6

Fast Gas Chromatography and Its Use in Pesticide Residues Analysis

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1. Introduction

Pesticides have been worldwide used for the protection of food crops against pests and diseases. It is common that residues of these pesticides occur in food products, especially agricultural commodities. Adverse effects on human health of pesticides residues remaining in food after they are applied to food crops are generally known. Possible health risk due to pesticide residues in the diet has deeply modified the strategy for the crop protection, with emphasis on food quality and safety. The widespread concern for the health of society led to the strict regulation of maximum residue limits (MRLs) of pesticide residues in food commodities. There are various organizations that set maximum residue limits (MRLs), such as European Commission (EC), Codex Alimentarius or national governments in Australia, Canada, Japan, USA, etc. Individual limits for different active substance per food commodity combinations are being set by EC within the range of 0.0008-50 $mg.kg^{-1}$ (Directive 91/414/EEC). Newly discovered ecotoxicological problems, particularly the knowledge on endocrine disrupting effects (Colborn et al., 1993; Lintelmann et al., 2003) related also to pesticide residues, emphasise the acute requirement of analytical methods development with increased sensitivity and reliability for monitoring, confirmation and quantification of lower residue levels. Analysis close to these levels corresponds to the ultra-trace analysis. This calls for urgent attention in two areas: (a) legislative requirements continuously decreasing the maximum acceptable concentration levels in food, and (b) the apparent importance of methods development in the area of pesticide residues analysis. The urgent requirement for low-level analyses promotes also contribution to the science – in the field of separation methods for ultra-trace analysis of organic pollutants in complex mixtures. The method development heads to speeding up the analysis (what leads to reduction of financial demands) while preserving the efficiency of conventional approaches or getting even better efficiency. In pesticide residues analysis additionally there is ever increasing interest to analyse as many analytes as possible in a single analysis. In the case of semivolatile pesticide residues analysis gas chromatography (GC) still plays an important role. Scientifically valid methods for the analysis at low concentration levels are currently still often very close to limits of detections (LODs). The most efficient approach to pesticide analysis involves the use of multiclass, multiresidue methods (MRMs). The sample preparation procedure should be taken into consideration together with the chromatographic analysis and detection in many aspects, mainly in limit of quantifications (LOQs) and selectivity. In multiresidue pesticides analysis used for an inspection of the

presence and/or violation of MRLs in a great number of pesticide residues, usually several chromatographic runs are necessary for qualitative and quantitative analyses. Positive samples exceeding the MRLs value require a subsequent confirmation. Nowadays, the use of mass spectrometry as universal detection method that has identification capability with mass spectral information and high selectivity with extracted ion trace or selected ion monitoring seems to become indispensable for identification purposes.

Gas chromatography – mass spectrometry (GC-MS) with electron ionization (EI) and the combination of liquid chromatography (LC) with tandem mass spectrometry (LC-MS/MS) using electrospray ionization (ESI) are identified as techniques most often applied in multi-residue methods for pesticides at present (Alder et al., 2006). For GC-amenable semivolatile pesticides GC methods are still preferred over LC (liquid chromatography) methods due to higher resolution. After a major advance of recent years in ultra-high performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS), which have been demonstrated to reliably quantify and identify hundreds of pesticides in less than 10 min (Romero-Gonzalez et al., 2008), the establishment of faster GC methods instead of conventional GC methods reaching separation in 25-45 min is a necessary continuation of the development. Especially fast GC techniques satisfy the present-day demands on faster and cost-effective analysis (Korytár et al., 2002; Dömötörová & Matisová, 2008). Analysis time and the cost are the most important aspects that should be considered in the choice of analytical method in routine application.

This contribution is devoted to the fast gas chromatography in pesticide residues analysis. Classification according to the GC speeding-up strategies is mentioned and the main part of the chapter is devoted to the fast GC in the analysis of pesticide residues with the use of narrow-bore columns (internal diameter I.D. <0.2 mm). Specificity of pesticide residues analysis as well as problems associated with analysis of pesticides in general are discussed. Sample preparation mainly from the point of view of time requirements and feasibility for fast GC is briefly outlined. Special attention to the selectivity enhancement by the negative chemical ionization approach is devoted. Applicability of fast GC for pesticide residues in real-life samples is demonstrated.

2. Classification of faster GC

During the last decade fast GC has acquired a real importance in the pesticide residues analysis. Classification of faster GC based on speed enhancement factor was suggested by Dagan & Amirav, 1996 and the terms fast GC, very fast GC and ultrafast GC are commonly used at present days. The speed enhancement factor shows the gain in speed compared to conventional capillary GC. Van Deursen et al., 2000 suggested a classification based on the peak half width and the total analysis time. Every reduction of analysis time results in an identical reduction of the chromatographic zone width due to the shorter residence time of the components in the column. It is reasonable to use a definition that takes account of the degree of separation per time. In classification, valuable information based on a peak width is very useful also from the point of view of the major requirements for instrumentation. The summarisation of both approaches to the classification of faster GC is in Table 1.

