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Journal of Chromatography A, 1084 (2005) 63–70
JOURNAL OF CHROMATOGRAPHY A
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Search on ruggedness of fast gas chromatography–mass spectrometry in pesticide residues analysis

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Available online 5 November 2004

Abstract

In this study, suitability of fast gas chromatography–mass spectrometry (GC–MS) on a narrow-bore column with a programmed temperature vaporizer for the analysis of pesticide residues in non-fatty food was evaluated. The main objectives were ruggedness and stability of chromatographic system with regards to co-extractives injected. The chromatographic matrix induced response enhancement was found to be strongly dependent on the concentration of residues and is reaching up to 700% compared to the pesticides solutions in a neat solvent. However, the responses of pesticides in matrix-matched standards at different concentration levels do not significantly change during 130 injections. Response enhancement/or decrease is influenced by the sample preparation technique. External calibration with matrix-matched calibration standards should, therefore, provide results with good precision also at the concentration level of 0.005 mg kg^{-1}. Special attention is given to the performance of the chromatographic column and retention gap with regards to peak widths, peak tailing and different sample preparation methods. During approximately 460 matrix sample injections, the performance of the analytical column was acceptable. GC–MS set-up with 0.15 mm i.d. column can be successfully utilized for the pesticide residues analysis.

Keywords: Fast GC–MS; Programmed temperature vaporizer; Pesticide residues; Matrix effects

1. Introduction

In multiresidue pesticides analysis used for an inspection of the presence and/or violation of maximum residual limit (MRLs) in a great number of pesticide residues, usually several chromatographic runs are necessary for qualitative and quantitative analyses. Analysis time with conventionally used 30 or 60 m long chromatographic columns with 0.25 μm i.d. may take longer than 1 h. The use of fast gas chromatography (GC) with run times in orders of minutes brings with it the promise of providing faster, more cost-effective analytical answers [1,2]. Another advantage of fast GC is that a total system can be better described if more analytical data are available. Many replicate analyses are performed in the same time that it would take to perform a single conventional GC run. This can be associated with better analytical precision [1]. The majority of papers published on the topic of fast GC methods present advantages, state-of-the-art of the instrumentation and future possibilities rather than the actual use of the fast GC in real-life applications [3].

In pesticide residues analysis the injected sample contains a large amount of unavoidably present co-extractives, which are responsible for matrix effects occurring on the injector, column and/or detector site [4]. In order to decrease the matrix effects on the detector site, efficient separation of analytes from the matrix components is important. It can be carried out using highly efficient columns. Therefore, the option of fast GC without a loss of the separation efficiency should be employed, fast GC utilizing narrow-bore capillary columns [1,2]. However, they suffer from low capacity that may sooner affect the column performance deterioration represented by the peak broadening, tailing, adsorption, reactivity and even ghost peaks [4]. Moreover, the pesticide residues analysis is, in addition, complicated by the co-injected matrix constituents responsible for the matrix induced chromatographic

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doi:10.1016/j.chroma.2004.10.043

response enhancement or a subsequent decrease of the response. Inlet systems and their operation have a significant influence on the performance of GC systems in the pesticide residues analysis, which was already studied on a conventional GC set-up. The worst performance was obtained in an on-column inlet system (14 injections, extract of wheat). A splitless inlet system operating with a pressure pulse provided a reasonable performance (87 injections); however, a programmed temperature vaporizer (PTV) in a solvent vent mode allowed up to 136 injections with reliable quantitation [5].

The fast GC with the splitless injection technique was already applied to compounds of a broad range of volatilities and polarities, including pesticides. Optimal conditions were found for good solute focusing and repeatability of the peak area measurements [6]. The fast GC-ECD was applied to real sample pesticide residues measurements [7]. For separation a narrow-bore column, 0.15 mm i.d. was chosen instead of 0.1 mm i.d. The 0.15 mm i.d. columns can be used in the majority of GC instruments, and they offer more flexibility with respect to the flow, sample transfer, loadability, type of detection systems and easier operation [6].

The aim of this work was to study the robustness and long term stability of the fast gas chromatography–mass spectrometry (GC–MS) system with a 0.15 mm i.d. capillary column equipped with PTV. It mainly focused on its tolerance towards co-injected matrix components in the analysis of real-life pesticide residues samples at ultra-trace concentration level.

