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MSPD Combined With Fast GC for Ultratrace Analysis of Pesticide Residues in Non-Fatty Food

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Abstract

Matrix solid phase dispersion (MSPD) sample preparation method was combined with fast gas chromatography (GC) to determine pesticide residues of different volatility and polarity at ultratrace concentration level. Apples as representatives of a non-fatty food were chosen as a matrix; they are also a common raw material for baby food production. At fast GC conditions with electron capture detection (ECD) several parameters of MSPD procedure were optimised. Sample is homogenized with sorbent Florisil, pesticides are eluted with the optimised volume of etylacetate. After evaporation of solvent to dryness, reconstitution of the rest to toluene follows and the final extract is injected utilising splitless injection. These optimised procedure leads to recoveries ≥ 90% (at concentration level of 60 μg kg^{-1}) and limits of quantification (*LOQs*) < 47 μg kg^{-1} (except of diazinon) utilizing ECD. Except of dimethoate all *LOQs* are lower than related maximum residual limits (*MRLs*) set for commodity apple. Also the possibilities of mass spectrometric (MS) detection were studied. Even at the half pre-concentration factor *LOQs* for all pesticides were lower than 10 μg kg^{-1}, the *MRL* for baby food. Acceptable recoveries were obtained even at concentration level of 5 μg kg^{-1} (≥ 79%).

Key words: MSPD, fast GC, pesticide residues, apples, matrix-effects

Introduction

Analysis of pesticide residues has recently become one of the priorities in the food chain control. The usage of chemical pesticides is known to have a significant positive impact on crop yields; however, the residues of pesticides have a negative impact on human health. Therefore, European Commission strictly regulates the level of pesticide residues in various food commodities through the maximum residue limits (*MRLs*).[1]

The most suitable approaches in determination of pesticide residues content at ultratrace level (<1 mg kg^{-1}, or <0.0001%, w/w)[2] in food material are chromatographic methods connected with various sample preparation methods. Especially fast GC techniques provide faster, cost-effective analytical answer.[3,4] Practically, the advantage of increased throughput of fast separation method can be fully taken only in combination with fast and effective sample preparation method, therefore, matrix solid-phase dispersion (MSPD) was chosen as sample preparation technique for the analytes of apple samples. MSPD offers several advantages over other sample preparation methods including simplicity, relatively low consumption of organic solvents. It performs cell disruption, homogenization, extraction and clean-up in one step, what is related with better precision.[5,6]

In this work, MSPD sample preparation procedure was connected with fast GC utilizing selective detections: electron capture (EC) and mass spectrometric (MS) detectors. Several parameters of sample preparation method were optimized at on the most common raw plant material for baby food production - apple. The objective of this work is to reach satisfactory limits of quantification (*LOQs*) and recoveries meeting the requirements of Council Directive 91/414 EEC (particularly the guidance documents establishing *MRLs*[1] for selected fruits and establishing requirements on validation[7]).

Experimental

1. Reagents and materials

The pesticides diazinon, terbuthylazine, dimethoate, pyrimethanil, chlorpyrifos-methyl, fenitrothion, chlorpyrifos, cyprodinyl, penconazole, methidathion, kresoxim-methyl, myclobutanil, tebuconazole, phosalone, bitertanol, cypermethrin,

etofenprox were of > 95% purity from various sources (Table 1). Bitertanol and cypermethrin consist of isomers. Stock solution of pesticides with concentration of 0.5 μg L^{-1} was prepared by dissolving 5 mg of each compound in 10 mL of toluene (Suprasolv, Merck, Darmstad, Germany) and was stored at –18 °C. Standards were weighted on Sartorius Analytic MC1 balances (Sartorius, Götingen, Germany) with a precision of ± 10 μg.

The stock solution of pesticides was diluted with acetone (Suprasolv, Merck, Darmstad, Germany) to get appropriate pesticide standard solutions for the preparation of spiked samples and matrix-matched standards. Ethyl acetate and dichloromethane were of gas chromatography grade (Suprasolv, Merck, Darmstad, Germany). Magnesium sulfate (anhydrous powder) was from Lachema (Neratovice, Czech Republic). The sorbent used was Florisil (60–100 mesh) from Rotichrom, Roth, Karlsruhe, Germany. Apples were mixed with blender Braun MX 2050 (Kronberg, Germany).