Nowadays fast GC can be performed on commercial gas chromatographs, which are standard equipped with high-speed injection systems, electronic gas pressure control, rapid oven heating/cooling and fast detection (Korytár et al., 2002, Matisová & Dömötörová, 2003). Fast GC technique has been established to real sample analysis very slowly. In the last

few years the number of publications offering application of fast GC in real analysis has increased (Dömötörová & Matisová, 2008, Donatao et al., 2007).

Type of analysis	Analysis time range	Peak width at half height	SEF	Efficiency (N)
fast	minutes	1-3 s	5-30	≥comparable to conventional GC
very fast	seconds	30-200 ms	30-400	25 000
ultra fast	sub-seconds	5-30 ms	400-4000	7 000

SEF – speed enhancement factor, N – plate number

Table 1. Classification of faster capillary GC.

3. Strategies of fast GC

Numerous options exist for pushing the speed of capillary gas chromatography as it was summarized in a few reviews (Matisová & Dömötörová, 2003; Dömötörová & Matisová, 2008; Maštovská & Lehotay, 2003). The most often approaches use i) narrow-bore columns, ii) fast temperature programming, iii) low-pressure gas chromatography (LP-GC), or iv) comprehensive GCxGC.

3.1 Narrow-bore columns

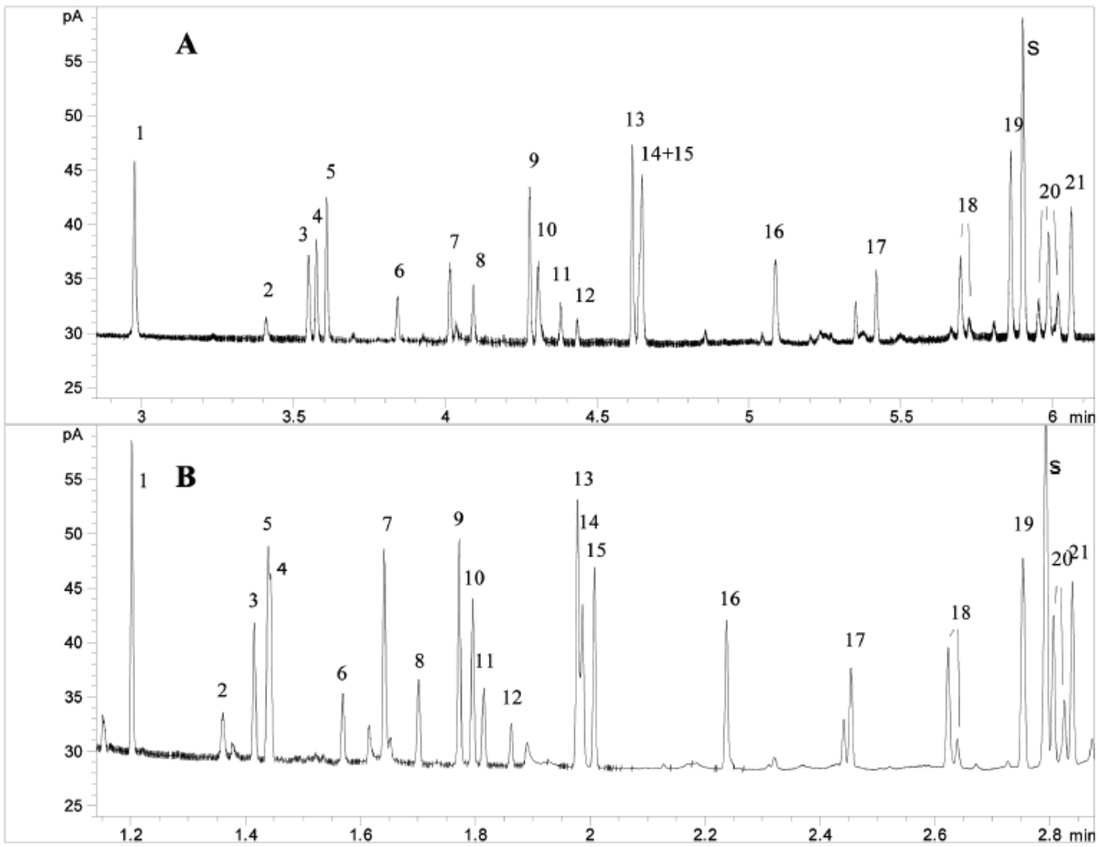
According to recent review by Donato et al., 2007, the wide majority of high-speed GC applications described in literature have been carried out by means of reduced columns I.D. (internal diameter). The reduction of column I.D. is usually combined with strategies as: changing column geometry (column shortening approach, thinner stationary phase), or its operating parameters (higher heating rates, above optimum carrier gas flow rate and in some cases usage of hydrogen as a carrier gas) what corresponds to the theoretical concept for the practical optimization of analysis speed of routine fast GC proposed by Klee & Blumberg, 2002. Theory of capillary gas chromatography has already demonstrated that the application of narrow-bore capillary columns has a number of advantages. Reduction of the column diameter can increase the efficiency (and consequently, the resolution) and drastically reduces analysis times. When the I.D. is reduced, optimal average linear velocity is also faster, what additionally contributes to the higher speed of analysis. The penalty to be paid is a much lower sample capacity which may result in higher LODs and LOQs and related higher maintenance frequency is needed.