2. Experimental

Chromatographic experiments were performed on a GC–MS Agilent 6890N equipped with a PTV, autoinjector Agilent 7683 and a Mass Selective Detector 5793 (MSD). A non-polar deactivated retention gap (1 m long, 0.32 mm i.d., Supelco, Bellefonte, USA) was coupled via a press-fit connector with a narrow-bore chromatographic column CP-Sil 8 CB Low-Bleed/MS (15 m long, 0.15 mm i.d., 0.15 μm film thickness) obtained from Varian (Middelburg, The Netherlands). Helium was used as a carrier gas. PTV was used in a cold splitless mode with the following temperature programme, 120 °C; hold, 0 min; ramp, 400 °C min^{-1} to 300 °C; hold, 1.2 min; then second temperature ramp, 100 °C min^{-1} to 350 °C to release the less volatiles from the deposit in the liner to the split vent (opened after 1.5 min, before the second temperature ramp started). The purge flow was set to 160 ml min^{-1}. An injection volume was 2 μl. Chromatographic separation was performed under a temperature programme, 100 °C; hold, 1.5 min; ramp, 30 °C min^{-1} to 290 °C; hold, 6 min and a constant carrier gas flow, 0.5 ml min^{-1}. MSD in an electron impact ionization mode (70 eV) was operated in selected ion monitoring mode (SIM). For each pesticide two specific ions were selected and sorted into groups by max. four ions, the used dwell time was 25 ms; pesticides were sorted according to the elution order into SIM groups presented in Table 1.

Pesticides belonging to different chemical classes were used (Table 1). Pesticides and PCB standards were obtained from different sources and were of purity >95%.

Table 1
List of pesticides, chemical classes, elution times, target and qualifier ions used for SIM, SIM groups start times and determination coefficients (from calibration)

Pesticide	Chemical class	Elution time (min)	Target, qualifier ions	SIM group start time (min)	$R^2_{toluene}$	R^2_{matrix}
Dimethoate	Organophosphate	5.86	*87*, **125**	3.00	0.9981	0.9994
Terbuthlyazine	Triazine	6.02	**214**, *229*	5.94	0.9968	0.9993
Diazinon	Organophosphate	6.02	*276*, **304**		0.9964	0.9993
Pyrimethanil	Anilinopyrimidine	6.11	**198**, *199*	6.06	0.9955	0.9993
Chlorpyrifos-methyl	Organophosphate	6.41	**286**, *288*	6.21	0.9961	0.9994
Fenitrothion	Organophosphate	6.62	*260*, **277**	6.51	0.9893	0.9995
Chlorpyrifos	Organophosphate	6.72	*286*, **314**		0.9969	0.9994
Cyprodinyl	Anilinopyrimidine	6.96	*224*, **225**	6.81	0.9979	0.9994
Penconazole	Triazole	7.00	**248**, *250*		0.9982	0.9993
Captan	Phtalimide	7.13	**79**, *264*	7.09	0.9968	0.9648
Methidathion	Organophosphate	7.18	**145**, *302*		0.9989	0.9994
Kresoxim-methyl	Oximinoacetate	7.41	**131**, *132*	7.26	0.9990	0.9991
Myclobutanil	Triazole	7.43	**179**, *245*		0.9990	0.9992
Tebuconazole	Triazole	8.03	**250**, *252*	7.51	0.9984	0.9993
Phosalone	Organophosphate	8.55	*182*, **367**	8.26	0.9984	0.9991
Bitertanol	Triazole	9.01 9.14	*168*, **170**	8.81	0.9975	0.9992
Cypermethrin	Pyrethroid	9.54 9.66 9.73	*163*, **181**	9.31	0.9987	0.9985
Etofenprox	Non-ester pyrethroid	9.85	**163**, *376*		0.9991	0.9989

Target ions data are in bold and the qualifier ions data are in italic. $R^2_{toluene}$, coefficients of determination obtained from calibration performed with standards in neat toluene; R^2_{matrix}, coefficient of determination obtained from calibration performed with matrix-matched standards.

For the sample preparation of apple samples two different methods were used. The apple samples were prepared by a modified procedure [8] described by Schenck et al. [9] based on an acetonitrile extraction followed by salting out and purification on SPE–NH_2 columns and solvent exchange to toluene; 1 ml of a final solution corresponds to 2.5 g of the apple sample. For comparison, the QuEChERS method published by Anastassiades et al. [10] based on acetonitrile extraction and dispersive SPE cleaning with PSA sorbent without any solvent exchange step was utilized. A volume of 1 ml of the final solution in acetonitrile corresponds to 1 g of the sample.

Apples free of pesticide residues were obtained from field experiments where no chemical treatment was applied. Purity of apple samples was confirmed by GC–MS.

A stock solution of pesticide standards was prepared in a toluene at a concentration of 0.5 mg ml^{-1}. Solutions of standards in a neat toluene were prepared by adding the appropriate volume of the stock solution of pesticide standards to the neat toluene. 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 first method (with SPE clean-up). Similarly, control matrix-matched standards were prepared by adding the appropriate volume of the pesticide standard stock and a PCB standards solution to the extract of the blank apple sample prepared by the first method.

3. Results and discussion

Measurements were performed under the conditions of the fast GC with optimized settings of cold splitless PTV, as described in Section 2. Special attention was given to the optimization of quadrupole MS in SIM. For each pesticide, two ions were selected with regards to the background noise and S/N ratio of a blank apple matrix extract compared to spiked samples at the lowest concentration studied (0.0125 ng μl^{-1}). Dwell time of 25 ms was selected according to the sufficient number of data points per peak obtained and good repeatability of the peak area measurements [11]. To decrease the number of active sites in the chromatographic system and to stabilize the system, a blank apple matrix prepared by the first method was injected five times before any set of measurements with the matrix. All set of measurements of standards prepared in neat toluene without the presence of any matrix was performed with a new liner and retention gap to eliminate the influence of matrix low and non-volatile components.

