 9.1	88.7 ± 13.7	92.6 ± 20.4
Clethodim isomer 2	112.1 ± 19.3	82.5 ± 10.3	95.1 ± 16.1	91.5 ± 14.5
Clothianidin	111.3 ± 15.1	110.9 ± 15.0	98.6 ± 7.8	102.9 ± 13.8
Cyazofamid	113.6 ± 10.1	115.8 ± 7.1	104.9 ± 12.7	115.4 ± 11.0
Cycluron	101.9 ± 8.0	89.7 ± 5.0	84.8 ± 9.9	90.8 ± 9.2
Cyproconazole isomer 1	100.1 ± 3.7	83.8 ± 14.0	101.0 ± 6.3	102.0 ± 3.2
Cyproconazole isomer 2	113.1 ± 9.3	50.4 ± 7.3	99.3 ± 9.1	102.4 ± 14.4
Desmedipham	87.6 ± 6.8	91.2 ± 2.5	94.4 ± 11.4	89.1 ± 9.1
Diclobutrazol	92.7 ± 10.6	88.6 ± 2.5	83.6 ± 12.4	93.6 ± 7.5
Dicrotophos-1	106.4 ± 5.3	98.1 ± 6.2	96.6 ± 7.7	98.5 ± 5.3
Diethofencarb	109.5 ± 19.1	86.7 ± 9.0	91.5 ± 15.7	92.4 ± 10.8
Difenoconazole isomer 1	81.3 ± 8.0	72.6 ± 9.1	73.4 ± 11.6	81.6 ± 7.9
Dimethoate	115.2 ± 9.5	100.7 ± 2.4	95.5 ± 8.7	100.0 ± 8.9
Dimethomorph isomer 1	101.9 ± 14.1	99.5 ± 8.4	98.0 ± 8.2	103.1 ± 9.9
Dimethomorph isomer 2	110.4 ± 6.1	94.6 ± 6.8	93.5 ± 2.5	99.0 ± 4.4
Dimoxystrobin	108.7 ± 15.1	95.1 ± 10.5	100.0 ± 6.9	104.2 ± 8.4
Diniconazole	72.1 ± 16.4	63.5 ± 18.0	28.7 ± 24.2	out of specification*
Dinotefuran	107.3 ± 14.9	110.4 ± 16.9	83.4 ± 22.3	116.0 ± 16.4
Diuron	72.2 ± 17.0	82.6 ± 18.9	73.6 ± 23.5	77.5 ± 16.4
Epoxiconazole	99.3 ± 11.8	92.0 ± 10.1	89.9 ± 9.9	94.6 ± 10.4
Eprinomectin	79.7 ± 24.0	70.0 ± 18.8	52.3 ± 23.1	72.3 ± 24.0
Etaconazole isomer 1	103.2 ± 14.1	92.2 ± 8.3	81.1 ± 9.5	95.2 ± 9.8
Ethiofencarb	111.5 ± 4.3	86.3 ± 5.2	103.1 ± 7.2	95.3 ± 2.4
Ethiprole	109.9 ± 13.5	110.1 ± 14.0	116.9 ± 6.9	80.0 ± 8.6
Etoxazole	99.1 ± 4.1	92.3 ± 4.5	91.7 ± 6.7	90.8 ± 12.6
Fenamidone	103.1 ± 7.2	106.9 ± 5.7	107.1 ± 5.9	101.7 ± 6.2
Fenarimol	101.5 ± 8.7	96.6 ± 9.0	out of specification*	99.2 ± 15.3
Fenazaquin	8.1 ± 22.2	10.2 ± 9.8	10.1 ± 19.0	15.1 ± 20.0
Fenbuconazole	97.8 ± 15.6	82.1 ± 19.6	102.4 ± 4.3	98.3 ± 11.7
Fenhexamid	109.0 ± 12.7	82.2 ± 12.5	91.0 ± 13.5	80.5 ± 8.0
Fenobucarb	101.2 ± 13.1	85.2 ± 18.2	91.0 ± 10.1	89.7 ± 11.0
Fenoxycarb	109.0 ± 6.3	103.3 ± 13.3	111.3 ± 6.8	100.9 ± 13.2
Fenpropimorph	69.9 ± 10.8	54.0 ± 8.7	57.2 ± 5.0	62.3 ± 8.2
Fenpyroximate	52.7 ± 4.6	37.8 ± 6.7	41.3 ± 13.5	50.3 ± 21.5

