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Multiresidue screening methods for the determination of pesticides in plant materials

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Abstract

The determination of pesticides in plant materials and related matrices is of great importance in environmental chemistry. To meet the increasing requirements for fast and reliable analytical procedures, a multiresidue screening method for the determination of pesticides in various plant materials has been developed. For samples with a low fat content, preconcentration of the analytes was carried out by solid-phase extraction (SPE) after extracting the samples with an acetone–water mixture; the ethyl acetate eluate was further cleaned up using Florisil. Gas chromatography with electron-capture detection or mass spectrometric detection in the negative chemical ionization mode (GC–NCI-MS) was employed for the separation and quantification of the pesticides. The first step of this procedure had to be modified for materials containing high amounts of fat, such as olive oil or corn germ oil. In this case, 0.5 g of these samples were blended with silica particles, which were then placed over a layer of poly(styrene–divinylbenzene) particles in an SPE cartridge and eluted with acetonitrile saturated with *n*-hexane. The eluate was dried with sodium sulfate, cleaned up with Florisil and determined by GC–NCI-MS. Using this method, no interferences were encountered in the matrices investigated. The method has been tested for various plant materials spiked with up to 28 pesticides and the recoveries obtained were generally in the range of 85 to 110%, with relative standard deviations below 7%.

Keywords: Plant materials; Multiresidue analysis; Extraction methods; Environmental analysis; Oils; Pesticides

1. Introduction

Pesticides are applied worldwide to a broad variety of crops for field- and post-harvest protection. Due to an increasing awareness of the possible risks involved with the widespread use of pesticides, strict regulation of maximum residue limits (MRLs) and total dietary intakes has been introduced for most food commodities. To be able to supervise these limits, a constantly increasing number of multiresidue methods for pesticides have been developed, which are aimed at the determination of one or more of the main groups of pesticides in different sample matrices [1–4].

The main difference between existing methods lies in the sample clean-up step; the final determination is usually carried out by gas chromatography in combination with one or more element-specific detectors. Most of the early methods use liquid–liquid extraction to separate the analytes from interfering coextractives [5–8], with many of the more recent methods using solid-phase extraction (SPE) to achieve this goal [9–12]. Gel permeation chromatography has been one of the preferred techniques, in addition to one or more extraction steps to clean up the primary extracts [7,8,13–15]. Recently, a new variation of SPE, matrix solid-phase dispersion

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(MSPD), was introduced into several multiresidue methods [16–19]. It substitutes the primary solvent extraction of the sample matrix and one or even several extraction steps and thereby manages to further reduce time and solvent consumption during sample preparation.

Sample matrices can be divided into those containing mainly apolar coextractives, like oils, and those that lead to coextractives that are more polar than the analytes. This has to be taken into consideration when choosing the polarity of the extraction media and allows a further differentiation into methods for the analysis of samples with a high amount of oils and fat and into those for samples with only very low amounts of apolar constituents, but, quite often, a high content of water. Very few multiresidue methods have been described that are claimed to be suitable for both kinds of matrices, and these methods are very time- and solvent-consuming [6,7].

In a previous paper, a method for the determination of 23 pesticides in plant materials was described. Since then, this method has been slightly modified to allow the determination of several new pesticides and has been tested for a variety of new matrices. Plant materials with a high amount of oils necessitated the development of a new approach to extraction and clean-up using MSPD in conjunction with the original Florisil clean-up step. Gas chromatography with either electron-capture detection (GC–ECD) or mass spectrometric detection in the negative chemical ionization mode (GC–NCI-MS) were used for the final determination. Using these two methods, it was possible to determine all 28 pesticides selected for this work at concentrations in the range of 10 μg/kg or lower in plant materials as diverse as apple, grass, wheat, flour, olive oil or pumpkin seeds.