The list of latest applications of narrow-bore fast GC for analysis of pesticide residues in food samples is given in Table 2. Various groups of pesticides were investigated by fast GC, for instance carbamate, organochlorine, organophosphorous, organothiophosphate, organotin, triazine and others. Prior to GC analysis, pesticide samples (standard solutions or extracts) were injected to the system using split, splitless, on-column or PTV (programmed temperature vaporization) injector mainly in cold splitless or in solvent vent mode. Helium and exceptionally hydrogen were the most frequently used carrier gases. MS detector in SIM mode is used preferably, specific and selective detectors as ECD (electron capture detector) and universal as FID (flame ionization detector) are also used.

Inlet systems and their operation have a significant effect on the performance of GC systems in pesticide residues analysis. The most frequently used technique of injection in trace analysis is a classic hot splitless injection. This injection technique has been employed in GC analysis due to its robustness. It has some restrictions such as small sample capacity and it may have a negative affect on results of quantitative analysis of pesticide residues, including discrimination, adsorption and degradation of analytes, which can subsequently influence the sensitivity. It was shown by Kirchner et al., 2004 that for the compounds with a broad range of volatilities and polarities good solute focusing and repeatability of the peak area measurements was obtained. Additionally, the pre-column to protect the analytical column from excessive contamination was suggested. However, PTV injector provides the best protection against effects of co-extracted compounds and operating in solvent vent mode allows even larger sample volume introduction resulting in excellent LOQs. It significantly eliminates matrix effects by releasing high-boiling co-extracted compounds through the split vent and/or trapping in a liner. Hada et al., 2000 showed that PTV with solvent vent mode was useful for large-volume injection (40 µl) into a narrow-bore capillary column because the injected solvent volume could be reduced to less than 2 µl. The introduction of a large sample volume is a simple and efficient way to increase sensitivity and useful way to analyze low-level concentrations. This approach is utilisable mainly for relatively "clean" matrices.

For a number of reasons (as sample capacity, inlet pressure values required, temperature-programmable rates), 0.1 mm I.D. columns seem to represent the current limit for the routine use (Matisová & Dömötörová, 2003). Properties of two narrow columns with I.D.s of 0.15 and 0.1 mm (15 m length and 0.15 µm film thickness, resp. 10 m length and 0.10 µm film thickness) compared Dömötörová et al., 2006 with regards to their advantages, practical limitations and applicability for fast GC on commercially available instrumentation. The two columns have the same phase ratio and the same separation power (length to I.D. ratio) to allow the method translation with preserved resolution (Klee & Blumberg, 2002). 0.1 mm I.D. column provided speed gain of 1.74 and significantly narrower peaks, but all other parameters investigated were better for 0.15 mm I.D. column concerning more efficient sample transfer from inlet to the column using splitless injection. Comparison of pesticides separation on columns with different I.D.s is shown in Fig. 1. Better sample capacity (3 times higher for 0.15 mm than for 0.10 mm I.D. column) resulted in improved ruggedness (up to 450 matrix sample injections with acceptable performance of analytical column (Kirchner et al., 2005 *a*) and simpler fast GC- MS method development. The use of 0.1 mm I.D. column in comparison to conventional one increased the detection limit as the peaks become sharper (Kempe & Baier, 2002).

Trends in GC are ever-increasing need for positive identification and for more flexible methods that enable analysis of a wide variety of samples in one system. These trends clearly result in the need for MS detection (van Deursen et al., 2000), because it enables structural elucidation for analyte identification. To obtain the low LODs and LOQs required for regulation purposes, selected ion monitoring (SIM) must be used. Unfortunately, when this sensitive mode of detection is used a part of the spectral information is lost. TOF is generally considered to be the detector of choice for applications with columns of I.D. ≥ 0.1 to < 0.2 mm (Maštovská & Lehotay, 2003) due to their fast data acquisition rates reaching up to 500 Hz and the subsequent possibilities of chromatographic and spectral deconvolution.



Elution order (1) C_{16}, (2) dimethoate, (3) terbutylazine, (4) diazinon, (5) pyrimethanil, (6) chlorpyrifos-methyl, (7) fenitrothion, (8) chlorpyrifos, (9) cyprodinyl, (10) penconazole, (11) captan, (12) methidathion, (13) C_{22}, (14) kresoxim-methyl, (15) myclobutanil, (16) tebuconazole, (17) phosalone, (18) bitertanol, (19) C_{28}, (20) cypermethrin, (21) ethofenprox; S, impurity from solvent.