3.1. Calibration

Parameters such as linearity and repeatability of responses were studied in a wide range of concentrations of pesticides in calibration standards prepared in neat toluene and a blank apple matrix extract, matrix-matched calibration standards.

Calibration was performed with solutions of standards prepared in neat toluene at the following concentration levels: 0.0125, 0.025, 0.125, 0.25, 1.25, 2.5 ng μl^{-1}. Each concentration was measured five times. The values of the determination coefficient (R^2) are presented in Table 1. They are worse compared to the measurements of matrix-matched standards except of captan, cypermethrin and etofenprox. Repeatability of the peak areas expressed as relative standard deviation (R.S.D.) in range from 0.48 up to 17%, however, R.S.D.s are not significantly dependent on the concentration injected.

Similarly, calibration was performed with matrix-matched standards. For the calibration, the same concentration levels were used, which corresponds to 0.005–1 mg kg^{-1} of pesticide residues in the original apple sample, $n = 5$. Linearity of responses was proved by the determination coefficient (R^2) ranging from 0.9995 for fenitrothion to 0.9985 for cypermethrin and thermally labile captan 0.9648, as shown in Table 1. Repeatability of the peak areas expressed as R.S.D. ($n = 5$) was as expected, slightly worse for the lowest concentration level corresponding to 0.005 mg kg^{-1} of pesticide residues typically ranging from 1.7 to 6.6%. For the higher concentration levels, R.S.D. were generally in the ranges 0.5–4.8% for all pesticides except captan.

3.2. Chromatographic matrix induced response enhancement

The importance of chromatographic matrix induced response enhancement is illustrated in Fig. 1, where extracted ion chromatograms ($n = 5$) of several pesticides obtained from the standard solution in neat toluene (lower responses) is overlaid with matrix-matched calibration standard chromatograms (higher responses) of the same concentration injected under identical conditions ($n = 5$).

The whole series of measurements of matrix-matched standards were performed in the order of increasing concentration. After measurements of the highest concentration 2.5 ng μl^{-1}, the solution with the lowest concentration 0.0125 ng μl^{-1} was re-measured. The differences in the peak areas between the 1st measurements and the latest were very low; the maximal difference observed was 11% for myclobutanil.

In Table 2, the average peak areas of the studied pesticides in matrix-matched standard are expressed as a relative peak area to standards prepared in neat toluene in percentage. As can be seen, chromatographic induced response enhancement is very dependent on the concentration of solutes. For the lowest concentration level (0.0125 ng μl^{-1}, corresponding to 0.005 mg kg^{-1} in original sample), the enhancement is very strong for all studied pesticides and is reaching up to 700% for bitertanol. However, for the highest concentrations studied (1.25 and 2.5 ng μl^{-1}) the presence of matrix constituents had also an adverse effect on the peak areas. Response enhancement induced in the inlet caused by the deactivation of the liner surface by the present matrix

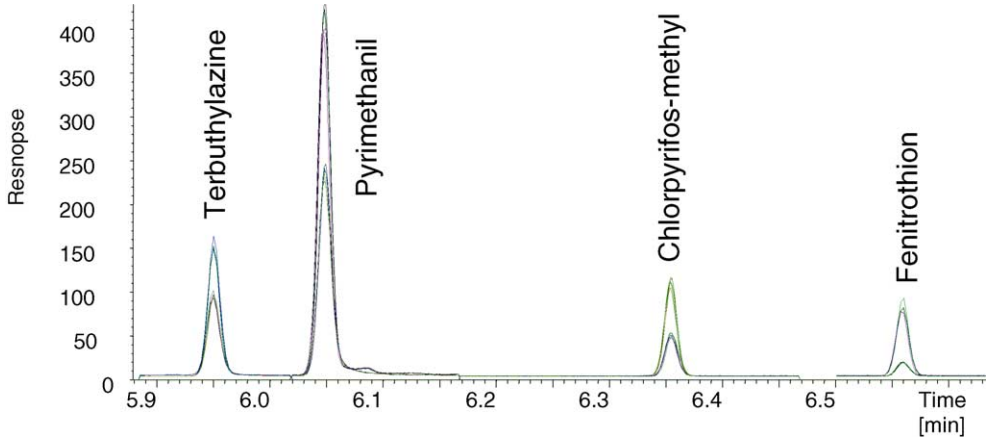

Fig. 1. Overlaid chromatograms ($n = 5$) of selected pesticide standards prepared in neat toluene (lower responses) and standards prepared in blank apple matrix-matched standards, matrix-matched calibration standards; both at concentration level 0.0125 ng μl^{-1}, corresponding to 0.005 mg kg^{-1} in apple sample.