2. Sample preparation

The sample used for this study was homogenously mixed chemically untreated apples (with peel) which were stored at –18 °C in a refrigerator. The whole optimised process of sample preparation is presented in Figure 1.

Solutions of matrix-matched standards were prepared by adding the appropriate volume of the pesticide stock solution to an extract of a blank apple sample prepared by the MSPD method.

3. Instrumentation

GC-ECD

GC measurements were performed on a HP 6890 gas chromatograph (Hewlett Packard, Avondale, PA, USA) equipped with an electron capture detector (ECD) operated at 320 °C. The rate of data acquisition was set to 50 Hz. The splitless injector with 2 mm i.d. liner (Agilent Technologies, USA) operated at 250 °C (split vent 100 mL min^{-1}, 1 min) was used for sample introduction. Injections were carried out by an autosampler using a 10 μL syringe (Hamilton, Reno, Nevada, USA). Hewlett Packard GC Chemstation software was used to control analysis, collect and process the data. For the experiments, a 25 m x 0.15 mm i.d. CP Sil 13 CB fused silica capillary column with a 0.4 μm 14% phenyl, 86% dimethylpolysiloxane stationary phase (Varian, Middelburg, The Netherlands) was used and it was coupled with a 1 m x 0.32 mm i.d. non-polar deactivated fused silica pre-column (Supelco, Bellefonte, PH, USA). For a pre-column - analytical column connection a glass press-fit connector (0.32/0.20, Agilent Technologies, USA) was utilized and sealed with a polyimide resin according to the manufacturers instructions (Supelco, Bellefonte, USA). Measurements were performed under temperature-programmed conditions (initial temperature 100 °C, initial time 1 min, heating rate 65 °C min^{-1}, and final temperature 290 °C (4 min)). Hydrogen (purity >99.99%, Linde, Technoplyn, Bratislava, Slovak Republic) was used as a carrier gas. Carrier gas flow programming was used: 2.3 mL min^{-1} (5.5 min), 2 mL min^{-2}, 3.4 mL min^{-1}; an electronic pressure control was employed.

Table 1. List of pesticides, chemical classes, sources of pesticide standards and monitored ions utilizing GC-MS in SIM mode.

Pesticide*	Chemical class	Source of pesticides	Monitored ions in SIM mode **Target ion**
Diazinon	Organophosphorus	Argovita	**276**, 304 [a]
Terbuthylazine	Triazine	Ciba-Geigy, Basel, Switzerland	**214**, 229 [a]
Dimethoate	Organophosphorus	Cheminova Agro, Denmark	**87**,125 [a]
Pyrimethanil	Anilinopyrimidine	Schering, Germany	**198**, 199 [a]
Chlorpyrifos-methyl	Organophosphorus	Dr. Ehrenstorfer, Germany	**286**, 288 [b]
Fenitrothion	Organophosphorus	Sumimoto Chemical Co., Japan	260, **277** [b]
Chlorpyrifos	Organophosphorus	Dow Chemical Company, USA	286, **314** [b]
Cyprodinil	Anilinopyrimidine	Ciba-Geigy, Basel, Switzerland	224, **225** [c]
Penconazole	Triazole	Ciba-Geigy, Basel, Switzerland	**248**, 250 [c]
Methidathion	Organophosphorus	Ciba-Geigy, Basel, Switzerland	**145**, 302 [c]
Kresoxim-methyl	Oximinoacetate	BASF, Germany	**131**, 132 [d]
Myclobutanil	Triazole	Dow Agro Science, USA	**179**, 245 [d]
Tebuconazole	Triazole	Argovita	**250**, 252 [e]
Phosalone	Organophosphorus	Dr. Ehrenstorfer, Germany	182, **367** [f]
Bitertanol	Triazole	Bayer, Germany	168, **170** [g]
Cypermethrin	Pyrethroid	Argovita	163, **181** [g]
Etofenprox	Non-ester pyrethroid	Mitsui Toatsu Chemicals, Japan	**163**, 376 [g]

* pesticides are arranged according to retention times; [a], [b], [c], [d], [e], [f], [g] denote ions monitored in one SIM group; Target ion - used for quantification.