Fig. 1. Chromatogram of GC-FID analysis of n-alkanes and pesticides in toluene on the narrow-bore column CP-Sil 8 CB (A) 15 m x 0.15 mm I.D. x 15 µm. (B) 10 m x 0.1 mm I.D. x 10 µm. Injected volume 2 µl of solution 0.25 ng.µl^{-1} of each analyt in toluene. (Dömötörová et al., 2006).

Quadrupole instruments have been most widely used with conventional capillary GC. Dalüge et al., 2002 utilized quadrupole MS as a detector in the resistively heated GC, the scan speed of the quadrupole mass spectrometer (16 spectra per second in the range m/z 50-310) was found to be sufficient for a proper reconstruction of the chromatographic peaks, and good-quality mass spectra were obtained. Six scans across a peak were sufficient for peak integration. In pesticide residue analysis with narrow-bore fast GC, Kirchner et al., 2005 b found that the spectra acquisition rate has a great impact on sensitivity (peak areas, peak shapes and S/N (signal-to-noise) ratios). The quality of the obtained spectra was not significantly influenced in the full scan monitoring mode for the fastest scan rates. For quantitative analysis a SIM mode was able to acquire the sufficient number of data-points for the proper peak shape reconstruction and good repeatability of peak areas measurements expressed by RSD (<5%) for all tested dwell times shorter than 75 ms. However, for shorter dwell times up to 10 ms, the S/N ratio is lower, while peak areas are not influenced. Proving the quadrupole MS ability for adequate detection of narrow peaks

without the loss of sensitivity gives the possibility to extend the use of the fast GC to routine laboratories.
Fast GC-MS methods using narrow-bore capillary columns have been developed and validated as effective substitutes for conventional capillary GC-MS for limited number of pesticides (Kirchner et al., 2005 *a*) and for multiresidue analysis of wide range of pesticides including carbamates, organochlorines, orhanophosphorous, triazoles and others (Húšková et al., 2008). The LOQs and ruggedness of fast GC-MS are sufficient for the analysis of pesticide residues even in baby food (Hercegová et al., 2006; Kirchner et al., 2008). The method for the determination of 29 pesticides proved or suspected to be endocrine disrupting chemicals was developed and validated by Húšková et al., 2010 *a*. LOQs in the range of 0.04 to 10 $\mu g.kg^{-1}$ for majority of pesticides were obtained, dicofol, linuron and prochloraz gave LOQs ≤ 21 $\mu g.kg^{-1}$ using matrix-matched standards for calibration.

3.2 Fast temperature programming

Combined approaches to realize the analysis faster are usually applied. Fast temperature programming and narrow-bore column utilization was shown by Ochiai et al., 2006 and subsequently modified by Samsamoto et al., 2007. 82 pesticides in natural water by fast screening method employing dual SBSE (stir bar sorptive extraction) – termal desorption (TD)-GC-MS were analyzed. Fast temperature programming (75 $°C.min^{-1}$) using a 0.18 mm I.D. narrow-bore capillary column and fast scanning (10.83 $scan.s^{-1}$) quadrupole MS were employed. The method showed high sensitivity with LODs < 10 $ng.l^{-1}$ and remarkable precision for most of the target pesticides.
Very fast temperature programming is realized by inserting capillary column into a resistively heated metal tube, or column enclosed in a resistively heated toroid-formed assembly, allowing heating rate of 1800 $°C.min^{-1}$ and a cool-down time of less than 1 min (Dalüge et al., 2002). Maštovská et al., 2001 used the flash GC technique (resistive heating of a short capillary column 5 m x 0.25 mm I.D.) for the analysis of 15 organophosphorus pesticides, the GC analysis time was reduced by a factor of more than 10 compared to the conventional GC technique (moderate oven temperature programming of a six times longer high resolution capillary column). Due to much narrower peak widths, improved detectability of analytes (higher S/N) was achieved. In comparison with the alternative fast temperature programming technique realized by a conventional GC oven, significantly better retention time repeatability was observed.

3.3 Low-pressure gas chromatography

Typically, LP-GC-MS involves the use of a short narrow uncoated restriction capillary (3 m x 0.15 mm I.D. or 0.1 m x 0.1 mm I.D.) connected between the inlet and a relatively short wide-bore analytical column (5-10 m x 0.53 mm I.D. x 1 µm film thickness). This column is maintained under vacuum conditions due to pumping from the MS system, which causes the helium carrier gas to have shifted the optimal flow velocity from the van Deemter equation to greater flow rate. Meanwhile, the restriction capillary allows normal operating pressure at the inlet (de Zeeuw et al., 2000). Detailed review on LP-GC was recently published by Ravindra et al., 2008. The main drawback of this technique is the loss of separation efficiency. Wider peaks compared to other approaches of fast GC do not require high acquisition rate of MS detectors, therefore, common detection techniques are adequate.

