MACHEREY-NAGEL
Chromatography application note

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Determination of pesticide residues in Cannabis sativa using an optimized QuEChERS method with a low amount of carbon in the clean-up mix

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Abstract

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

Introduction

There is an increasing interest in the determination of pesticide residues in marijuana. 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 drinkable or edible forms) have grown year by year in North America and also in other countries [1]. To saturate the huge demand for marijuana the cultivation of hemp gets professional to improve growth yields. The use of pesticides is a common tool for this monocultural plant production.

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 removed by optimized clean-up mixes. On the other side, the composition of the clean-up mix has to ensure high recovery rates for pesticides, as well as adequate matrix removal properties. Therefor the respective mix needs to contain a sufficient amount of carbon adsorbent.

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 for clean-up from competitors

Competitor 1:

QuEChERS dispersive kit, 15 mL centrifuge tube, 1200 mg $MgSO_4$, 400 mg PSA, 400 mg C_{18} ec, 45 mg GCB

Competitor 2:

QuEChERS SPE Q-sep, 15 mL centrifuge tube, 900 mg $MgSO_4$, 300 mg PSA, 300 mg C_{18}, 45 mg GCB

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 XLIX (REF 7300000)
- 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
Flow rate:	0.7 mL/min
Temperature:	30 °C
Injection volume:	2 µL

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Pesticide residues in cannabis with a low amount of carbon

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]
Cyromazine.1	0.88	167.1	85.1
Cyromazine.2	0.88	167.1	125.1
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
Carbendazim.1	1.98	192.1	160.1
Carbendazim.2	1.98	192.1	132.1
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
Aldicarb sulfone.1	2.10	240.0	86.0
Aldicarb sulfone.2	2.10	240.0	148.0
Oxamyl.1	2.22	237.2	90.0
Oxamyl.2	2.22	237.2	72.1
Flonicamid.1	2.36	230.2	203.1
Flonicamid.2	2.36	230.2	174.0
Methomyl.1	2.39	163.1	106.0
Methomyl.2	2.39	163.1	88.1
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
Ethirimol.1	2.68	210.2	140.2
Ethirimol.2	2.68	210.2	98.1
Dicrotophos.1	2.70	238.1	112.1
Dicrotophos.2	2.70	238.1	193.0
Pirimicarb.1	2.75	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
Cymoxanil.1	3.17	199.2	128.1
Cymoxanil.2	3.17	199.2	111.0
Simetryn.1	3.27	214.2	124.2
Simetryn.2	3.27	214.2	144.1
Prometon.1	3.31	226.2	142.1
Prometon.2	3.31	226.2	86.0
Terbumeton.1	3.32	226.2	170.0
Terbumeton.2	3.32	226.2	100.0
Secbumeton.1	3.33	226.2	170.0
Secbumeton.2	3.33	226.2	100.0
Mevinphos isomer 2.1	3.34	225.1	127.0
Mevinphos isomer 2.2	3.34	225.1	192.9
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
Imazalil.1	3.40	297.1	201.0
Imazalil.2	3.40	297.1	159.0
Thiacloprid.1	3.40	253.1	126.0
Thiacloprid.2	3.40	253.1	99.1
Butocarboxim.1	3.43	213.0	75.0
Butocarboxim.2	3.43	213.0	116.0
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
Oxadixyl.1	3.58	279.1	219.1
Oxadixyl.2	3.58	279.1	132.1
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

Pesticide residues in cannabis with a low amount of carbon

Analyte	RT [min]	Q_1 Mass [Da]	Q_3 Mass [Da]
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
Propoxur.1	3.76	210.1	168.1
Propoxur.2	3.76	210.1	111.0
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
Bendiocarb.1	3.83	224.1	167.1
Bendiocarb.2	3.83	224.1	109.0
Thidiazuron.1	3.84	221.1	102.1
Thidiazuron.2	3.84	221.1	127.9
Sulfentrazone.1	3.85	387.0	307.0
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
Terbutryn.1	4.02	242.2	186.0
Terbutryn.2	4.00	242.2	68.1
Pyrimethanil.1	4.02	200.2	107.0
Pyrimethanil.2	4.02	200.2	82.2
Ethiofencarb.1	4.04	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	4.15	302.2	123.0
Chlorotoluron.1	4.15	213.1	72.2
Chlorotoluron.2	4.15	213.1	46.0
Propham.1	4.15	180.1	138.1
Propham.2	4.16	180.1	120.1
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