2. Experimental

2.1. Gas chromatography

A Carlo Erba (Milan, Italy) Model HRGC 5300 Mega Series gas chromatograph equipped with an ECD 400 electron-capture detector, an on-column injector and a Chrompack CP-Sil 8 column (60 m×0.25 mm I.D., film thickness 0.25 μm) was used for GC–ECD measurements. The instrumentation for GC–MS consisted of a Hewlett Packard (Palo Alto, CA, USA) Model HP 5890 gas chromatograph equipped with a split/splitless injector and a Chrompack CP-Sil 8 column (60 m×0.25 mm I.D., film thickness 0.25 μm), which was coupled to a Hewlett-Packard HP 5989 MS-Engine quadrupole mass spectrometer. Negative chemical ionization was used with methane as the reagent gas and an ionization energy of 240 eV.

2.2. Materials for solid-phase extraction

Poly(styrene–divinylbenzene) (PS–DVB) particles with a particle size of about 20 μm were synthesized according to a procedure published elsewhere [20]. Silicagel 60 H, particle size 5–40 μm (Merck, Darmstadt, Germany) was used for MSPD; Supelclean LC-Florisil (Supelco, Bellefonte, PA, USA) was used for sample clean-up.

The SPE materials were packed into glass columns (60×10 mm I.D.) equipped with glass fiber frits (Macherey-Nagel, Düren, Germany).

2.3. Reagents

All organic solvents were of Ultra Resi analyzed quality (J.T. Baker, Phillipsburg, NJ, USA); water was obtained from an Elix3 system (Millipore, Malborough, MA, USA). Pesticide standards were obtained from Riedel-de Haen (Seelze, Germany). Stock solutions were prepared by dissolving the pesticides in ethyl acetate to obtain concentrations of about 1 mg/ml, and further dilutions were made with ethyl acetate. All other chemicals used were of analytical reagent grade quality.

2.4. Sample preparation

2.4.1. Method A

A 10-g amount of the homogenized sample was blended with 66 ml of acetone. Water was added to obtain a total volume of 100 ml and the mixture was chopped and homogenized with an Ultra Turrax T25 (Ika, Staufen, Germany). A 3-g amount of Celite was added and the extract was filtered through a Buchner funnel (fitted with fast speed filter paper) with the aid of a gentle vacuum.

A 5-ml volume of the extract was diluted with water to 80 ml in a glass reservoir and passed through the SPE column containing 250–500 mg of the PS–DVB particles with a flow-rate of approximately 5 ml/min. Before use, the SPE column was washed and conditioned with 2–3 ml each of ethyl acetate, methanol and water.

Most of the residual water was removed from the column by blowing nitrogen through the column for 1 min at a pressure of 1 bar. Afterwards, the pesticides were eluted with 4 ml of ethyl acetate at a flow-rate of about 1 drop/s by applying a small pressure to the head of the column; a 5-min break was introduced after about 1 ml had passed through the column to ensure that there was optimum contact between the solvent and the solid-phase. The eluate was dried and cleaned up by passing it through an additional column containing 1 g of Florisil and, above that, about 1 g of sodium sulfate. For determination with GC–NCI-MS, the extract was concentrated from 4 ml down to 200 μl under a gentle stream of nitrogen before injection.

2.4.2. Method B

About 10 g of the sample were chopped and homogenized with a Braun MX32 kitchen blender for 3 min. A 0.5-g amount of the sample was transferred to a glass mortar and carefully blended with 1 g of silica using a glass pestle. In the case of liquid samples like olive oil, the sample was added dropwise onto the silica particles with a pasteur pipette to avoid direct contact between the sample and the mortar before blending. The mixture was then poured into a glass extraction column that had already been filled with PS–DVB particles that had previously been washed and activated with *n*-hexane and acetonitrile. A 2-ml volume of acetonitrile saturated with *n*-hexane was applied to the column; after several drops had passed through, the column was closed on both ends and sonicated in an ultrasonic bath for several minutes. Afterwards, it was eluted dropwise using an additional 3 ml of acetonitrile saturated with *n*-hexane, by applying a small pressure to the head of the column. For some matrices, a total of up to 10 ml of acetonitrile had to be used. The eluate was dried and cleaned up by passing it through an additional column containing 1 g of Florisil and, above that, about 1 g of sodium sulfate. Afterwards, the eluate was brought almost to dryness with a gentle stream of nitrogen and made up to the required volume (about 2 ml for GC–ECD, 200 μl for GC–NCI-MS) with ethyl acetate.