Another advantage is the lower elution temperature that is beneficial for thermally unstable analytes and stationary phases, enhancement of S/N ratio leads to the improved detection limits and it offers a 3-5-fold reduction in analysis time in comparison to conventional GC. LP-GC–MS using a quadrupole MS instrument was developed and evaluated for the fast analysis of 57 pesticides in food crops by Maštovská et al., 2004. The further study for fast LP-GC-MS employing TOF for determination of 100 analytes was developed by Čajka et al., 2008. The sample throughput of combination of QuEChERS sample preparation technique followed by LP-GC/TOF-MS (time-of-flight mass spectrometry) was checked by Koesukwiwat et al., 2010.

3.4 Comprehensive GCxGC

Comprehensive two-dimensional gas chromatography (GC × GC) is a powerful separation technique in which two gas capillary columns with different separation mechanism are coupled via an interface called modulator. This modulator is used to focus and efficiently transfer (i.e. re-inject) the entire effluent from the first column into the second one as consecutive narrow chromatographic bands. The fast GC separation that takes place in the second column depends on the nature of stationary phase, its length and the offset of temperature between this column and the main oven. Advanced detection methods, as a consequence, necessitate rapid acquisition capacities. Flame ionization detector (FID) systems are characterized by rapid data acquisition rates (250 Hz max) and are the most commonly used. Time-of-flight mass spectrometers (TOF MS) have a demonstrated effectiveness for the positive identification of comprehensive GC analytes (Tranchida et al., 2004). This type of MS possesses a higher scan speed in respect to traditional quadrupole systems and is capable of supplying sufficient spectra per peak (at least 10) for reliable component assignment.

The main features of GC × GC, the influence of the experimental parameters in the final peak capacity and separation power as well as the main advantages of GC × GC as compared to other multidimensional chromatographic separation techniques for different application fields have been discussed in the recent reviews (Adahchour et al., 2006; Adahchour et al., 2008).

Ramos et al., 2009 evaluated the feasibility of using GC×GC-μECD (micro electron capture detection) in combination with a miniaturised generic matrix solid-phase dispersion-based sample preparation method for the fast monitoring of pesticides in real samples. The comparison of LODs with conventional GC-MS (quadrupole mass analyzer) screening triazines, organophosphorus pesticides (OPPs) and pyrethroids, in different types of fruits was evaluated. GCxGC provided lower LODs values.

4. Specificity of pesticide residues analysis

Despite of great efforts in the research of GC amenable pesticide residues analysis the analysis is complicated by the co-injected matrix constituents responsible for the matrix-induced chromatographic response enhancement or the subsequent decrease of the response. When a real sample is injected, the matrix components tend to block active sites in the GC injector and column, thus reducing losses of susceptible analytes caused by adsorption or degradation on active sites. This phenomenon results in ordinarily higher analyte signals in matrix-containing, versus matrix-free solutions (Hajšlová & Zrostlíková, 2003).

analytes /sample	column	carrier gas	temperature conditions	injection technique	detec techn
17 pesticides / water	HP-1, 10 m x 0.1 mm I.D. x 0.1 µm	He, const. press. 70.12 psi	80°C, 3.7 min, 100°C.min^{-1} to 150°C, 30°C.min^{-1} to 250°C, 3 min	LVI, PTV, solvent vent	MS (SIM)
15 organophosphor. pesticides / wheat	DB-5MS, TDX-RTX5, 5 m x 0.25 mm I.D. x 0.25 µm	He, const. flow 1 ml.min^{-1}	resist. heating	splitless	NPD FPD
pesticides / apples	DB-5, 5m x 0.1 mm I.D. x 0.1 µm	He, const. press. 300 kPa	resist. heating 100, 200 or 400°C.min^{-1}	split, splitless	MS (SIM)
organophosphor. and sulphur pesticides	SGE DB5 , 10 m x 0.1 mm I.D. x 0.4 µm	H_2, linear velocity 120 cm.s^{-1}		splitless	FPD,
6 multiclass pesticides / lettuce	J&W DB5-MS, 20 m x 0.18 mm I.D. x 0.18 µm	He, 1 ml.min^{-1}	60°C, 7.5 min, 30°C.min^{-1}to 280°C	LVI-DMI-PTV, solvent vent	TOF (20 H
15 organochlorine pesticides / tap and ground water	HP1-MS, 15 m x 0.1 mm I.D. x 0.4 µm	H_2, 1.1 ml.min^{-1}	45°C, 3.4 min, 120°C.min^{-1}to 280°C, 6 min	LVI- PTV, solvent vent	MS (
20 pesticides / peach	DB5-MS, 20 m x 0.18 mm I.D. x 0.18 µm	He, 1 ml.min^{-1}	70°C, 1 min, 2.5°C.min^{-1} to 200°C, 10°C.min^{-1} to 280°C, 9.8 min	splitless	TOF
20 organophosphor. pesticides / peach, sweet pepper	RTX 1701, 5 m x 0.25 mm I.D. x 0.25 µm	He, const. press. 3.8 psi	EZ flash, 60°C, 158°C.min^{-1} to 200°C, 24°C.min^{-1} to 240°C, 141°C.min^{-1} to 280°C, 88 s	splitless	FPD
18 pesticides / baby food	a) CP-Sil 13 CB, 25 m x 0.15 mm I.D. x 0.4 µm b) CP-Sil 8 Low-BleedMS, 15 m x 0.15 mm I.D. x 0.15 µm	a) H_2, progr. flow 2.3 ml.min^{-1} (5.5 min), 2 ml.min^{-2}, 3.4 ml.min^{-1}; b) He, const. flow, 0.5 ml.min^{-1}	a) 100°C, 1 min, 65°C.min^{-1} to 290°C, 8 min; b) 120°C, 1min, 30°C.min^{-1} to 290°C, 5 min	a) splitless b) cold splitless	a) EC b) MS
18 pesticides / apples	CP-Sil 8 Low-BleedMS, 15 m x 0.15 mm I.D. x 0.15 µm	He, const. flow 0.5 ml.min^{-1}	100°C, 1.5 min, 30°C.min^{-1} to 290°C, 6 min	PTV, cold splitless	MS (