Analyte	RT [min]	Q_1 Mass [Da]	Q_3 Mass [Da]
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
Forchlorfenuron.1	4.29	248.1	129.0
Forchlorfenuron.2	4.29	248.1	93.0
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
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
Cyprodinil.1	4.49	226.2	93.0
Cyprodinil.2	4.49	226.2	76.9
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
Dimethomorph isomer 1.1	4.55	388.2	300.9
Dimethomorph isomer 1.2	4.55	388.2	164.9
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

Pesticide residues in cannabis with a low amount of carbon

Analyte	RT [min]	Q_1 Mass [Da]	Q_3 Mass [Da]
Carfentrazone-ethyl.1	4.56	412.0	328.0
Carfentrazone-ethyl.2	4.56	412.0	356.0
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 2.1	4.61	388.2	300.9
Dimethomorph isomer 2.2	4.61	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
Cyproconazole isomer 1.2	4.66	292.2	125.1
Emamectin-benzoate B_1a.1	4.66	886.5	158.2
Emamectin-benzoate B_1a.2	4.66	886.5	82.2
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	4.68	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
Spirotetramat.1	4.71	374.2	330.2
Spirotetramat.2	4.71	374.2	302.2
Acibenzolar-S-methyl.1	4.72	211.1	136.1
Acibenzolar-S-methyl.2	4.72	211.1	91.0
Chloroxuron.1	4.72	291.1	72.1
Chloroxuron.2	4.72	291.1	218.1
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
Fluoxastrobin.1	4.76	459.1	427.0
Fluoxastrobin.2	4.76	459.1	188.1

Analyte	RT [min]	Q_1 Mass [Da]	Q_3 Mass [Da]
Fenarimol.1	4.77	331.0	268.0
Fenarimol.2	4.77	331.0	81.0
Fipronil.1	4.78	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	4.79	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
Diflubenzuron.1	4.85	311.2	158.2
Diflubenzuron.2	4.85	311.2	141.1
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
Kresoxim-methyl.1	4.96	314.2	116.1
Kresoxim-methyl.2	4.96	314.2	131.1
Famoxadone.1	4.97	392.0	331.0
Famoxadone.2	4.97	392.0	238.0
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
Metconazole.1	4.99	320.2	70.1
Metconazole.2	4.99	320.2	125.1

Pesticide residues in cannabis with a low amount of carbon

Analyte	RT [min]	Q_1 Mass [Da]	Q_3 Mass [Da]
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	5.10	326.3	70.0
Indoxacarb.1	5.10	528.3	202.9
Thiobencarb.1	5.10	258.3	125.0
Thiobencarb.2	5.10	258.3	89.1
Indoxacarb.2	5.11	528.3	218.0
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
Ipconazole isomer 2.1	5.14	334.5	70.0
Ipconazole isomer 2.2	5.14	334.5	125.1
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
Clofentezine.1	5.17	303.2	138.1
Clofentezine.2	5.17	303.2	102.1
Clethodim isomer 1.1	5.19	360.3	164.0
Clethodim isomer 1.2	5.19	360.3	268.1
Metaflumizone.1	5.22	507.3	177.9
Metaflumizone.2	5.22	507.3	287.1
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
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
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	5.48	540.0	158.0
Fenpyroximate.1	5.57	422.2	366.2
Fenpyroximate.2	5.57	422.2	134.9