2.5. GC–ECD and GC–NCI-MS

The determination by GC–ECD was carried out by injecting 1 μl of the final extract directly onto the column. Pentabromoethylbenzene was used as the internal standard; it was added after the last clean-up step. The following temperature program was used: 55 to 173°C at 10°C/min, 173°C for 1 min, 173 to 203°C at 1.1°C/min, 203 to 300°C at 20°C/min, 300°C for 23 min.

The same internal standard was used for GC–NCI-MS. Final extract (2–3 μl) was injected using the splitless mode after concentrating the extract to 200 μl as mentioned above. The following temperature program was used: 125°C for 1 min, 125 to 180°C at 8°C/min, 180°C for 1 min, 180 to 203°C at 0.7°C/min, 203 to 300°C at 30°C/min, 300°C for 20 min.

The measurement was carried out in the selected ion monitoring (SIM) mode using at least one specific ion for each pesticide. The time segments and the ions measured therein are given in Table 1.

3. Results and discussion

At the beginning of this work, a multiresidue screening method, described previously [10], was tested for its applicability to additional matrices and pesticides. This method, to a large degree consistent with method A as described above, allowed the determination of 23 pesticides in 19 different plant materials. Most of these matrices could be analyzed using GC–ECD, although for some matrices, a mass spectrometer in the negative chemical ionization mode had to be used as a detector to eliminate background interferences. No modifications of this method were necessary to determine the 23 pesticides in sample materials like apple, grass, wheat and flour. The use of the larger PS–DVB particles with a mean diameter of 20 μm as described in the present work instead of the smaller ones with a mean diameter of 4.5 μm that had been used before had several advantages. Higher flow-rates could be

Table 1
Segments with pesticides and ions measured therein for the determination by GC–NCI-MS in the selected-ion monitoring mode

Segment number	Start time (min)	Pesticides	Ions measured (m/z)
1	18.00	α-Hexachlorocyclohexane, hexachlorobenzene	71, 255, 284, 286
2	20.50	β-Hexachlorocyclohexane, lindane, terbutylazine, quintozene, δ-hexachlorocyclohexane	71, 228, 255, 265
3	25.00	Chlorpyriphosmethyl, heptachlor	214, 266, 285, 300
4	30.00	Aldrin, malathion, metolachlor	35, 157, 172, 248
5	36.00	Pendimethalin, heptachloroepoxide, captan, folpet	35, 146, 150, 281
6	40.00	*o,p*-DDE, α-endosulphan	35, 246, 372, 406
7	41.75	Dieldrin, *p,p*-DDE, *o,p*-DDD	35, 37, 318, 346
8	43.00	Endrin, β-endosulphan, *p,p*-DDD, *o,p*-DDT	35, 248, 346, 406
9	44.75	Internal standard, propiconazole, *p,p*-DDT	35, 81, 248, 256
10	47.00	Deltamethrin	79, 81, 297, 307

achieved while up to 1 g of the particles could be packed into the column without excessive back-pressure. At the same time, the danger of clogging could be reduced and the recoveries obtained with the new material were as good as or better than those that had been measured with the smaller particles.