DMI – difficult matrix introduction, ECD – electron capture detector, FID-flame ionization detector, FPD-flame photometric detector, FTD- flame thermo-ionic detector, LVI-large volume injection, MS – mass spectrometry, NPD-nitrogen-phosphorus detector, PFPD-pulsed flame photometric detector, PTV – programmed-temperature vaporization (injector), SIM-selected ion monitoring, TDU – thermal desorption unit, TOF-time-of-flight. Highlighted items use the fast temperature programming.

Table 2. A narrow-bore column and resistive heating fast GC approaches to the pesticide residues analysis

analytes /sample	**column**	**carrier gas**	**temperature conditions**	**injection technique**
pesticides	HP-1 MS, 5 m x 0.1 mm I.D. x 0.4 µm	H_2, const. press., 413 kPa	80°C, 0.65 min, 65°C.min^{-1} to 300°C	on-column
pesticides	CP-Sil 8 CB: a) 15 m x 0.15 mm I.D. x 0.15µm; b) 10 m x 0.10 mm I.D. x 0.10µm	I. H_2, const. press., a) 260 kPa b) 437 kPa II. He a) 363.5 kPa b) 0.5 ml.min^{-1}, 9 min, 5 ml.min^{-2}, 0.8 ml.min^{-1}	I. a) 100°C, 1 min, 65°C.min^{-1} to 290°C, 8 min; b) 120°C, 1 min, 30°C.min^{-1} to 290°C, 5 min II. a) 130°C, 1.13 min, 27.25°C.min^{-1} to 290°C, 6 min; b) 115°C, 1.88 min, 27.6°C.min^{-1} to 290°C, 5.78 min	I. split; spl II. PTV in splitless
82 multiclass pesticides / brewed green tea	DB-5, 10 m x 0.18 mm I.D. x 0.18 µm	He, const. flow 1.1 ml.min^{-1}	40°C, 2 min, 75°C.min^{-1} to 300°C, 2 min	PTV in splitless, T
20 pesticides / apples, baby food, processed samples	CP-Sil 8 Low-BleedMS, 15 m x 0.15 mm I.D. x 0.15 µm	He, const. flow 1.2 ml.min^{-1}	130°C, 1.13 min, 27.25°C.min^{-1} to 290°C, 6 min	PTV, cold splitless
pesticides / fruit and vegetables	CP-Sil 8 Low-BleedMS 15 m x 0.15 mm I.D. x 0.15 µm	He, const. flow 1.2 ml.min^{-1}	60°C, 1.75 min, 60°C.min^{-1} to 150°C, 23.8°C.min^{-1} to 300°C, 1.9 min	PTV, solve vent

Ways to compensate the matrix effects include: (i) use of isotopically labelled internal standards, (ii) method of standard addition, (iii) use of matrix-matched standards, and (iv) use of analyte protectants (APs). The most widely used method in laboratories nowadays is the use of matrix-matched standards. This approach is, however, complicated by the fact, that the composition of matrix-matched standard should be as close as possible to the composition of real sample matrix in order to provide good compensation of matrix effects.
The principle of "analyte protectants" use is to find masking agents that would mask active sites in the GC system and thus would provide strong response enhancement of pesticides. More than 90 compounds belonging to different chemical classes were evaluated in order to protect coinjected analytes against degradation and/or adsorption in GC system (Anastassiades et al., 2003 *b*). Ethylglycerol, gulonolactone and sorbitol have been chosen as the most promising substitute of fruit and vegetable matrix.
The influence of chromatographic matrix induced response enhancement in fast GC with narrow-bore column was studied by Kirchner et al., 2005 *a* and it is illustrated in Fig. 2,