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

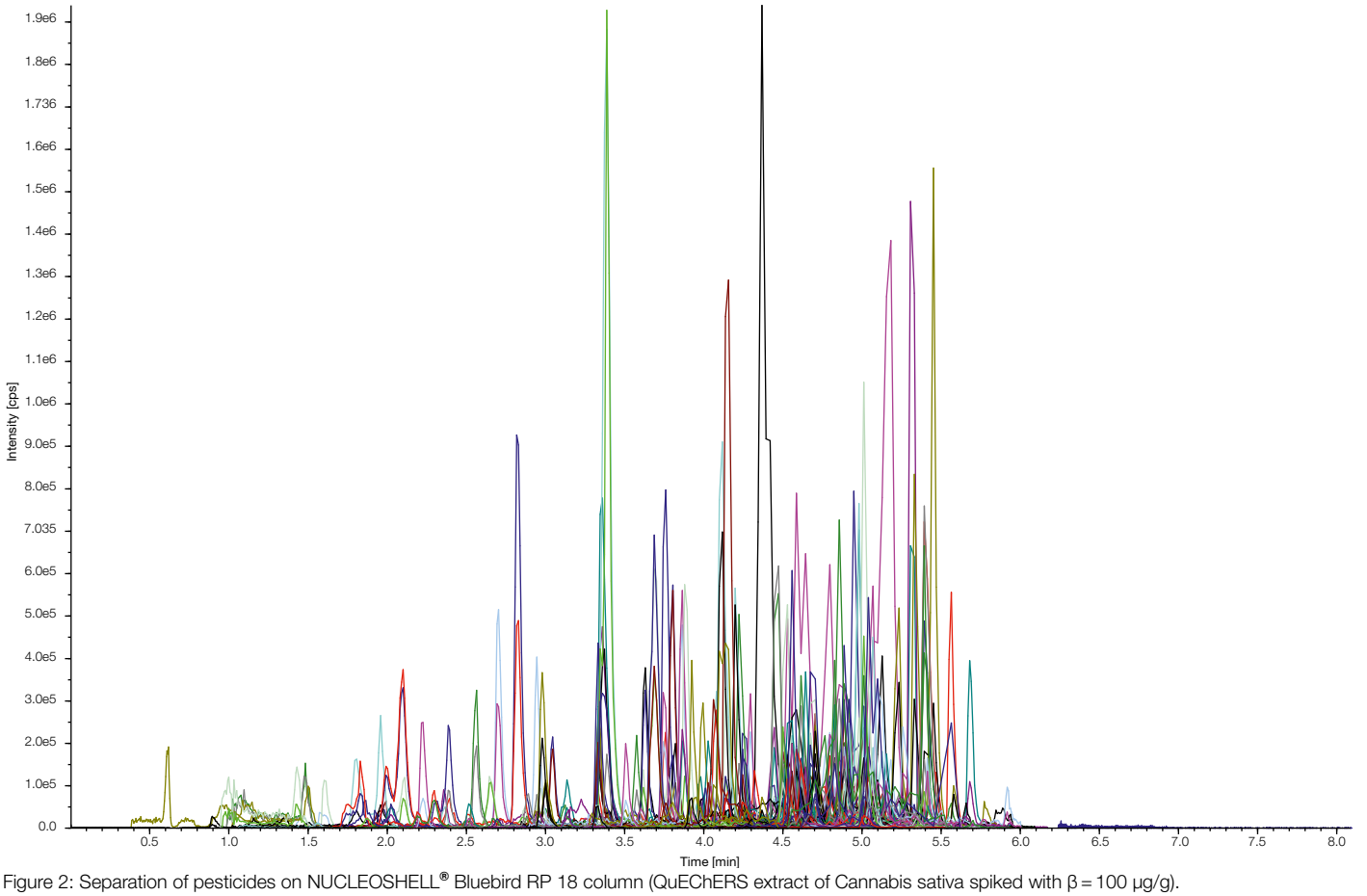

Figure 2: Separation of pesticides on NUCLEOSHELL® Bluebird RP 18 column (QuEChERS extract of Cannabis sativa spiked with β = 100 µg/g).

Pesticide residues in cannabis with a low amount of carbon

Matrix reduction

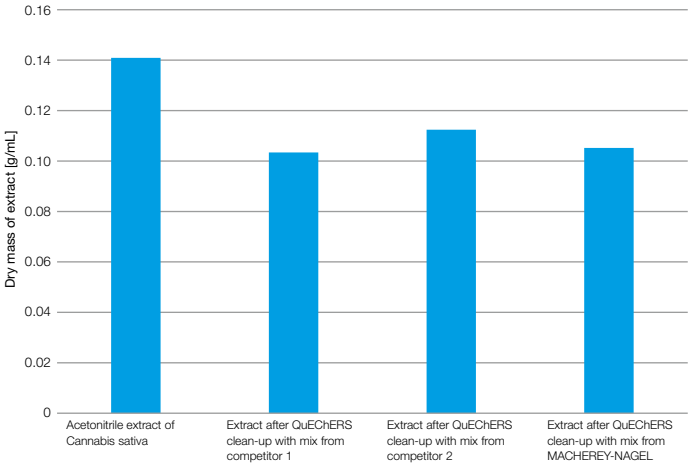

Figure 3: Comparison of drying residue of extracts before and after using clean-up.