Pesticide residues in cannabis with high matrix reduction

	QuEChERS clean-up mix from MACHEREY-NAGEL	QuEChERS clean-up mix from competitor 1	QuEChERS clean-up mix from competitor 2	QuEChERS clean-up mix from competitor 3
Analyte	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]
Fenuron	108.1 ± 10.6	94.5 ± 7.0	101.7 ± 10.1	96.4 ± 11.5
Fipronil	112.7 ± 18.3	out of specification*	out of specification*	out of specification*
Flonicamid	109.7 ± 6.4	97.3 ± 6.0	105.3 ± 7.9	105.1 ± 4.2
Flubendiamide	109.6 ± 13.1	100.1 ± 7.1	112.5 ± 9.4	98.2 ± 12.8
Flufenacet	108.6 ± 2.0	117.3 ± 8.4	114.3 ± 5.1	111.2 ± 9.7
Fluometuron	106.4 ± 4.2	100.2 ± 12.0	105.8 ± 4.3	108.6 ± 7.6
Fluoxastrobin	107.2 ± 6.8	out of specification*	109.7 ± 8.5	out of specification*
Fluquinconazole	108.8 ± 18.0	90.4 ± 10.5	116.8 ± 20.4	100.7 ± 9.3
Flusilazole	113.2 ± 13.5	92.2 ± 12.5	95.7 ± 13.2	101.3 ± 9.2
Flutolanil	106.2 ± 9.9	108.3 ± 1.8	112.7 ± 7.1	113.0 ± 4.5
Flutriafol	96.8 ± 6.3	96.3 ± 2.7	102.6 ± 7.5	97.6 ± 6.8
Formetanate HCl	77.0 ± 5.1	77.5 ± 9.2	68.4 ± 8.9	79.0 ± 7.1
Fuberidazole	53.9 ± 17.9	out of specification*	24.0 ± 19.1	41.1 ± 10.3
Furalaxyl	112.4 ± 10.1	105.8 ± 6.5	116.7 ± 11.9	101.7 ± 7.2
Furathiocarb	101.1 ± 7.6	93.4 ± 6.1	98.4 ± 6.9	94.2 ± 15.8
Halofenozide	112.2 ± 16.9	105.0 ± 13.9	107.9 ± 14.9	99.0 ± 14.3
Hexaconazole	106.6 ± 14.2	98.2 ± 10.2	97.1 ± 15.2	99.4 ± 23.5
Hexythiazox	84.4 ± 13.0	out of specification*	102.0 ± 14.7	out of specification*
Hydramethylnon	3.7 ± 7.2	out of specification*	2.1 ± 5.3	out of specification*
Imazalil	40.5 ± 21.9	41.9 ± 19.1	48.3 ± 9.3	44.7 ± 16.7
Imidacloprid	104.0 ± 12.3	103.2 ± 10.1	104.8 ± 4.5	95.4 ± 9.0
Iprovalicarb isomer 1	102.1 ± 17.5	89.0 ± 16.6	105.0 ± 8.0	96.6 ± 5.1
Iprovalicarb isomer 2	100.8 ± 8.8	102.4 ± 5.4	106.3 ± 6.1	99.1 ± 5.7
Isoprocarb	100.7 ± 12.3	96.0 ± 23.6	88.0 ± 11.9	101.0 ± 14.5
Isoproturon	105.9 ± 4.6	95.2 ± 5.3	97.7 ± 4.5	98.5 ± 9.1
Linuron	119.6 ± 10.8	116.8 ± 15.5	114.3 ± 7.2	110.3 ± 14.5
Lufenuron	74.9 ± 15.5	out of specification*	out of specification*	out of specification*
Mandipropamid	111.4 ± 11.8	109.8 ± 9.8	104.1 ± 9.4	112.5 ± 9.1
Mefenacet	93.1 ± 9.1	69.0 ± 8.5	77.4 ± 14.4	79.9 ± 11.4
Mepronil	96.7 ± 8.5	84.8 ± 15.6	87.3 ± 9.1	81.2 ± 14.5
Mesotrione	103.0 ± 8.1	88.0 ± 5.9	65.4 ± 8.9	80.7 ± 3.6
Metalaxyl	109.4 ± 5.2	95.0 ± 7.6	100.5 ± 5.4	97.6 ± 5.0
Metconazole	87.7 ± 9.8	67.0 ± 16.4	62.9 ± 6.0	71.1 ± 8.1
Methabenzthiazuron	39.8 ± 8.6	35.4 ± 11.5	40.7 ± 6.9	50.6 ± 3.9
Methiocarb	110.7 ± 12.0	103.5 ± 7.3	100.6 ± 7.3	100.5 ± 1.8
Methoprotryne	31.8 ± 7.1	22.3 ± 6.1	15.7 ± 12.5	24.3 ± 7.2
Methoxyfenozide	113.3 ± 11.4	103.5 ± 3.7	112.3 ± 9.6	106.1 ± 8.7
Metobromuron	97.8 ± 8.6	102.4 ± 11.1	104.6 ± 6.7	97.8 ± 9.8
Metribuzin	101.1 ± 9.2	102.7 ± 8.0	116.6 ± 14.9	98.9 ± 9.2
Mevinphos isomer 1	101.1 ± 6.6	98.4 ± 22.1	93.7 ± 11.4	96.1 ± 13.6
Mexacarbate	100.0 ± 6.5	103.6 ± 10.1	111.0 ± 7.7	97.5 ± 5.7
Monocrotophos	108.6 ± 11.4	96.8 ± 9.8	92.7 ± 9.1	104.6 ± 11.6
Monolinuron	108.5 ± 5.9	96.0 ± 6.9	95.3 ± 8.3	96.7 ± 9.6
Moxidectin	92.7 ± 15.5	87.3 ± 23.9	out of specification*	out of specification*
Myclobutanil	98.3 ± 5.9	104.6 ± 5.9	101.4 ± 8.7	99.2 ± 9.8
Neburon	81.5 ± 10.0	70.6 ± 16.3	72.6 ± 3.6	78.8 ± 14.1
Nitenpyram	103.1 ± 18.3	86.6 ± 6.2	87.0 ± 16.2	91.1 ± 11.3
Nuarimol	105.8 ± 16.1	93.3 ± 7.5	92.1 ± 7.5	109.0 ± 15.4