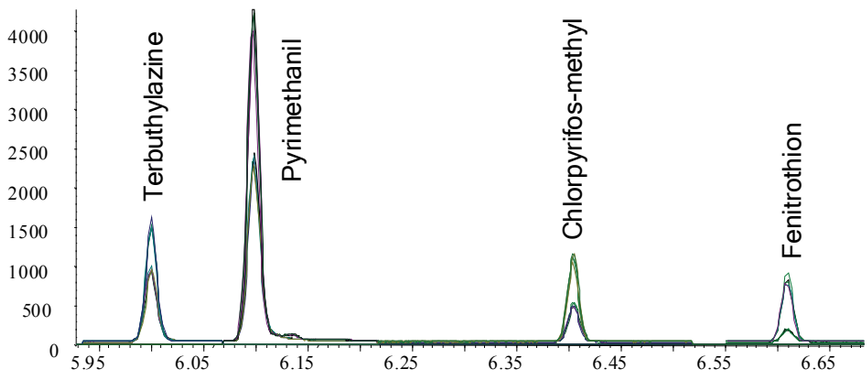


Fig. 2. Overlaid chromatograms (n=5) of selected pesticide standards prepared in neat toluene (lower responses) and standards prepared in blank apple matrix-matched standards, both at concentration level 0.0125 ng.µl^{-1}, corresponding to 5 µg.kg^{-1} in apple matrix, Kirchner et al., 2005 *a*.

where extracted ion chromatograms (n=5) of several pesticides obtained from the standard solution in a neat solvent (lower responses) is overlaid with matrix-matched calibration standard chromatograms (higher responses) of the same concentration injected under identical conditions (n=5). The chromatographic matrix induced response enhancement was found to be strongly dependent on the concentration of residues mainly in the lowest concentration region and is reaching up to 700 % compared to the pesticides solutions in a neat solvent. Selected results are shown in Table 3. 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. However, it was shown that fast GC-MS utilizing narrow-bore columns with 0.15 mm I.D. shows acceptable stability of the separation system and the responses of pesticides in matrix-matched standards at different concentration levels do not significantly change during 130 injections with the proper maintenance of inlet liner and retention gap. Illustrative chromatograms of fast GC separation with narrow-bore column showing the influence of matrix-matched standards use and the use of analyte protectants in comparison to the chromatogram without matrix compensation is given in

Fig. 3. In a neat solvent (acetonitrile MeCN) the shapes of pesticide peaks are very poor, whereas the chromatogram of matrix-matched standards and also the chromatogram with APs, which have been utilised for the elimination of matrix effects in real sample analysis, are suitable for evaluation. It should be pointed out, that measurements in a neat solvent were performed in a "dirty" chromatographic system. The instrument noise seems to be comparable to matrix-matched standards and standards in a neat solvent.

However, responses in matrix-matched standards improve significantly. In order to compare the performance of APs with matrix-matched standards (Kirchner et al., 2008) calibration curves of selected pesticides were searched in terms of linearity of responses, repeatability of measurements and reached LOQs utilizing the following calibration standards in the concentration range 0.001 – 0.5 $\mu g.kg^{-1}$: in a neat solvent (MeCN) with/without addition of APs, matrix-matched standards with/without addition of APs. For APs results are in a good agreement with matrix-matched standards. To evaluate errors of determination of pesticide concentration in samples at the concentration level of pesticides 0.05 $\mu g.kg^{-1}$ synthetic sample were analyzed and quantified. For less troublesome pesticides very good estimation of concentration was obtained utilizing APs, while for more troublesome pesticides such as methidathion, malathion, phosalone and deltamethrin significant overestimation reaching up to 80 % was occurred (Fig. 4).

Pesticide	Relative average peak area in %					
	Concentration ($ng.\mu l^{-1}$)					
	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
Myclobutanil	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

Table 3. 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 solvent, in % (n=5), Kirchner et al., 2005 *a*.