In addition to the 23 pesticides tested previously, the five commonly used pesticides terbutylazine, metolachlor, pendimethalin, propiconazole and deltamethrin were studied in this work. Only small changes were necessary to allow the simultaneous determination of all 28 pesticides. One of these changes was the modification of the eluting solvent of the SPE procedure. Instead of a mixture of ethyl acetate–*n*-hexane (1:1, v/v), ethyl acetate alone had to be used to elute all of the pesticides, otherwise, pendimethalin in particular would not have been eluted quantitatively from the Florisil column. Another modification was necessary for the GC temperature program to optimize the separation of all compounds, although this resulted in a rather long retention time for deltamethrin and considerably longer GC runs. Applying these changes led to method A as described in Section 2, exhibiting all the advantages mentioned in the original method, like short sample preparation times, low solvent consumption and little use of glassware [10]. Using this procedure in combination with the GC–ECD system, up to 28 pesticides could be quantitatively recovered and determined from spiked samples of apple, grass, wheat and flour. Some problems were encountered with the gas chromatographic separation when ECD was employed: despite the use of a high resolution column with a length of 60 m, peak overlapping occurred between terbutylazine and quintozene, and the signal of *p,p*-DDT could not be separated from one of the two signals obtained for propiconazole within reasonable retention times. Therefore, these two pairs of pesticides could not be determined separately within one run. The results of these measurements are given in Table 2, and a chromatogram of the 28 pesticides spiked to and recovered from wheat is shown in Fig. 1. By changing to the GC–NCI-MS system, this problem could be solved. The use of the very specific SIM mode allowed the separate quantification of all 28 pesticides within one chromatographic run, even in the case of total peak overlapping.

While method A worked well for samples with a low content of lipids, recoveries were severely diminished for samples containing high amounts of fats or oils. The losses occurred when the primary acetone–water extract was diluted with water to an acetone content of about 4%. Small droplets of oil were formed that were no longer miscible with the aqueous solution. These droplets, containing considerable amounts of pesticides, formed a film on the walls of the glass container and thereby led to losses of the pesticides contained within. Even rinsing the glass container with small quantities of ethyl acetate before applying it to the SPE column did not increase the recoveries sufficiently. A new approach had to be taken for these kinds of matrices. The pesticides had to be separated from the apolar lipids

Table 2
Recoveries for plant materials fortified with 28 pesticides at concentrations from 1 to 4 μg/g, SPE with PS–DVB and Florisil, determination with GC–ECD

No.	Pesticide	Grass		Apple		Wheat		Flour	
		Recovery (%)	R.S.D.	Recovery (%)	R.S.D.	Recovery (%)	R.S.D.	Recovery (%)	R.S.D.
1	α-Hexachlorocyclohexane	112	3.1	99	3.6	100	1.0	99	3.1
2	Hexachlorobenzene	96	2.7	88	4.1	89	1.1	85	5.6
3	β-Hexachlorocyclohexane	110	7.7	100	0.1	98	3.4	96	7.4
4	Lindane	88	0.7	104	6.1	100	1.9	103	1.9
5	Terbutylazine	–[a]	–[a]	–[a]	–[a]	–[a]	–[a]	–[a]	–[a]
6	Quintozene	91	3.5	94	5.6	96	0.7	94	2.5
7	δ-Hexachlorocyclohexane	102	6.9	100	2.9	99	1.9	97	3.3
8	Chlorpyriphosmethyl	110	2.7	100	3.8	96	2.5	94	3.0
9	Heptachlor	106	0.9	91	3.5	91	1.3	92	3.7
10	Aldrin	100	0.9	89	4.8	102	0.9	90	2.7
11	Malathion	123	5.4	107	4.7	92	2.5	103	0.9
12	Metolachlor	101	3.9	112	12.0	95	1.1	93	5.2
13	Pendimethalin	102	8.8	100	3.4	98	3.4	95	5.3
14	Heptachloroepoxide	105	0.5	95	5.2	101	0.2	98	0.9
15	Captan	106	3.2	98	5.5	90	1.7	90	5.9
16	Folpet	98	4.6	79	3.7	85	4.2	82	10.7
17	*o,p*-DDE	99	1.0	103	7.1	95	2.2	94	4.3
18	α-Endosulphan	104	1.1	96	4.7	100	0.6	97	1.8
19	Dieldrin	104	0.5	93	3.5	95	0.4	93	5.7
20	*p,p*-DDE	104	0.9	93	4.2	98	1.1	97	2.6
21	*o,p*-DDD	105	1.8	93	3.8	92	2.1	93	1.8
22	Endrin	94	3.8	92	3.2	96	2.5	92	2.6
23	β-Endosulphan	102	0.7	92	3.5	99	0.7	95	1.5
24	*p,p*-DDD	104	1.6	96	4.4	93	1.7	92	2.1
25	*o,p*-DDT	100	1.6	94	3.0	99	3.9	93	5.6
26	Propiconazole	100	0.7	108	3.9	100	7.9	100	3.8
27	*p,p*-DDT	100	0.7	108	3.9	100	7.9	100	3.8
28	Deltamethrin	105	6.0	102	1.4	88	3.9	89	5.0