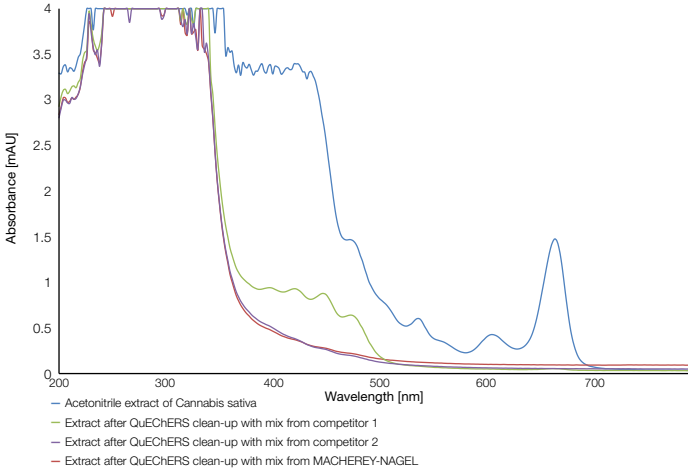

Figure 4: Comparison of spectra of extracts before and after using clean-up.

Recovery rates

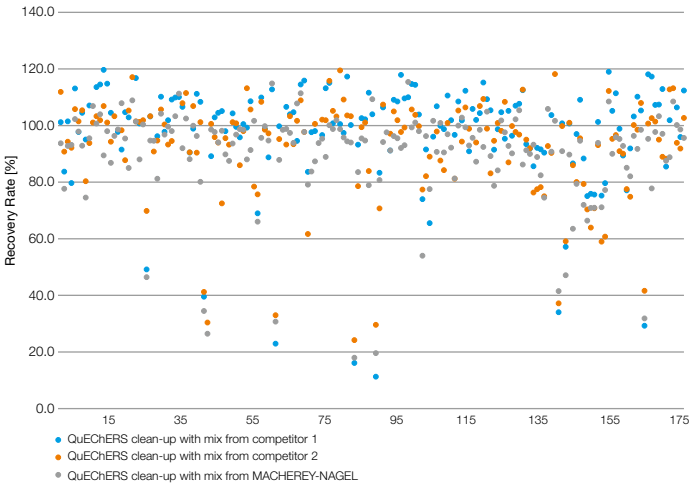

Figure 5: Comparison of recovery rates between MACHEREY-NAGEL and different competitors.

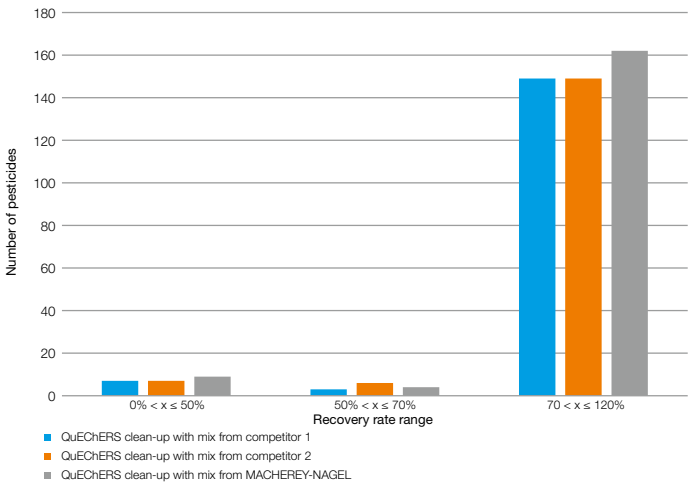

Figure 6: Comparison of distribution of recovery rates between MACHEREY-NAGEL and different competitors.

	QuEChERS clean-up mix from MN	QuEChERS clean-up mix from comp. 1	QuEChERS clean-up mix from comp. 2
Analyte	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]
3-Hydroxycarbofuran	93.7 ± 15.0	101.2 ± 12.8	111.9 ± 20.3
Acephate	77.7 ± 14.3	83.7 ± 11.8	90.8 ± 17.4
Acetamiprid	92.8 ± 3.8	101.5 ± 6.7	94.3 ± 10.0
Acibenzolar-S-methyl	93.2 ± 24.7	79.7 ± 21.0	92.2 ± 17.6
Aldicarb sulfone	102.3 ± 10.3	113.1 ± 10.7	105.8 ± 16.5
Aldicarb sulfoxide	97.9 ± 8.0	97.8 ± 15.9	101.5 ± 15.2
Aldicarb	92.9 ± 8.4	104.5 ± 6.8	105.4 ± 17.5
Ametryn	74.6 ± 14.3	95.1 ± 9.4	80.4 ± 5.1
Aminocarb	95.5 ± 12.9	107.1 ± 6.5	93.8 ± 6.5
Amitraz	106.9 ± 18.6	out of specification*	101.1 ± 16.4
Azoxystrobin	100.7 ± 4.8	113.6 ± 7.3	103.3 ± 4.0
Benalaxyl	104.0 ± 6.3	114.5 ± 9.9	101.9 ± 8.2
Bendiocarb	89.5 ± 11.2	119.7 ± 10.7	106.9 ± 13.1
Benzoximate	98.0 ± 13.6	114.8 ± 21.0	101.1 ± 13.8
Bifenazate	86.8 ± 11.8	104.5 ± 13.6	94.3 ± 8.9
Bitertanol	96.4 ± 4.1	out of specification*	103.3 ± 9.7
Boscalid	98.6 ± 17.6	97.8 ± 17.5	out of specification*
Bromucanozole isomer 1	107.9 ± 12.4	91.5 ± 8.3	98.4 ± 16.3