Pesticide residues in cannabis with high matrix reduction

	QuEChERS clean-up mix from MACHEREY-NAGEL	QuEChERS clean-up mix from competitor 1	QuEChERS clean-up mix from competitor 2	QuEChERS clean-up mix from competitor 3
Analyte	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]
Omethoate	115.4 ± 12.7	93.4 ± 11.2	97.7 ± 16.2	103.1 ± 15.6
Paclobutrazol	96.9 ± 3.8	95.6 ± 3.2	92.7 ± 6.1	89.2 ± 4.7
Penconazole	96.4 ± 6.3	85.0 ± 9.1	92.7 ± 3.9	92.4 ± 5.7
Phenmedipham	81.4 ± 13.6	95.2 ± 13.7	89.0 ± 9.6	95.8 ± 10.1
Picoxystrobin	108.6 ± 6.1	113.7 ± 4.8	100.2 ± 4.8	105.0 ± 15.7
Piperonyl butoxide	96.1 ± 8.5	88.7 ± 8.9	99.9 ± 6.6	88.4 ± 9.7
Pirimicarb	117.1 ± 9.6	82.2 ± 5.6	84.6 ± 7.4	90.4 ± 6.1
Prochloraz	55.6 ± 10.2	39.9 ± 9.6	38.3 ± 8.7	48.6 ± 12.5
Promecarb	91.5 ± 16.5	75.8 ± 11.8	93.9 ± 13.2	88.6 ± 6.6
Prometon	44.9 ± 9.8	22.0 ± 10.5	24.7 ± 7.5	34.6 ± 9.2
Prometryne	52.6 ± 6.4	32.9 ± 6.2	33.2 ± 2.8	40.3 ± 5.1
Propamocarb	84.8 ± 7.1	59.8 ± 19.5	50.4 ± 6.6	71.9 ± 17.8
Propargite	110.8 ± 22.0	out of specification*	119.3 ± 13.9	114.0 ± 13.1
Propiconazole isomer 1	105.3 ± 17.6	76.3 ± 16.4	84.0 ± 14.4	85.0 ± 6.3
Prothioconazole	82.8 ± 15.1	76.3 ± 18.3	out of specification*	out of specification*
Pymetrozine	12.1 ± 10.7	out of specification*	6.1 ± 8.3	3.1 ± 24.6
Pyraclostrobin	90.9 ± 10.8	65.6 ± 10.1	81.0 ± 9.9	78.6 ± 6.7
Pyridaben	88.8 ± 11.1	103.8 ± 9.7	102.7 ± 16.0	99.3 ± 20.3
Pyrimethanil	8.7 ± 17.9	6.4 ± 10.6	7.5 ± 7.0	5.9 ± 15.0
Pyriproxyfen	86.2 ± 11.1	86.0 ± 7.6	92.4 ± 3.7	92.1 ± 6.6
Quinoxyfen	9.6 ± 7.3	11.0 ± 3.6	7.8 ± 10.0	10.2 ± 15.0
Secbumeton	35.2 ± 14.3	23.9 ± 6.2	24.4 ± 13.8	33.4 ± 9.9
Siduron	99.9 ± 8.4	99.3 ± 6.1	96.5 ± 3.5	96.5 ± 6.5