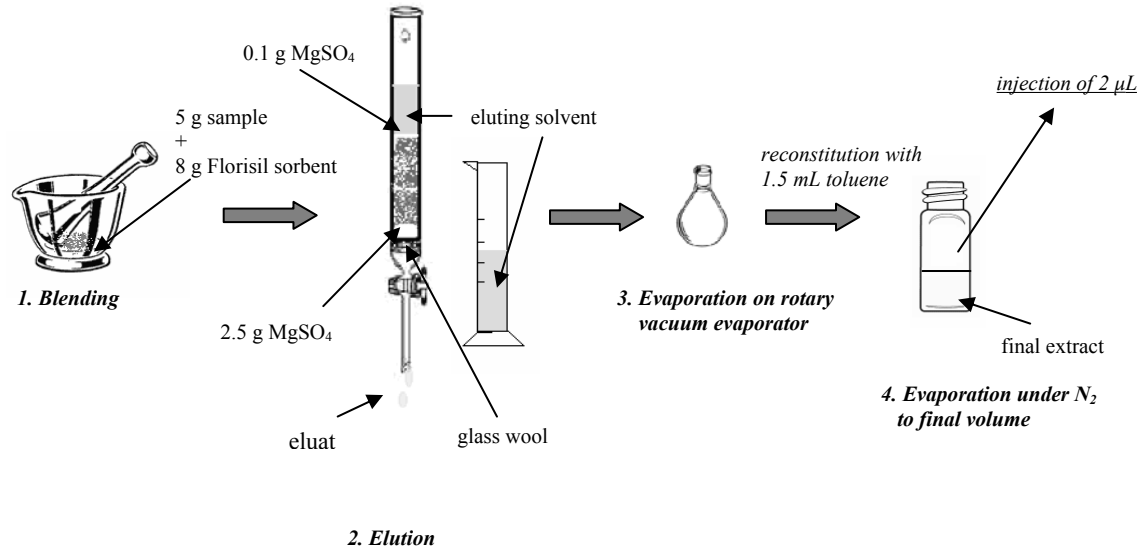


Figure 1. Scheme of the whole apple sample MSPD preparation process.

GC-MS

GC–MS measurements were performed on an Agilent 6890N GC coupled to 5973 MSD (Agilent Technologies, Avondale, PA, USA) equipped with a programmed temperature vaporizer (PTV) and autoinjector Agilent 7683. MS with electron impact ionization (EI) mode (70 eV) was operated in SIM mode; for each pesticide two specific ions were selected and sorted into groups (maximal number of ions in one group was 8); the used dwell time was 10 ms. PTV was operated in cold splitless mode. An injection volume was 2 μL. Helium with purity 5.0 (Linde Technoplyn, Bratislava, Slovak Republic) was used as a carrier gas. Narrow bore chromatographic columns CP-Sil 8 CB (Varian, Middelburg, The Netherlands) with 5% diphenyl 95% dimethylsiloxane stationary phase 15 m x 0.15 mm I.D. x 0.15 μm was utilised. It was connected to a non-polar deactivated pre-column. Constant pressure mode 363.5 kPa was used until the elution of the last analyte (ethofenprox, 7.90 min), additional pressure ramp (1000 kPa min^{-1}, 685 kPa) was used to speed-up elution of higher boiling matrix co-extractives. Chromatographic separation was performed under a temperature program, 130 °C (1.13 min), 27.25 °C min^{-1}, 290 °C (8 min). PTV conditions: temperature program, 150 °C, 400 °C min^{-1}, 300 °C (2 min), 400 °C/min, 350 (5 min); split vent open time 1.13 min.