Pesticide residues in cannabis with a low amount of carbon

	QuEChERS clean-up mix from MN	QuEChERS clean-up mix from comp. 1	QuEChERS clean-up mix from comp. 2
Analyte	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]
Bupirimate	95.4 ± 8.3	104.7 ± 8.2	87.8 ± 8.3
Buprofezin	85.0 ± 1.0	102.9 ± 10.7	105.3 ± 10.6
Butafenacil	108.9 ± 10.0	out of specification*	117.1 ± 8.9
Butocarboxim	101.4 ± 9.4	116.8 ± 12.7	101.5 ± 15.0
Butoxycarboxim	88.1 ± 7.3	100.7 ± 17.8	101.3 ± 14.8
Carbaryl	100.4 ± 10.9	out of specification*	101.9 ± 12.0
Carbendazim	46.4 ± 21.4	49.2 ± 16.6	69.8 ± 13.0
Carbetamide	94.7 ± 6.0	103.2 ± 4.1	103.3 ± 3.2
Carbofuran	94.6 ± 7.4	out of specification*	90.8 ± 8.7
Carboxin	81.2 ± 6.1	96.2 ± 8.5	94.7 ± 7.9
Carfentrazone-ethyl	104.2 ± 4.5	110.2 ± 4.1	105.7 ± 12.4
Chlorantraniliprole	96.8 ± 6.9	97.8 ± 12.2	100.4 ± 16.2
Chlorotoluron	99.6 ± 7.2	101.9 ± 10.5	93.3 ± 10.8
Chloroxuron	98.0 ± 7.2	109.2 ± 10.0	94.6 ± 4.5
Clethodim isomer 1	103.3 ± 13.8	109.9 ± 23.2	out of specification*
Clofentezine	111.3 ± 14.1	110.1 ± 9.2	out of specification*
Clothianidin	92.0 ± 13.2	106.6 ± 11.2	107.9 ± 6.7
Cyazofamid	102.5 ± 9.9	out of specification*	111.5 ± 9.3
Cycluron	88.1 ± 11.9	90.5 ± 5.3	90.5 ± 8.6
Cymoxanil	100.0 ± 15.5	98.9 ± 24.4	106.9 ± 23.3
Cyproconazole isomer 1	96.3 ± 7.0	111.2 ± 8.4	90.4 ± 10.9
Cyproconazole isomer 2	80.1 ± 8.0	108.4 ± 22.8	101.2 ± 10.1
Cyprodinil	34.5 ± 7.6	39.5 ± 4.5	41.2 ± 18.7
Cyromazine	26.5 ± 11.0	out of specification*	30.4 ± 20.1
Desmedipham	98.6 ± 22.5	89.2 ± 11.5	100.6 ± 21.6
Diclobutrazol	97.7 ± 7.0	102.9 ± 7.1	95.9 ± 10.0
Dicrotophos-1	94.1 ± 9.0	104.5 ± 12.5	94.0 ± 11.1
Diethofencarb	98.2 ± 7.4	105.1 ± 12.0	72.5 ± 9.0
Difenoconazole isomer 1	89.8 ± 7.8	98.0 ± 3.5	95.6 ± 7.7
Diflubenzuron	87.5 ± 24.7	out of specification*	93.3 ± 18.7
Dimethoate	93.7 ± 12.8	104.3 ± 6.4	101.2 ± 10.9
Dimethomorph isomer 1	96.8 ± 8.0	99.6 ± 4.8	100.8 ± 15.7
Dimethomorph isomer 2	98.7 ± 9.6	95.8 ± 5.6	86.0 ± 8.3
Dimoxystrobin	98.5 ± 4.0	100.5 ± 9.3	98.1 ± 9.8
Diniconazole	88.0 ± 19.6	99.3 ± 12.1	113.2 ± 19.8
Dinotefuran	91.4 ± 8.5	108.6 ± 8.7	105.7 ± 12.2
Diuron	101.7 ± 16.4	out of specification*	78.4 ± 19.1
Emamectin-benzoate B_1a	66.0 ± 15.9	69.0 ± 10.4	75.7 ± 6.4
Epoxiconazole	95.7 ± 8.0	109.9 ± 8.7	108.4 ± 10.2
Etaconazole isomer 1	99.8 ± 8.6	98.9 ± 5.7	98.5 ± 6.8
Ethiofencarb	94.7 ± 6.6	88.8 ± 2.0	97.2 ± 3.0
Ethiprole	114.9 ± 15.0	112.8 ± 6.7	out of specification*
Ethirimol	30.7 ± 11.5	23.0 ± 11.9	33.0 ± 12.4
Etoxazole	87.9 ± 14.0	99.7 ± 9.9	95.2 ± 15.6
Famoxadone	98.5 ± 20.5	out of specification*	out of specification*
Fenamidone	98.8 ± 5.1	106.6 ± 7.6	93.3 ± 5.9
Fenarimol	97.4 ± 4.9	104.0 ± 13.9	103.3 ± 12.1
Fenbuconazole	93.9 ± 16.0	104.7 ± 18.1	93.4 ± 11.7
Fenhexamid	107.8 ± 9.6	94.6 ± 16.1	101.7 ± 19.2
Fenobucarb	111.4 ± 18.2	114.5 ± 22.0	108.9 ± 21.2
Fenoxycarb	97.8 ± 11.2	115.9 ± 8.1	97.7 ± 10.2