[a] Not determined.

as well as from polar interferences. To achieve this, a combination of MSPD and Florisil clean-up was used. The sample was chopped if necessary, then blended carefully with 1 g of silica and packed over a layer of PS–DVB particles into an SPE column. The blending with the silica particles had to be done very carefully to avoid losses resulting from the formation of oily films on the surface of the mortar. The blending served three purposes: the silica acted as a support to produce a homogeneous and completely accessible bed for extraction and elution of the analytes; in the case of some plant materials, it helped with cellular disruption; and the silica particles served as an adsorbent to hold back polar interferences. The eluent, acetonitrile saturated with *n*-hexane, was chosen as it had been proved to be useful for elution of pesticides from an Extrelut column loaded with olive oil dissolved in *n*-hexane [21,22] or for the liquid–liquid extraction of pesticides from olive oil dissolved in *n*-hexane [23]. A 5-ml volume of this eluent was sufficient to quantitatively elute all of the pesticides, with the possible exception of hexachlorobenzene. For some matrices, for example pumpkin seeds, as much as 10 ml of the eluent were necessary to remove the latter analyte quantitatively from the column, which, in turn, led to a significant increase in the carry-over of lipids. Adding ethyl acetate to the eluent to increase the solvent strength did not improve the elution of the pesticides, but again increased the carry-over of coextractives. Ultrasonication helped to improve the extraction of the pesticides; about 3 min of ultrasoni-

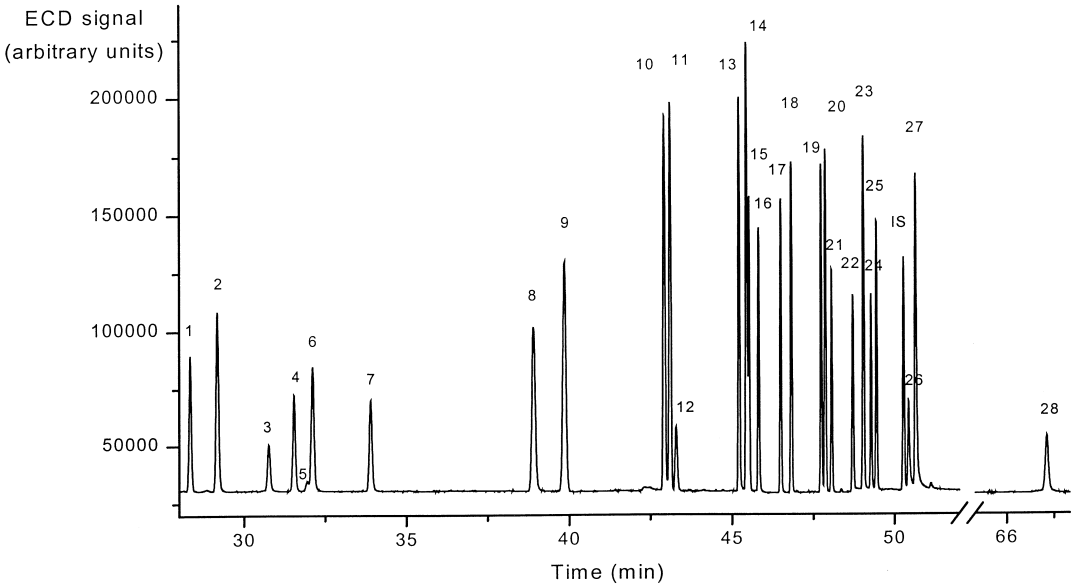

Fig. 1. ECD chromatogram of an extract from wheat fortified with 28 pesticides listed in Table 2. IS=internal standard pentabromoethylbenzene, sample preparation by method A, for chromatographic conditions see Section 2.