should be characterized mainly by the increase of the peak area and peak height if the peak tailing is not excessive. Response enhancement induced by the column deactivation or by the protective effect of co-eluting matrix components is supposed to be characterized by the decreased peak tailing as adsorption is moderated [12]. In Table 3, the relative average peak heights of matrix-matched standards to the standards prepared in neat toluene ($n = 5$) expressed in percentage are shown. The highest values of the peaks heights increase are observed for the following pesticides: dimethoate, fenitrothion, methidathion, myclobutanil, tebuconazole phosalone and bitertanol (Table 2). For the majority of the mentioned compounds also the increase of the peak areas was observed (Table 3). In Table 4, the average tailing factors calculated at 10% of the peak height are presented for selected pesticides ($n = 5$). Calculation of tailing factors was not possible in all cases, because baseline-to-baseline separation of pesticides from the matrix background or isomers was not always reached (the baseline was disturbed by the matrix mainly at low analytes concentrations). Generally, the peak tailing is decreasing if matrix is present or pesticides are present at higher concentrations. The highest improvement of the peak tailing is gained for penconazole, myclobutanil and etofenprox. As can be seen by comparison of the results in Tables 2–4, the response enhancement is for some pesticides

Table 2
Dependence of chromatographic matrix induced response enhancement on concentration of pesticides measured, expressed as relative peak area of matrix-matched standard to standard prepared in neat toluene ($n = 5$)

Pesticide	Concentration (ng μl^{-1})					
	0.0125	0.025	0.125	0.25	1.25	2.5
Dimethoate	419.7	295.5	209.6	152.9	101.0	89.2
Terbuthylazine	150.2	144.0	129.6	112.3	91.8	76.5
Diazinone	178.7	177.5	148.9	125.3	95.9	79.6
Pyrimethanil	155.8	153.8	134.5	115.2	91.5	74.2
Chlorpyrifos-methyl	227.8	227.6	188.2	152.0	102.9	85.8
Fenitrothion	489.3	487.8	414.1	288.8	130.1	101.0
Chlorpyrifos	228.6	229.3	188.9	148.3	106.0	89.6
Cyprodinyl	163.2	168.1	150.2	118.9	98.3	84.2
Penconazole	198.4	203.7	167.4	130.4	103.8	89.9
Captan	–	–	23.8	18.05	18.4	22.3
Methidathion	332.3	307.5	192.4	135.8	99.9	90.0
Kresoxim-methyl	218.6	220.4	161.1	129.4	107.2	94.8
Myclobuthanil	438.7	350.8	190.4	141.8	107.8	95.2
Tebuconazole	464.5	433.5	279.0	194.5	127.5	113.2
Phosalone	367.5	377.1	237.8	165.3	112.6	99.3
Bitertanol 1	758.2	700.8	531.1	293.2	160.5	150.9
Bitertanol 2	772.3	709.7	393.6	219.9	111.0	116.8
Cypermethrin 1	378.7	380.0	317.6	193.3	140.1	126.9
Cypermethrin 2	395.7	346.6	278.3	161.6	119.7	104.4
Cypermethrin 3	571.1	419.1	253.9	153.3	113.9	96.0
Etofenprox	222.9	202.7	153.1	131.5	113.7	99.7

The data represent the average peak area (%).

Table 3
Relative average ($n = 5$) peak heights of matrix-matched standards to standards prepared in the neat toluene expressed in percentage

Pesticide	Concentration (ng μl^{-1})		
	0.0125	0.125	1.25
Dimethoate	303.2	244.5	103.2
Terbutylazine	162.0	138.4	90.7
Diazinone	175.7	148.9	96.8
Pyrimethanil	175.2	143.4	91.4
Chlorpyrifos-methyl	227.3	193.2	101.7
Fenitrothion	492.4	420.8	120.8
Chlorpyrifos	230.4	191.1	107.4
Cyprodinyl	210.3	167.1	101.5
Penconazole	272.5	238.4	122.2
Captan	–	36.2	18.6
Methidathion	373.9	213.5	102.0
Kresoxim-methyl	247.5	178.2	108.8
Myclobuthanil	530.4	260.6	127.5
Tebuconazole	525.4	398.3	174.4
Phosalone	404.2	276.0	126.5
Bitertanol 1	797.0	639.9	185.0
Bitertanol 2	803.4	549.1	173.7
Cypermethrin 1	351.2	376.0	193.8
Cypermethrin 2	376.6	338.2	174.3
Cypermethrin 3	382.8	315.5	163.1
Etofenprox	287.8	264.0	181.8

The data represent the ratio, $H_{matrix}/H_{toluene}$; H_{matrix}, peak height of pesticide obtained from matrix-matched standard; $H_{toluene}$, peak height of pesticide obtained from solution of standards in the neat toluene.