Pesticide residues in cannabis with a low amount of carbon

	QuEChERS clean-up mix from MN	QuEChERS clean-up mix from comp. 1	QuEChERS clean-up mix from comp. 2
Analyte	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]
Fenpropimorph	79.1 ± 7.5	83.7 ± 6.3	61.7 ± 9.9
Fenpyroximate	83.8 ± 21.5	97.7 ± 18.0	out of specification*
Fenuron	87.4 ± 5.7	98.1 ± 12.8	100.6 ± 17.2
Fipronil	93.8 ± 22.2	out of specification*	out of specification*
Flonicamid	95.4 ± 8.9	96.7 ± 8.8	102.1 ± 10.9
Flubendiamide	89.0 ± 8.4	113.2 ± 13.9	101.9 ± 7.0
Flufenacet	100.1 ± 7.7	115.1 ± 8.5	115.8 ± 10.0
Fluometuron	98.8 ± 6.7	100.8 ± 10.6	105.2 ± 14.2
Fluoxastrobin	101.9 ± 8.6	out of specification*	103.2 ± 8.0
Fluquinconazole	98.7 ± 14.0	100.5 ± 19.5	119.5 ± 9.0
Flusilazole	95.8 ± 10.5	97.4 ± 11.9	109.2 ± 8.5
Flutolanil	94.4 ± 4.8	117.3 ± 6.0	103.6 ± 5.5
Flutriafol	94.0 ± 3.9	100.2 ± 4.4	103.3 ± 6.8
Forchlorfenuron	18.0 ± 12.9	16.1 ± 8.5	24.2 ± 10.2
Formetanate HCl	83.6 ± 10.3	93.3 ± 11.3	78.6 ± 6.5
Furalaxyl	95.5 ± 4.2	102.6 ± 8.2	99.4 ± 10.1
Furathiocarb	94.7 ± 4.8	102.2 ± 9.4	101.1 ± 19.5
Hexaconazole	78.9 ± 22.3	111.6 ± 9.8	83.9 ± 14.2
Hexythiazox	109.3 ± 23.4	104.0 ± 17.9	out of specification*
Hydramethylnon	19.6 ± 9.2	11.3 ± 7.2	29.6 ± 5.5
Imazalil	80.8 ± 8.2	83.3 ± 4.1	70.7 ± 14.6
Imidacloprid	94.2 ± 10.7	106.4 ± 11.6	107.4 ± 7.5
Indoxacarb	97.6 ± 12.8	out of specification*	out of specification*
Ipconazole isomer 2	91.2 ± 16.3	91.2 ± 17.4	97.1 ± 8.3
Iprovalicarb isomer 1	96.3 ± 21.5	109.1 ± 12.0	105.0 ± 13.8
Iprovalicarb isomer 2	95.5 ± 5.3	108.5 ± 7.2	101.9 ± 9.0
Isoprocarb	92.1 ± 10.1	117.9 ± 13.1	97.7 ± 17.5
Isoproturon	93.1 ± 6.1	109.6 ± 10.9	99.3 ± 8.1
Kresoxim-methyl	115.4 ± 15.8	110.0 ± 13.5	out of specification*
Linuron	99.3 ± 8.6	114.7 ± 17.9	105.7 ± 7.6
Mandipropamid	101.1 ± 14.0	114.4 ± 8.3	103.8 ± 13.6
Mefenacet	98.0 ± 15.4	103.9 ± 12.9	99.8 ± 8.4
Mepanipyrim	54.0 ± 8.3	74.0 ± 13.8	77.4 ± 6.5
Mepronil	96.3 ± 3.6	91.6 ± 8.2	82.1 ± 14.4
Mesotrione	77.6 ± 13.3	65.5 ± 10.1	89.0 ± 3.5
Metaflumizone	101.7 ± 19.3	96.1 ± 18.8	out of specification*
Metalaxyl	90.7 ± 2.9	106.8 ± 3.3	97.9 ± 4.1
Metconazole	100.9 ± 9.7	99.9 ± 8.6	87.7 ± 4.9
Methabenzthiazuron	90.5 ± 6.7	98.7 ± 5.7	84.3 ± 11.4
Methiocarb	96.9 ± 2.8	110.6 ± 10.9	100.9 ± 8.2
Methomyl	92.2 ± 3.6	101.9 ± 17.9	out of specification*
Methoprotryne	81.3 ± 10.9	96.7 ± 9.8	81.2 ± 7.0
Methoxyfenozide	100.0 ± 6.7	108.5 ± 8.5	105.3 ± 3.7
Metobromuron	102.8 ± 10.8	101.8 ± 11.0	94.3 ± 16.9
Metribuzin	99.4 ± 9.8	112.3 ± 19.7	106.4 ± 8.2
Mevinphos isomer 1	93.0 ± 16.7	90.9 ± 12.9	98.9 ± 16.0
Mevinphos isomer 2	95.7 ± 15.0	105.9 ± 11.8	out of specification*
Mexacarbate	87.2 ± 7.3	102.0 ± 3.2	94.0 ± 8.8
Monocrotophos	98.5 ± 9.7	104.4 ± 7.6	106.9 ± 5.1
Monolinuron	92.4 ± 10.9	115.2 ± 7.0	109.4 ± 7.4
Myclobutanil	104.9 ± 4.6	109.3 ± 8.6	98.9 ± 5.3