Results and discussion

Pesticides belonging to the different chemical classes to include different chemical properties and polarities were selected (Table 1). For the separation of pesticides, capillary GC columns coated with non-polar to middle polar stationary phases have been utilized. A capillary with the internal diameter of 0.15 mm was chosen instead of 0.1 mm for the reason of the increased column capacity and/or carrier gas flow through the column. This column dimension can be used in the majority of GC instruments and offers more flexibility with respect to flow, loadability and practical operation. Conditions of fast GC-ECD were optimised with the mixture of selected pesticides and n-alkanes C_{10}-C_{28} in hexane at the concentration level of 10 mg L^{-1} of each compound.[8] The influence of the injection volume, type of liner, injection technique, retention gap length, type of solvent, oven temperature and column length on peak areas, peak shape and peak broadening of analytes was investigated. At these conditions all peaks were separated with the resolution ≥ 1.4. In the case of fast GC-MS analysis, the chromatographic method was developed with respect to the separation/speed trade-off based on key principles proposed by Klee at al.:[9] speed-optimised flow (*SOF*), and optimal temperature ramp rate 10 °C/t_M, t_M denotes void time.

Development of sample preparation method

A critical aspect of pesticide residue analysis is the sample extraction and purification, which are required to isolate the residues from the matrix components. The MSPD technique seems to be superior to other techniques used for this purpose.[10]

For purposes of development of MSPD sample preparation method in apples as non-fatty food representatives, fast GC-ECD configuration was utilised. Fruit sample free of pesticides were used for the preparation of a matrix matched standard prepared in blank extracts. The ECD shows that blanks were free of the selected pesticides (Figure 2A). First two solvents of different polarity - ethyl acetate and dichloromethane

were tested as eluents (80 mL). After eluent evaporation the final volume used for the residues reconstitution was 1 mL of toluene. The recoveries of pesticides using fortified apples at the level of 120 μg kg^{-1} ranged between 97–113% for ethyl acetate and 83–97% for dichloromethane. The difference in background of chromatograms for the two solvents was not significant; therefore, ethyl acetate was used as eluting solvent in further experiments.

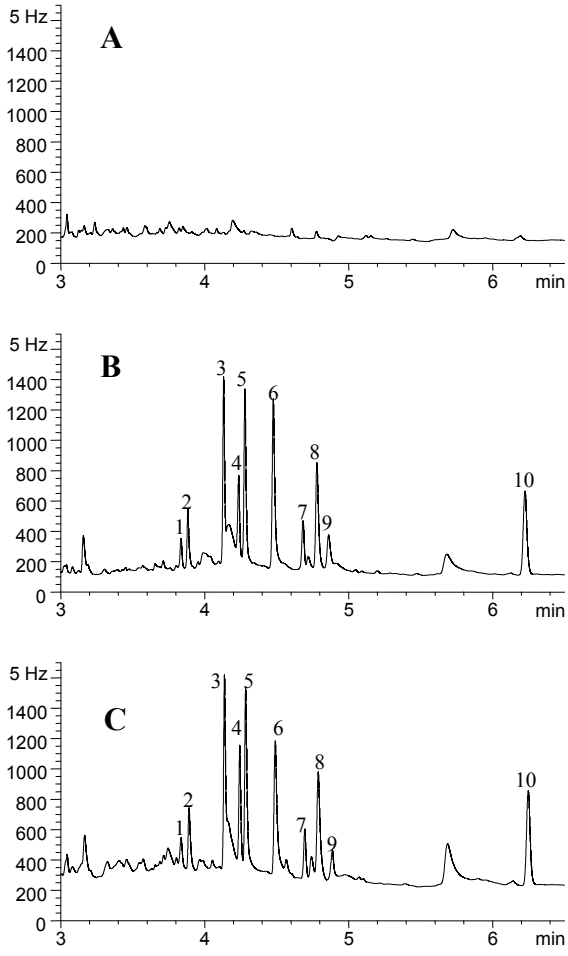


Figure 2. Chromatograms of apple sample extracts prepared by MSPD (A) blank apple sample; spiked apple samples: (B) 120 μg kg^{-1} with final volume of solvent 1 mL used for reconstitution of residues and (C) 60 μg kg^{-1} with final volume 0.5 mL, **1**: diazinon, **2**: dimethoate, **3**: chlorpyrifos-methyl, **4**: fenitrothion, **5**: chlorpyrifos, **6**: penconazole, **7**: methidathion, **8**: kresoxim-methyl, **9**: myclobutanil, **10**: phosalone.