Table 4
Average tailing factors ($n = 5$) calculated at 10% of the peak height for selected pesticides at different concentration levels of solutions prepared in the neat toluene and matrix-matched standards

Pesticide	Concentration (ng μl^{-1})					
	0.0125		0.125		1.25	
	Toluene	Matrix	Toluene	Matrix	Toluene	Matrix
Terbuthylazine	1.114	1.1	1.08	1.03	0.95	0.94
Diazinon	0.97	0.95	1.02	1.03	1.03	1.03
Pyrimethanil	1.21	1.03	1.23	0.99	0.94	0.95
Chlorpyrifos-methyl	1.00	0.97	1.10	1.01	0.99	0.97
Fenitrothion	1.00	0.98	0.99	0.95	1.12	1.10
Chlorpyrifos	1.09	1.13	1.19	1.13	0.96	0.96
Cyprodynil	1.39	1.23	1.01	0.92	1.03	1.08
Penconazole	2.35	1.42	2.03	1.22	1.45	0.99
Methidathion	1.24	0.92	1.23	0.92	0.89	0.88
Kresoxim-methyl	1.32	0.98	1.05	1.08	1.03	0.89
Myclobutanil	2.59	1.41	2.30	1.04	1.44	0.99
Phosalone	1.34	1.12	1.12	1.06	1.22	0.93
Etofenprox	3.05	1.55	2.99	1.18	2.51	0.99

caused preferably by the deactivation of the inlet surface with matrix components as the peak areas and heights increased compared to the measurements in neat toluene, while the peak shapes expressed as tailing are not significantly influenced (terbuthylazine, diazinon, chlorpyrifos-methyl, fenitrothion, chlorpyrifos, cyprodinyl). For other pesticides, the peak tailing is improved significantly, while the peak area is increased to a lower extent (penconazole, myclobutanil and etofenprox).

The situation is different for pesticide captan, which undergoes decomposition in the inlet [13].

3.3. Influence of matrix co-extractants on analytes responses

The study of the influence of the co-injected matrix co-extractants amount characterized by the number of injections performed on peak areas and their repeatability is important for the routine performance of a quantitative analysis.

To check the reproducibility of measured parameters, a special control matrix-matched standard of pesticides fortified with PCB 149 at two concentration levels was used. PCB 149 was added for the verification of results as PCBs are significantly less polar than pesticides and the influence of the chromatographic matrix induced response enhancement is not expected to such an extent as for polar pesticides.

Before any sequence of measurements, the blank apple matrix was injected five times to decrease the number of active sites in an inlet and a column. Then, the set of pesticides control matrix-matched standards at two different concentration levels 0.025 and 1.75 ng μl^{-1} with added PCB 149 were injected in triplicate. Afterwards the real samples were analyzed, always in pairs with the matrix-matched calibration standard (number of measurements $n = 3$ for each vial). The pairs of analytes and their matrix-matched standards rotated with control matrix standards in the sequence. In Figs. 2 and 3, the average peak areas ($n = 3$) of control matrix-matched standards for sequences consisting of 130 injections with one retention gap and 70 injections after the retention gap exchange are presented at a lower (Fig. 2) and a higher (Fig. 3) concentration level.