Pesticide residues in cannabis with a low amount of carbon

	QuEChERS clean-up mix from MN	QuEChERS clean-up mix from comp. 1	QuEChERS clean-up mix from comp. 2
Analyte	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]
Neburon	89.2 ± 9.5	105.4 ± 14.6	83.1 ± 13.8
Nitenpyram	78.7 ± 4.1	91.5 ± 8.1	94.6 ± 12.7
Omethoate	84.2 ± 8.9	98.7 ± 12.6	100.9 ± 20.7
Oxadixyl	101.8 ± 6.5	104.7 ± 12.3	98.1 ± 6.2
Oxamyl	97.6 ± 9.5	95.3 ± 9.0	108.4 ± 13.0
Paclobutrazol	92.8 ± 3.3	105.2 ± 5.1	87.0 ± 10.5
Penconazole	90.2 ± 7.2	96.4 ± 4.5	99.8 ± 7.8
Phenmedipham	102.2 ± 10.4	107.0 ± 9.7	97.8 ± 9.9
Picoxystrobin	105.4 ± 15.8	107.7 ± 10.2	96.8 ± 7.0
Piperonyl butoxide	86.2 ± 11.7	112.5 ± 6.8	112.7 ± 18.7
Pirimicarb	91.3 ± 8.0	93.4 ± 8.1	95.0 ± 5.9
Prochloraz	90.0 ± 10.0	91.8 ± 9.2	92.0 ± 15.2
Promecarb	93.3 ± 22.6	85.6 ± 8.5	76.3 ± 14.2
Prometon	88.9 ± 12.4	92.1 ± 13.0	77.5 ± 10.6
Prometryne	82.5 ± 3.5	91.6 ± 4.3	78.2 ± 12.2
Propamocarb	74.5 ± 6.8	90.4 ± 15.4	75.0 ± 7.1
Propham	105.9 ± 18.5	out of specification*	92.8 ± 9.0
Propiconazole isomer 1	90.8 ± 11.6	103.7 ± 12.3	90.4 ± 9.2
Propoxur	101.7 ± 10.2	out of specification*	118.2 ± 14.0
Pymetrozine	41.5 ± 14.1	34.0 ± 14.8	37.2 ± 16.8
Pyraclostrobin	90.9 ± 6.0	100.8 ± 12.9	99.8 ± 5.0
Pyrimethanil	47.1 ± 15.2	57.2 ± 5.0	59.1 ± 21.1
Pyriproxyfen	89.7 ± 11.2	100.7 ± 4.8	101.0 ± 16.5
Quinoxyfen	63.5 ± 20.7	86.6 ± 8.0	86.0 ± 20.3
Secbumeton	79.4 ± 8.1	97.0 ± 7.8	80.1 ± 9.3
Siduron	94.6 ± 10.0	109.1 ± 7.7	95.5 ± 6.8
Simetryn	72.0 ± 5.9	88.4 ± 7.3	79.4 ± 12.5
Spinetoram	66.4 ± 11.8	75.1 ± 12.8	70.4 ± 10.6
Spinosad (Spinosyn A)	70.9 ± 6.4	75.9 ± 12.2	64.0 ± 21.5
Spinosad (Spinosyn D)	71.0 ± 7.6	75.6 ± 15.6	70.8 ± 21.8
Spirotetramat	93.9 ± 11.0	101.3 ± 6.4	93.1 ± 8.7
Spiroxamine isomer 1	71.1 ± 6.5	75.2 ± 7.8	59.0 ± 6.8
Spiroxamine isomer 2	77.2 ± 7.8	79.7 ± 3.2	60.8 ± 14.7
Sulfentrazone	108.5 ± 13.2	119.0 ± 9.0	112.2 ± 12.7
Tebuconazole	90.0 ± 10.0	105.2 ± 13.7	95.3 ± 6.1
Tebufenozide	95.9 ± 12.6	111.4 ± 11.7	96.7 ± 7.8
Tebufenpyrad	95.3 ± 10.3	98.9 ± 7.0	90.9 ± 16.4
Tebuthiuron	92.8 ± 14.0	89.4 ± 17.3	90.1 ± 19.2