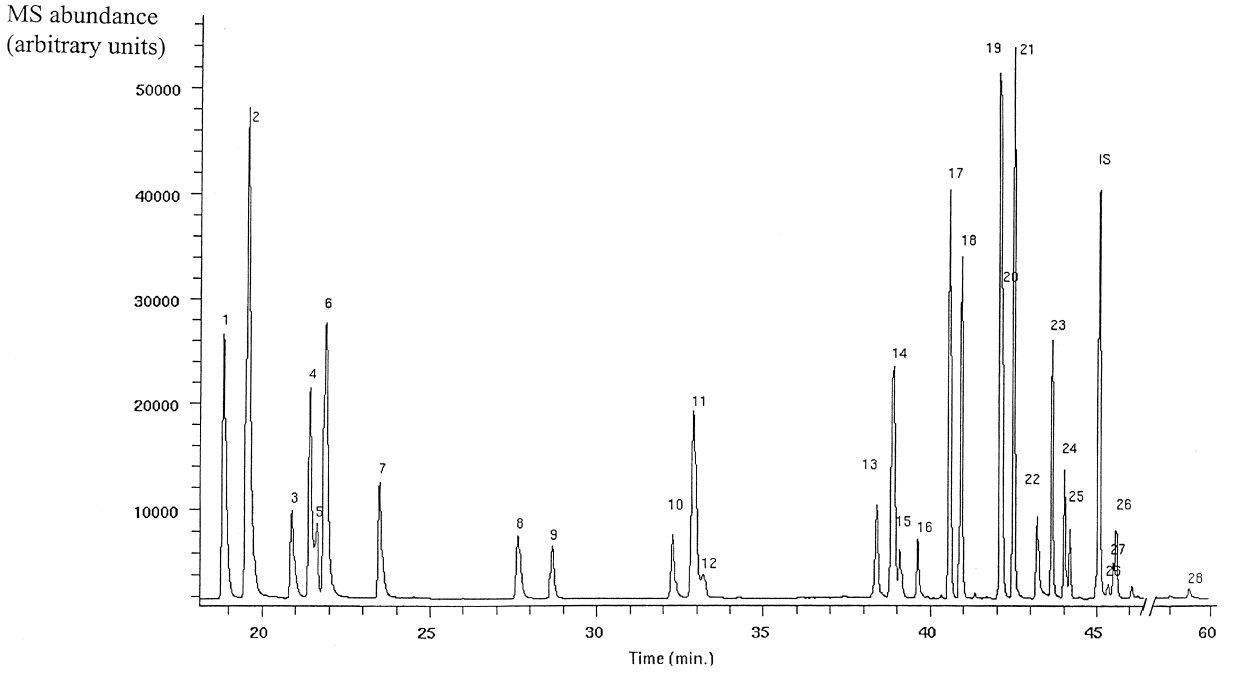

Fig. 2. GC–NCI-MS chromatogram of an extract from olive oil fortified with the 28 pesticides listed in Table 2. IS=the internal standard, pentabromoethylbenzene; sample preparation was by method B; for chromatographic conditions, see Section 2 and Table 1.

cation were able to replace 1 h of normal soaking of the sample in the eluent. The carry-over, determined by completely blowing off the solvent and weighing the residue, was normally between 5 and 10 mg from 500 mg of the sample used for MSPD. After the additional clean-up step on Florisil, which also served to remove most of the colored coextractives, the carry-over was lower than 3 mg for olive oil, corn germ oil and pumpkin seeds. While the final extract was still not clean enough to determine all of the pesticides at concentrations below 100 μg/kg by GC–ECD, no background interferences were encountered when using the GC–NCI-MS system. One problem resulting from residual lipids in the final extract was the considerable deterioration of GC column resolution after about 100 injections. Washing the column with ethyl acetate and *n*-hexane helped to improve the resolution, but it was not possible to regain the same results as at the beginning. Fig. 2, showing a GC–NCI-MS chromatogram of the 28 pesticides spiked to and recovered from olive oil, is typical for the state of the column after about 100 injections of samples extracted and cleaned up using method B. The installation of a precolumn and the regular removal of at least 20 cm of this precolumn is therefore strongly recommended.