Spinetoram	44.7 ± 12.8	14.4 ± 13.7	21.0 ± 20.9	45.0 ± 16.7
Spinosad (Spinosyn A)	51.7 ± 14.0	23.9 ± 10.0	29.8 ± 18.8	45.5 ± 10.6
Spinosad (Spinosyn D)	47.7 ± 14.1	21.3 ± 12.3	26.9 ± 11.3	45.5 ± 6.1
Spirotetramat	109.0 ± 8.5	92.4 ± 9.1	89.9 ± 12.1	96.9 ± 10.8
Spiroxamine isomer 1	54.6 ± 22.5	46.0 ± 13.1	46.0 ± 4.2	55.3 ± 11.3
Spiroxamine isomer 2	66.1 ± 3.6	44.3 ± 8.5	45.7 ± 3.7	57.5 ± 10.6
Tebuconazole	83.7 ± 8.8	71.6 ± 6.6	72.6 ± 10.0	76.5 ± 11.8
Tebufenozide	102.5 ± 7.7	103.8 ± 12.7	104.9 ± 5.3	110.9 ± 8.6
Tebufenpyrad	78.6 ± 9.1	82.7 ± 11.4	87.0 ± 9.4	88.8 ± 7.7
Tebuthiuron	97.5 ± 5.8	81.8 ± 9.0	82.6 ± 6.8	91.5 ± 9.2
Temephos	86.6 ± 21.3	out of specification*	out of specification*	90.1 ± 20.9
Terbutryn	49.5 ± 4.9	34.2 ± 4.5	34.4 ± 2.1	46.6 ± 3.6
Tetraconazole	108.6 ± 16.0	101.4 ± 7.7	105.9 ± 11.0	101.4 ± 5.8
Thiamethoxam	118.7 ± 9.2	96.6 ± 4.7	107.8 ± 10.9	113.6 ± 6.1
Thiobencarb	102.5 ± 10.6	out of specification*	102.9 ± 10.4	103.8 ± 17.1
Thiophanate-methyl	109.2 ± 8.0	107.9 ± 9.8	99.1 ± 8.5	95.4 ± 13.8
Triadimefon	104.8 ± 9.2	103.3 ± 9.4	104.6 ± 4.6	117.9 ± 9.3
Triadimenol	102.7 ± 7.4	102.2 ± 4.0	97.1 ± 8.6	102.3 ± 3.0
Trichlorfon	113.7 ± 17.4	99.9 ± 21.6	out of specification*	99.1 ± 5.8
Tricyclazole	24.2 ± 15.7	out of specification*	out of specification*	25.7 ± 18.1
Trifloxystrobin	108.0 ± 17.4	98.7 ± 5.8	out of specification*	102.2 ± 10.7
Triflumizole	113.7 ± 10.1	108.1 ± 14.3	93.2 ± 6.5	104.0 ± 12.0
Triflumuron	89.4 ± 11.6	88.0 ± 17.0	92.2 ± 7.6	105.8 ± 9.5
Triticonazole	93.9 ± 7.6	83.1 ± 5.9	77.7 ± 6.2	90.3 ± 10.1
Vamidothion	117.2 ± 14.0	94.4 ± 11.5	94.6 ± 13.4	91.1 ± 4.5
Zoxamide	103.1 ± 12.1	101.4 ± 6.3	114.6 ± 10.4	105.7 ± 7.0