Terbumeton	85.1 ± 7.7	77.1 ± 13.7	77.6 ± 4.4
Terbutryn	82.1 ± 7.9	91.9 ± 4.5	74.9 ± 12.3
Tetraconazole	96.4 ± 12.1	103.2 ± 5.7	100.2 ± 10.1
Thiacloprid	91.8 ± 15.5	110.2 ± 13.8	98.6 ± 12.6
Thiamethoxam	98.5 ± 8.9	105.3 ± 7.1	108.0 ± 13.3
Thidiazuron	31.9 ± 8.7	29.3 ± 13.3	41.6 ± 11.4
Thiobencarb	95.3 ± 22.0	118.1 ± 16.7	100.7 ± 9.1
Thiophanate-methyl	77.8 ± 14.1	117.3 ± 6.3	102.6 ± 15.8
Triadimefon	97.7 ± 11.1	107.3 ± 7.6	101.4 ± 11.0
Triadimenol	103.3 ± 7.9	107.4 ± 6.5	95.0 ± 9.6
Trichlorfon	97.1 ± 12.1	112.9 ± 21.0	89.0 ± 11.2
Tricyclazole	87.5 ± 9.7	85.5 ± 20.1	88.3 ± 18.5
Trifloxystrobin	88.8 ± 10.0	101.9 ± 9.1	112.8 ± 5.6

Pesticide residues in cannabis with a low amount of carbon

	QuEChERS clean-up mix from MN	QuEChERS clean-up mix from comp. 1	QuEChERS clean-up mix from comp. 2
Analyte	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]
Triflumuron	108.5 ± 9.9	out of specification*	113.2 ± 12.7
Triticonazole	100.2 ± 8.8	106.4 ± 8.3	93.9 ± 8.9
Vamidothion	98.6 ± 12.1	96.0 ± 12.0	91.9 ± 8.7
Zoxamide	95.6 ± 9.8	112.4 ± 8.4	102.7 ± 13.1

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

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 high recovery rates for pesticides. The presented QuEChERS method resulted in an average recovery rate of 90.2 % for 175 pesticides. Most of the pesticides (162 analytes) show recovery rates between 70 % to 120 %. On the other side, high matrix reduction yields are achieved by using the presented clean-up mix. The amount of dry substance after clean-up is reduced to less than 40 % of raw acetonitrile extracts. With this clean-up approach interfering substances (like e.g., lipids and pigments) are successfully removed due to optimized amounts of GCB and CHROMABOND® C_{18} ec adsorbents.

The chromatographic separation of pesticides was performed using core-shell particles that are well known for fast and high-efficient separations combined with a reasonably low backpressure. 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 7300000, CHROMABOND® QuEChERS clean-up mix XLIX

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