Then the eluting volume was tested and the volume of 60 mL is considered as sufficient to reach satisfactory recoveries (95%–105%).

Finally the final volume of toluene (Figure 2) was adjusted. In Figure 2 there is the comparison of two chromatograms with the final volume of 1 and 0.5 mL. Although the spiking concentration level for the final volume of 0.5 mL was two times lower then for 1mL to reach peaks of the same height, the background increased moderately related to the peak heights.

The recoveries were found over 90% (except diazinon) (Table 2). Further reduction of the final volume leads to significantly lower precision and higher background leading to problems with matrix induced enhancement effect. Therefore, the final volume adjusted to 0.5 mL is the best choice.

The choice of injection volume of samples with difficult matrices, such as plant extracts must be a compromise between:

- Required *LOQs*
- Degree of chromatographic system contamination. The injected matrix significantly affects chromatographic system and subsequently analytical results (matrix effects).[11]

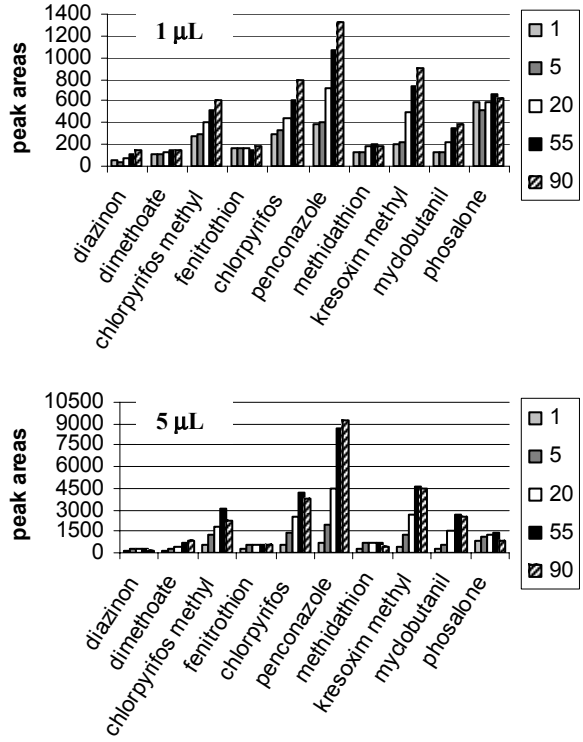


Figure 3. Graph of the dependence of peak areas of pesticides injected by autosampler on the number of performed injections studied/retention gap at the concentration of matrix matched standard 0.625 mg L^{-1} (corresponds to concentration 125 mg kg^{-1}).

90 injections of 1 and 5 μL of matrix matched standards (1 mg L^{-1}) were performed to study the changes in the peak areas and widths with the number of injections. The experiment started utilizing a new pre-column, inlet liner and septum. In general, peak areas increased with the number of injections in both cases (Figure 3). For the injection volume of 5 μL, the increase was more noticeable. The change in the

first five injections presents up to 12% increase of peak areas for the injection of 1 μL and mostly over 120% for 5 μL injection volume. The changes in peak areas in the whole range of 90 injections ranged from 6.9% for phosalone to 344% for kresoxim-methyl for injected volume of 1 μL and from –2.3% for phosalone to 1196% for penconazole for injected volume of 5 μL. The dependence of peak widths on the number of performed injections is presented in Figure 4. Evident increasing trend for all compounds except of diazinon was observed for the higher injection volume, for 1 μL injected the changes in the peak widths represent up to 20%.

Therefore, 2 μL was a good choice as a compromise as the injection volume for the combination of fast GC and MSPD. To minimize the impact of the matrix effect five injections of a blank apple sample were injected before alternation of injections of spiked samples and matrix matched standards. In this study, several other ways to reduce matrix effects were practised: addition of the final isothermal part of the oven temperature program to remove the high boiling components from a column and the utilization of a pre-column to protect the analytical column from an excessive contamination.