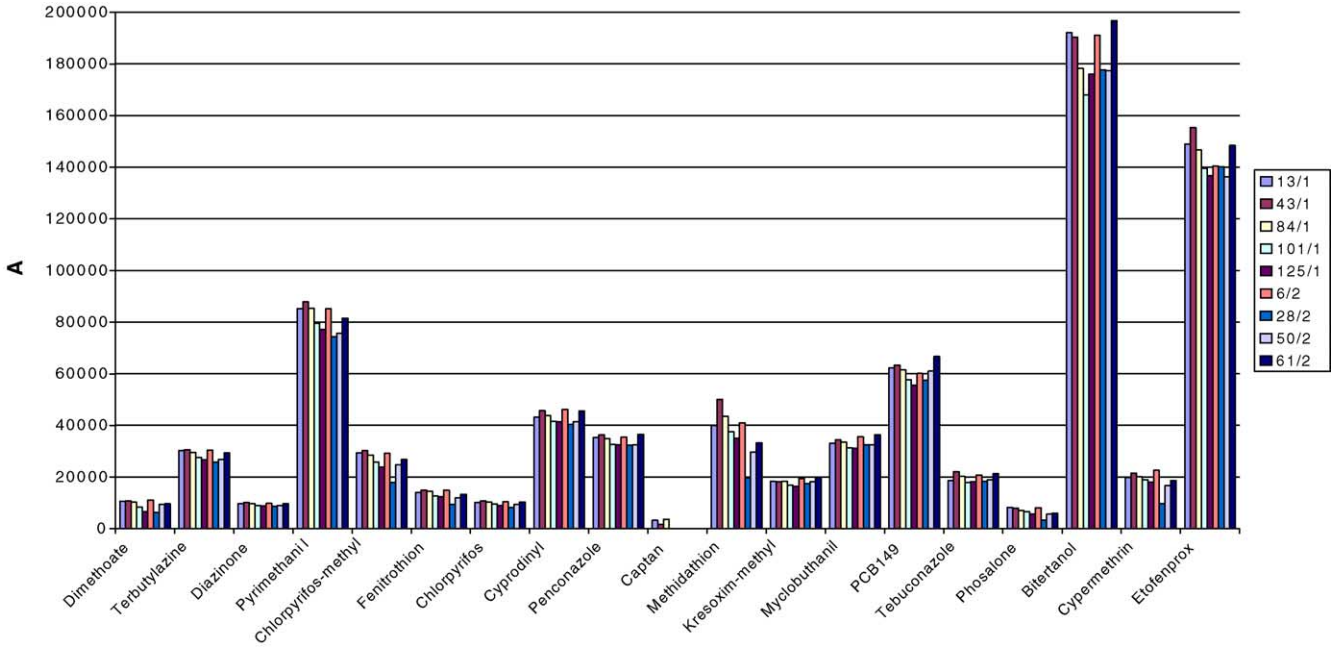

Fig. 2. Dependence of average peak areas of the control matrix-matched standards with concentration 0.025 ng μl^{-1} (corresponds to concentration 0.01 mg kg^{-1} before sample preparation) injected between analyses of real samples, $n = 3$, number of injections/retention gap.

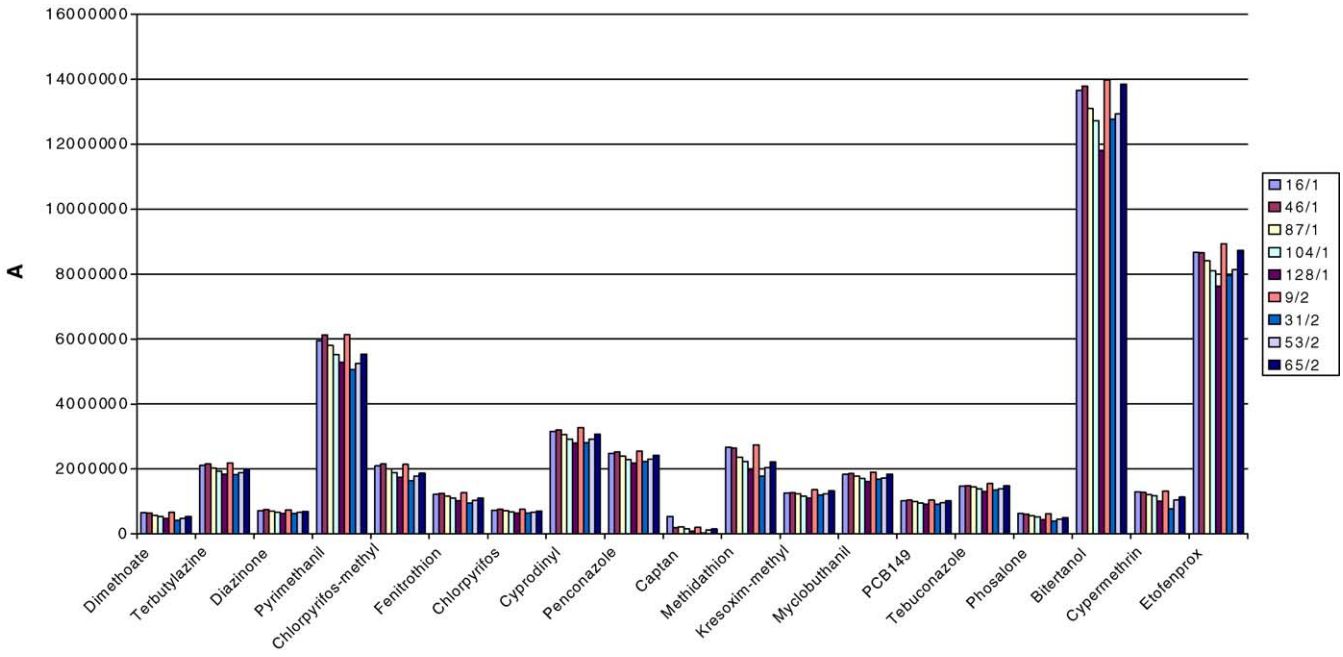

Fig. 3. Dependence of average peak areas of the control matrix-matched standards with concentration 1.75 ng μl^{-1} (corresponds to concentration 0.7 mg kg^{-1} before sample preparation) injected between analyses of real samples, $n = 3$, number of injections/retention gap.

Up to about first 40 injections the peak areas negligibly increased (except of captan, phosalone and biteranol) which is a consequence of the chromatographic matrix induced response enhancement. The increase of the peak area is not significant as it is represented at the most by 5%. The following decrease of the majority of analytes peak areas (Fig. 2: injections 84/1, 101/1, 125/1; Fig. 3: injections 87/1, 104/1, 128/1) is caused by the sorption of analytes by the deposit of non-volatile residues in the liner and the retention gap. This was verified as after the replacement of the retention gap and the liner after 130 runs the responses were close to the initial ones.