Table 2: Recovery rates for presented QuEChERS clean-up mixes. The recovery rates that are calculated by matrix matched standard calibration. *specification = 0 – 120 % ± 25 %

Pesticide residues in cannabis with high matrix reduction

Conclusion

This application note shows the reliable and successful determination of pesticide residues from marijuana samples with an optimized QuEChERS method. The optimized composition of QuEChERS salt clean-up mixes leads to high reduction of matrix components and to high recovery rates for pesticides. The presented QuEChERS method leads to an average recovery rate for pesticides of 92.3 % for 162 pesticides. Most of the pesticides (138 analytes) show recovery rates between 70 % to 120 %. On the other side, high matrix reduction yields were also possible by using the presented clean-up mix. The amount of dry substance after clean-up is reduced to less than 70 % of raw acetonitrile extracts. With this clean-up approach interfering substances (like e.g., lipids and pigments) are successfully removed due to high amounts of GCB and CHROMABOND® C_{18} ec adsorbents.

The chromatographic separation of pesticides was performed by using core-shell particles that are well known for fast and high-efficient separations combined with a reasonably low back pressure. In this work, a subsequent analytics was developed on a NUCLEOSHELL® Bluebird RP 18 column.

References

[1] R. L. Pacula, R. Smart, Annu. Rev. Clin. Psychol. 2017 May 8, 13: 397–419.

[2] M. Anastassiades, S. J. Lehotay, D. Stajnbaher, F. J. Schenck, J. AOAC Int. 86 (2003), 412–431.

Product information

The following MACHEREY-NAGEL products have been used in this application note:

REF 763432.46, EC 50/4.6 NUCLEOSHELL® Bluebird RP 18, 2.7 µm

REF 730970, CHROMABOND® QuEChERS extraction mix I

REF 730845, CHROMABOND® QuEChERS clean-up mix XLVII

REF 730223, CHROMABOND® centrifuge tubes with screw cap, 50 mL

REF 702293, Screw neck vials N 9, 1.5 mL

REF 702107, N 9 PP Screw cap, yellow, center hole, silicone white / PTFE red