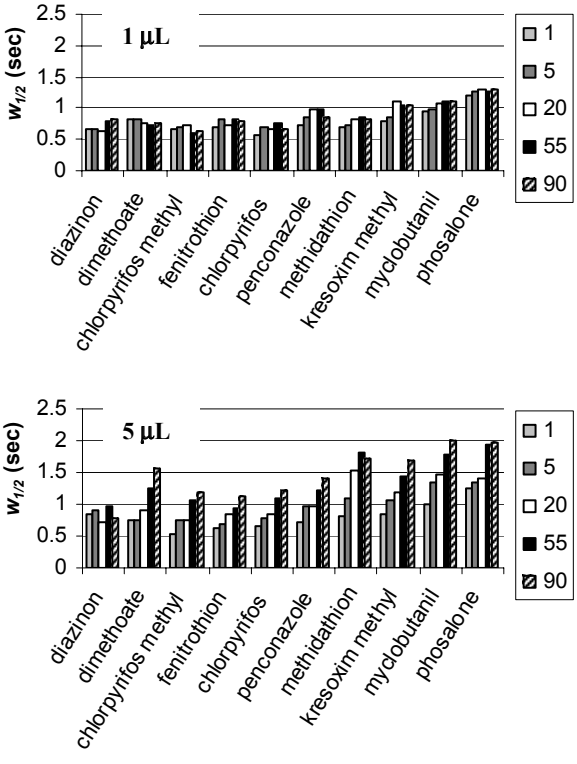


Figure 4. Graph of the dependence of peak widths at half height ($w_{1/2}$) of pesticides injected by autosampler on the number of performed injections studied/retention gap at the concentration of matrix matched standard 0.625 mg L^{-1} (corresponds to concentration 125 μg kg^{-1}).

Method validation

GC-ECD

For the recovery calculation responses of pesticide residues of matrix matched standards and spiked samples were used. The recovery data and *LOQs* under optimal conditions are shown in Table 2. Except of dimethoate all *LOQs* of the studied pesticides were lower than the required *MRL* established by European Commission for commodity apple.[1] Good recoveries (≥ 90%) were obtained, what is in an agreement with directives laid down by the European Commission (pesticides recoveries should be in 70–110% range with relative standard deviations (*RSD*) < 20%).[7] Repeatability of peak areas measurement by fast GC-ECD for all pesticides expressed as *RSD* (n=5) was in the range of 5.8–16.1% at the concentration level of 60 μg kg^{-1}. The obtained *MRLs* are, however, not sufficient for baby food control. Therefore, further research was performed.

Table 2. The GC-ECD results of the recovery and limits of quantification (*LOQs*) of selected pesticide residues from apples at the concentration level of 60 μg kg^{-1}.

Pesticide residue	Recovery %	*LOQ* [a] µg kg^{-1}	*MRL* [b] µg kg^{-1}
Diazinon	90	100.6	300
Dimethoate	98	37.1	20
Chlorpyrifos-methyl	92	13.8	500
Fenitrothion	96	46.2	500
Chlorpyrifos	91	8.8	500
Penconazole	92	2.0	200
Methidation	93	29.3	300
Kresoxim-methyl	90	12.8	200
Myclobutanil	93	31.2	500
Phosalone	92	30.8	2000

[a] $(LOQ)=\frac{s_0}{\bar{s}}\cdot 10$, s_0 - standard deviation of noise (peak height), $\bar{s}$ - detector response (height), [b] *MRL* - maximum residual limit for commodity apple.[1]

GC-MS

LOQs may be further reduced by utilising MS detection technique in SIM mode by measuring specific ions what significantly improves selectivity of detection. Extracted chromatograms of target ions of pesticides at concentration level of 10 μg kg^{-1} are shown in Figure 5.