After the retention gap was changed, again the control matrix-matched standards prepared in toluene were injected (denominated in Fig. 2: 6/2; in Fig. 3: 9/2) and followed by the samples prepared by the QuEChERS method published by Anastassiades et al. [10] (in acetonitrile) which were then analyzed under identical conditions. As can be seen from the following injections of control matrix-matched standards, a significant decrease of the peak areas occurs for several compounds, mainly for chlorpyfos-methyl, methidathion and cypermethrin (Fig. 2: injection 28/2; Fig. 3: injection 31/2). In the QuEChERS method, no solvent exchange step is involved. The injection solvent is acetonitrile, which contains also residual water (after drying with $MgSO_4$) that is supposed to be responsible for the creation of active sites in the chromatographic system; and thus, increasing the polar pesticides adsorption and a subsequent peak areas decrease.

After the control matrix-matched standard analyses in the range of 28–33 injections with the changed retention gap, again real samples prepared by the initial method (solvent exchange to toluene) were analyzed and the peak areas increased as active sites were deactivated by matrix constituents. Similar behaviour of pesticides was observed for both concentration levels of pesticides control matrix-matched standards (Fig. 2: injections 50/2, 61/2; Fig. 3: injections 53/2, 65/2).

The peak areas decrease and/or increase is more significant for the lower concentration level measurements. Only captan, as the most troublesome pesticide in our selection, significantly decomposed in the inlet and its peak completely disappeared after 50 injections for the lower concentration control standard with the first retention gap. In the case of the second retention gap, the condition of the inlet liner when "dirtier" samples were measured was poor to preserve captan from decomposition.

Repeatability of the peak areas expressed as R.S.D. was found to be generally in the ranges 0.1–4% for all compounds except captan ($n = 3$) for control matrix-matched standards at both concentration levels. The presented results have shown that external calibration with matrix-matched standards can be successfully utilized to obtain correct results of quantitative analysis.

3.4. Influence of matrix co-extractants on column performance

The studied parameters were peak half widths, peak tailing factors, retention times and target/qualifier ion ratios. According to the classification of faster GC analysis according to van Deursen et al. [14], the peak half width in fast GC is in the range of 0.2–3 s. The peak half widths of pesticides

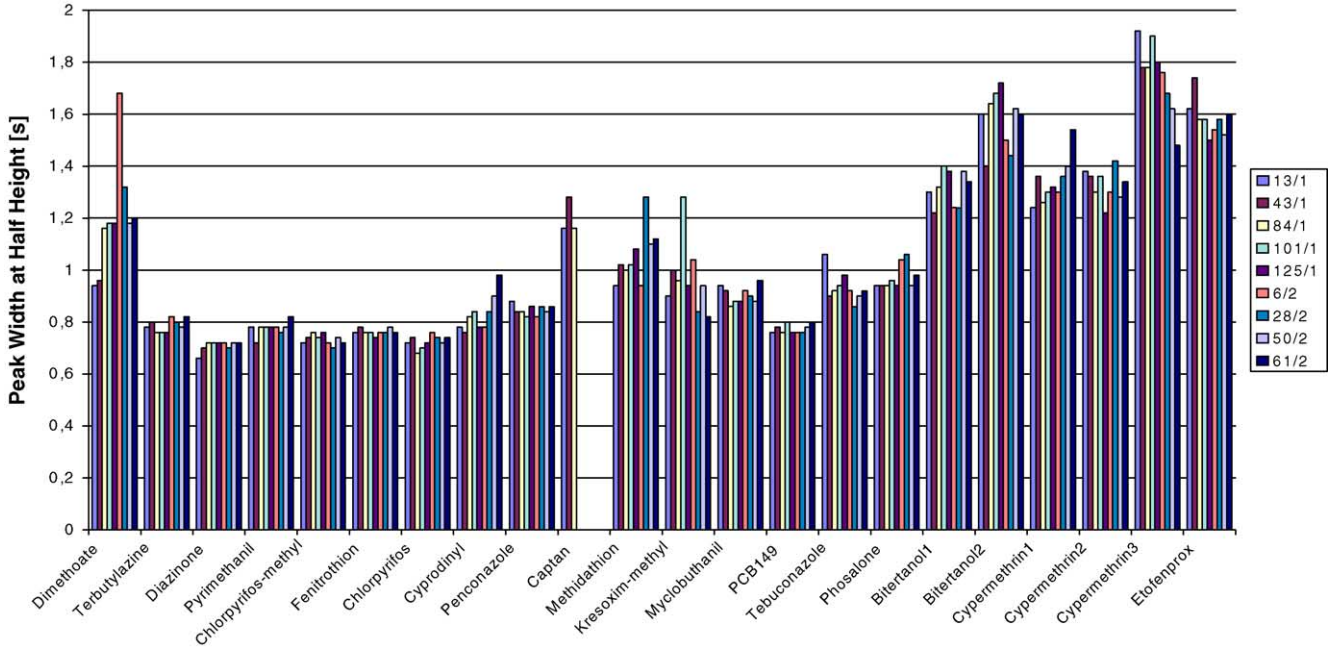

Fig. 4. Dependence of average peak widths at half height of pesticides on number of performed injections studied at concentration of control matrix-matched standard 0.025 ng μl^{-1} ($n = 3$).

studied were compounds-dependent and were in the range of 0.75–1.8 s. The peak half widths are influenced mainly by overloading the analytical column or by adsorption, which may occur on active sites or non-volatile matrix components.