Most of the 28 pesticides could be determined in olive oil, corn germ oil and in pumpkin seeds at a concentrations of 5 ng/g, with a signal-to-noise ratio higher then ten. For terbutylazine, malathion, metolachlor, captan, folpet, propiconazole and deltamethrin, 10 to 30 ng/g where necessary to achieve this signal-to-noise ratio. The recoveries and relative

Table 3
Recoveries for plant materials fortified with 28 pesticides at concentrations ranging from 50 to 200 ng/g, using MSPD with silica and PS–DVB, clean-up with Florisil and determination with GC–NCI-MS

Pesticide	Corn germ oil		Olive oil		Pumpkin seeds	
	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
α-Hexachlorocyclohexane	98	2.8	97	3.1	94	1.9
Hexachlorobenzene	82	6.2	87	5.4	86	6.7
β-Hexachlorocyclohexane	92	2.1	93	3.1	107	2.0
Lindane	109	1.0	106	2.1	108	1.6
Terbutylazine	93	3.5	94	2.9	91	3.6
Quintozene	101	4.2	101	4.1	93	3.0
δ-Hexachlorocyclohexane	92	2.9	95	3.6	99	4.0
Chlorpyriphosmethyl	96	3.1	100	3.3	102	4.1
Heptachlor	93	2.8	103	6.2	92	1.9
Aldrin	88	4.3	112	6.2	96	5.1
Malathion	98	2.8	97	2.6	103	4.0
Metolachlor	112	1.9	103	2.2	107	4.8
Pendimethalin	105	3.1	109	4.1	109	3.6
Heptachloroepoxide	98	2.0	92	2.1	91	1.2
Captan	89	2.3	99	3.1	96	5.2
Folpet	91	3.4	93	2.8	93	4.3
o,p-DDE	95	4.6	90	2.3	91	5.7
α-Endosulphan	106	2.1	102	2.0	98	4.1
Dieldrin	91	6.2	92	4.1	92	5.8
p,p-DDE	106	2.6	99	3.1	96	3.0
o,p-DDD	103	3.1	91	2.8	97	7.4
Endrin	94	2.8	96	3.7	105	3.1
β-Endosulphan	101	1.0	102	2.1	94	1.4
p,p-DDD	105	3.8	89	3.1	102	4.0
o,p-DDT	97	2.1	94	5.0	90	2.7
Propiconazole	89	2.5	92	4.3	104	2.8
p,p-DDT	99	4.1	92	2.6	97	3.7
Deltamethrin	100	5.1	92	2.6	106	4.9

standard deviations for a spiked olive oil sample are given in Table 3.

4. Conclusions

Using one of the two methods described in this paper, all of the tested plant materials, including fruits, herbs, vegetables and oils, could be analyzed for residues of 28 pesticides at concentrations down to 10 ng/g or even lower. Although our goal of being able to analyze all matrices with one universal multiresidue method has not yet been reached, the two procedures presented here differ only in the first extraction and SPE step. Method A, consisting of extraction with acetone–water, RP-SPE and Florisil clean-up, was used for samples containing low amounts of fat and oil. Method B, consisting of MSPD with silica and PS–DVB particles and Florisil clean-up, was used for samples with a high content of lipids. Final determination with GC–NCI-MS was necessary for most of the samples extracted and cleaned up with method B; almost all of the other samples could be determined by GC–ECD. The recoveries were satisfactory for all pesticides, with values for the most part being between 85 and 110% and standard deviations being below 7%; only hexachlorobenzene proved to be difficult to extract from some samples with a high content of oil.

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