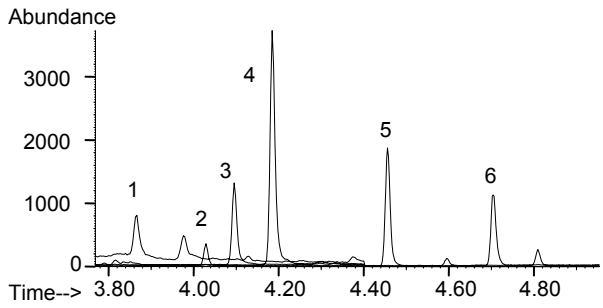
Table 3 presents *LOQs* obtained by GC-MS analysis in SIM mode as well as the results from the fortification experiment of apples. Recoveries at three spiking levels of 5, 10 and 100 μg kg^{-1} are presented. As the table shows, *LOQs* obtained with MS detection are 3–290 times lower compared to ECD (Table 3) and are lower than the required *MRL* for baby food 10 μg kg^{-1}. The recovery results fell within the commonly accepted range 70–110% recovery and ≤ 20% *RSD*[7] (except of tebuconazole at 5 μg kg^{-1} level with *RSD* 54%

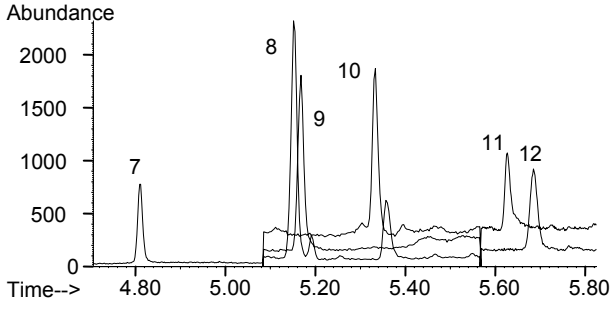
Table 3. Limits of quantification (*LOQs*), average recoveries (*R*) and relative standard deviations (*RSD*s) of fortified pesticides in apples at different concentrations 5, 10 and 100 μg kg^{-1} from the MSPD method with GC-MS analyses

Spiking level (µg kg^{-1})	*LOQ* µg kg^{-1}	5		10		100	
Pesticide		*R* %	*RSD* [a] %	*R* %	*RSD* [a] %	*R* %	*RSD* [a] %
Dimethoate	2.67	84	4.2	107	14	99	2.2
Terbuthylazine	0.25	101	7.7	99	1.7	96	0.8
Diazinon	0.36	93	5.4	91	6.6	93	8.0
Pyrimethanil	0.07	93	0.4	94	3.1	95	0.9
Chlorpyrifos-methyl	0.06	94	0.5	95	3.8	93	3.8
Fenitrothion	0.16	98	4.8	95	3.9	95	1.6
Chlorpyrifos	0.30	90	1.6	93	0.7	93	2.6
Cyprodinyl	0.65	92	2.3	90	1.0	94	0.7
Penconazole	0.60	86	4.5	99	0.9	96	0.2
Methidathion	2.76	99	0.9	106	1.7	96	0.5
Myclobutanil	0.68	96	9.3	99	0.9	96	0.2
Kresoxim-methyl	2.00	99	8.9	71	18	93	1.9
Tebuconazole	0.59	79	54	92	0.6	97	2.3
Phosalone	0.57	88	18	105	16	95	0.5
Bitertanol1	0.24	95	1.6	94	3.2	95	0.9
Bitertanol2	2.25	92	12	96	3.3	91	0.5
Cypermethrin1	1.42	108	2.2	92	13	92	5.9
Cypermethrin2	2.64	79	16	91	20	90	0.5
Cypermethrin3	5.03	79	17	96	1.0	95	7.2
Etofenprox	1.17	85	4.5	91	6.3	93	2.7

[a] *RSD* (n=2) of recovery experiments were calculated according to Eckschlager et al.[12]

due to interference). These satisfactory results were obtained even without final evaporation step (Figure 1); the evaporation on rotary vacuum evaporator was followed by reconstitution in 1 mL of toluene, what saves time and simplifies the overall sample preparation procedure. Besides that the burden on chromatographic system decreases.