The dependence of the peak half widths values on the number of injections was characterized by the control matrix-matched standards (as described above). The results are presented in Fig. 4. The most of the peak half widths were not significantly changing during the experiment consisting of 200 injections for both measured concentrations of control standards.

Some changes are noticeable, but mainly for thermally unstable captan and for cypermethrin and dimethoate as a result of a lack of sufficiently selective ions resulting in difficult integration. Noticeable peak broadening and peak area decrease occurs for methidathion after the samples with residual water were measured.

Also, peak tailing factors calculated at 10% of the peak height were evaluated for the lower concentration of the matrix-matched control standard (0.025 ng μl^{-1}). Tailing factors were not significantly influenced by the number of injections performed (200), but they were improved in comparison to toluene neat standard solutions in terms of the discussion above.

Retention times of the compounds analyzed were moderately shifting but differently for various compounds during the experiment with a very small effect of retention gap exchange. This is the most probably caused by changing physico-chemical properties of the stationary phase of the analytical column by the less-volatile residues; and thus, changing the selectivity of the used system. The change of the retention time was in the order of 1–2 s within 200 injections and no change of elution order was observed.

The improved stability of the used chromatographic system in comparison to conventional GC set-up [5] is supposed to be caused first by the elimination of the less volatile compounds to the split vent increasing the final temperature of PTV after opening the splitless vent. Another important parameter seems to be the prolonged isothermal period at the end of the oven temperature programming enabling the elution of the majority of semivolatile matrix components injected. The elution time of the last pesticide etofenprox was 10 min, but additional 6 min were necessary to obtain a relatively stable baseline without any further large peaks, low volatile matrix components, which is approximately half of the run time needed for the last pesticide elution. When compared to conventional GC, additional approximately 30 min would be needed. An important parameter influencing the performance of fast GC system is also the sample preparation procedure and the purity of the final extract, mainly with regards to the content of water.

The ratios of the target to the qualifier ions were also evaluated as they serve for identification purposes when SIM mode is used. The ions ratios were slightly dependent on the concentration injected, which leads to the need to use some medium concentration for setting the ion ratio values. The ratios were constant during all 200 injections. Better repeatability was observed for the control matrix-standard with the higher concentration 1.75 ng μl^{-1} (less than 4% R.S.D., $n = 3$) when compared to the lower concentration level 0.025 ng μl^{-1} (less than 14% R.S.D., $n = 3$).

4. Conclusions

The fast GC–MS on 0.15 mm i.d. capillary columns has provided good ruggedness for such a fairly complicated analysis as a pesticide residues analysis in a plant matrix is. The chromatographic matrix induced response enhancement effect is, at very low concentration levels, reaching up to 700% when responses of the matrix-matched calibration standards are compared to standards prepared in neat toluene. Response enhancement is caused primary by the deactivation of active sites in the inlet but some improvements of the peak shapes were observed also under the protective effect of co-eluting matrix components in the analytical column and retention gap.

For acceptable stability of the signal obtained, sample preparation procedure plays an important role. Responses of the pesticides investigated are changing only moderately with the number of injections of well-purified samples. Therefore, calibration with an external standard should provide sufficiently precise results. PTV inlet in the cold splitless mode under optimized conditions provided sample vaporization and sample transfer into the column with excellent repeatability. Repeatability of the peak areas (expressed as R.S.D.) at the lowest concentration level was not exceeding 6.6%.

Stability of the separation system verified by peak widths is also acceptable. It is important for holding column efficiency and, consequently, analytes separation from matrix components and quality of the obtained signal. A slower vaporization process in the PTV inlet is also responsible for a lower amount of very low volatile sample constituents vaporized and transferred to the column when compared to the classical hot splitless inlet, and so the lifetime of the retention gap and the analytical column is increased. Approximately 460 injections of real sample extracts have been performed with only mild deterioration of 0.15 mm ID CP-Sil 8 CB Low-Bleed/MS column performance. Common maintenance such as the inlet liner and retention gap exchange is necessary after approximately 120–150 injections.

The concentration levels investigated correspond to the ultra-trace concentration of pesticides in apples that are also covering the MRLs of pesticides in baby-food. The presented fast GC–MS setup provided very good performance with the run time of 16 min. LODs and LOQs less than 0.005 mg kg^{-1} were reached for all pesticides except thermolabile captan [7]. Fast GC–MS utilizing narrow-bore columns with 0.15 mm i.d. can be successfully utilized for pesticide residues analysis.

Acknowledgements

The authors gratefully acknowledge the support of a part of this research within the framework of the Slovak Grant Agency (Vega, Project No. 1/9126/02) and NATO Project No. SfP 977983.

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