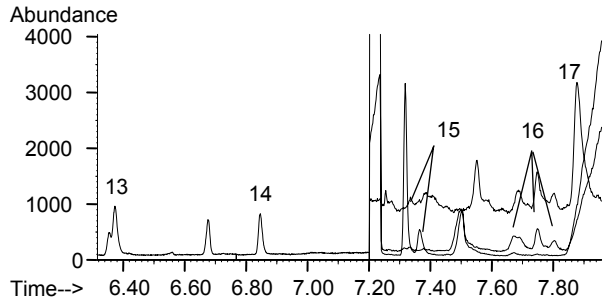


Figure 5. Extracted chromatograms of target ions of pesticides in matrix matched standard solution from fast GC-MS measurements; concentration of pesticides 10 μg kg^{-1}. **1**: dimethoate, **2**: terbuthylazine, **3**: diazinon, **4**: pyrimethanil, **5**: chlorpyrifos-methyl, **6**: fenitrothion, **7**: chlorpyrifos, **8**: cyprodinyl, **9**: penconazole, **10**: methidathion, **11**: kresoxim-methyl, **12**: myclobutanil, **13**: tebuconazole, **14**: phosalone, **15**: bitertanol, **16**: cypermethrin, and **17**: etofenprox.

The linearity of response of GC-MS in SIM mode was checked with calibration matrix matched standards in black extracts. Duplicate determinations at three concentration levels (0.025–0.5 mg L^{-1}, what corresponds to 5–100 μg kg^{-1} in apple sample) were carried out according to European Commission directives.[13] The obtained coefficients of determination R^2 were in the range of 0.9995–1, except of kresoxim-methyl (0.9985), tebuconazole (0.9911), and cypermethrin1 (0.9594).

Conclusions

Application of fast GC in combination with MSPD sample preparation to ultratrace analysis of pesticides in apple samples (non-fatty food) was performed. Several parameters of MSPD procedure were optimized utilising ECD detection. The elution solvent ethyl acetate with elution volume of 60 mL was selected for extraction purposes of pesticides from the homogenized sample with sorbent Florisil. The final volume of 0.5 mL was adjusted by evaporation of reconstituted solution under N_2. At these conditions recoveries in the range of 90–98% were obtained at the concentration level of 60 μg kg^{-1}. *LOQs* reached were between 2–100.6 μg kg^{-1}. Except of dimethoate *LOQs* of all pesticides did not exceed *MRLs* set by European Commission for commodity apple.

In the case of GC-MS measurements in SIM mode, the rest after the evaporation to dryness by rotary vacuum evaporator was reconstituted in 1 mL toluene, so the step of evaporation under N_2 was omitted. Good recoveries of pesticides at the concentration levels of 5, 10 and 100 μg kg^{-1} were achieved at all concentration levels. *LOQs* fulfil even the requirement on the analysis of baby food; the values are lower than 5 μg kg^{-1} (*MRL* set for baby food is 10 μg kg^{-1}). Good linearity (R^2 between 0.9995–1) is reached in the range of 0.025–0.5 mg L^{-1}, what corresponds to 5–100 μg kg^{-1} in apple sample.

Acknowledgements

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Povzetek

Za kromatografsko analizo ostankov pesticidov različnih polarnosti in hlapnosti smo uporabili predpripravo vzorca s pripravo mešanice matrice s sorbentom v trdni fazi. Kot primer nemastnega prehrambenega pridelka smo kot vzorec izbrali jabolka. Za plinsko kromatografsko detekcijo smo uporabili detektor na zajetje elektronov. Optimizirali smo več parametrov procesa predpriprave vzorca, kot je količina etilacetata, ki ga uporabimo za spiranje sorbenta Florisila, ki ga pripravimo v mešanici z vzorcem. Po odparevanju topila do suhega smo preostanek raztopili v toluenu in injecirali brez deljenja vzorca.

Izkoristki ekstrakcijskega postopka so nad 90% (pri vsebnosti ~60 μg kg^{-1}), meje določitve pa pod 47 μg kg^{-1} (razen za diazinon). Razen za dimetoat so vse meje določitve manjše kot so odgovarjajoče najvišje meje za preostanke pesticidov določene za jabolka široke potrošnje. Preučili smo tudi možnosti masno-spektrometrične določitve. Tudi pri polovičnem predkoncentracijskem kvocientu so bile meje določitve manjše kot 10 μg kg^{-1}, kar je meja za ostanke pesticidov v otroški hrani. Sprejemljive izkoristke smo dobili tudi pri vsebnostih ~5 μg kg^{-1} (≥79%).