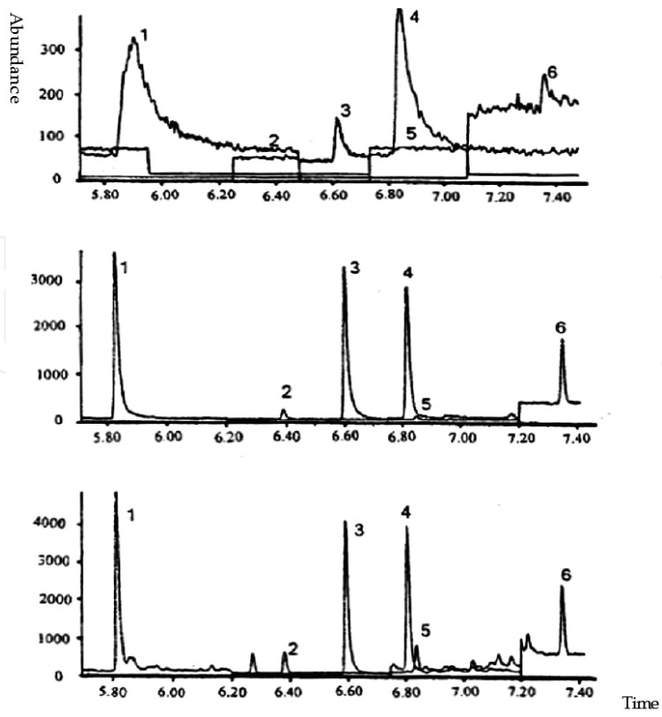


Fig. 3. Fast GC-MS chromatograms of pesticides obtained in SIM mode. A – standards in neat solvent (MeCN); B- standards in solvent with addition of analyte protectants (2 µg of 3-ethoxy-1,2-propanediol, 200 ng of D-sorbitol and L-gulonic acid γ-lactone); C – matrix-matched standards (matrix-apple prepared by QuEChERS method). Concentration level 10 µg.kg^{-1}, injected volume 2 µl, PTV injection. 1 - pyrimethanil, 2 - fenitrothion, 3 - tetraconazole, 4 – cyprodinil, 5 - tolylfluanid, 6 – kresoxim-methyl (Húšková et al., 2007)

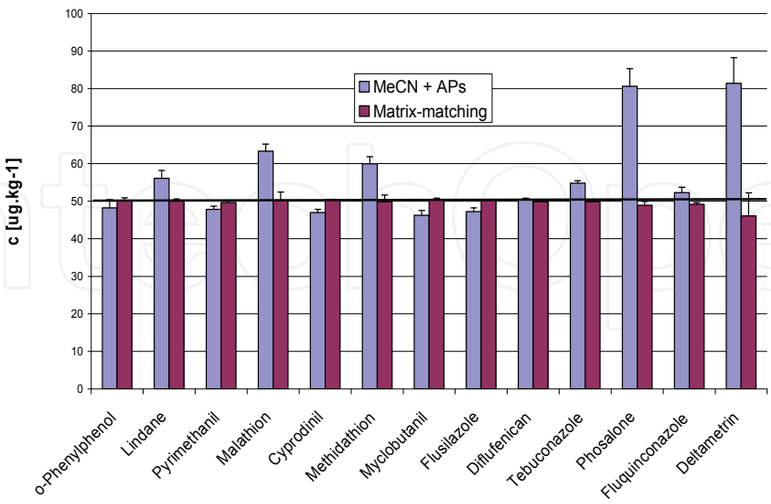


Fig. 4. Graf of calculated concentrations of pesticides in synthetic sample using MeCN with addition of APs and matrix-matched standards (both normalized to triphenyl phosphate) vs. expected concentration of 50 µg.kg^{-1}. Error bars on each column represent repeatability of measurements, (Kirchner et al., 2008).

5. Sample preparation in food samples analysis by fast GC

When considering the merits of developing and validating a routine GC method, the total run time involved in analysing the sample must be considered (Klee & Blumberg, 2002). The total run time is the sum of the time for sample preparation, sample introduction, separation and detection, cool down and reequilibrating and reporting.

Sample preparation is usually the limiting step of analytical method determining the sample throughput in pesticide residues analysis of food and environmental samples. Therefore, it is necessary to combine a fast chromatography technique with fast sample preparation technique; the total analysis time can be reduced significantly.

The sample preparation approach known as QuEChERS, which stands for "quick, easy, cheap, effective, rugged and safe", firstly introduced by Anastassiades et al., 2003 *a* represents a breakthrough in the field of sample preparation. QuEChERS approach use acetonitrile for extraction of a 10-15 g homogenized sample followed by salt-out partitioning of the water from the sample using anhydrous $MgSO_4$, NaCl, and/or buffering agents, and further clean-up using dispersive solid-phase extraction (d-SPE) or disposable pipette extraction (DPX) with anhydrous $MgSO_4$, primary secondary amine (PSA) and/or in combination with C_{18}, graphitized carbon black (GCB) sorbents. Ethyl acetate (EtOAc) is sometimes used as a substitute solvent in QuEChERS procedure, but generally it leads to less clean extracts and lower recoveries of numerous pesticides. Acetate-buffered MeCN version (relatively strong buffering at pH 5) exhibits advantages in comparison to non-buffered or weaker citrate buffered version, but both were accepted by scientific standards organizations – acetate version AOAC Official Method 2007.01 and citrate version European Committee for Standardization (CEN) Standard Method EN 15662. Intercomparison of unbuffered and both buffered methods (Lehotay et al., 2010) was evaluated in terms of pH-dependence, co-extracted matrix components, matrix effects and substitution of MeCN with EtOAc. It was shown, that the use of EtOAc leads to less clean extracts and lower recoveries of more pesticides, but for GC-amenable pesticides EtOAc gave equivalent results as MeCN.

The QuEChERS approach is very flexible and it serves as a template for modifications on the analyte properties, matrix composition, equipment and subsequent analytical technique. QuEChERS reached the worldwide acceptance, it serves as a base to create different permutations for the analyte(s)/matrix(es) applications.

Concerning throughput, according to Koesukwiwat et al., 2010, sample preparation of fruit and vegetables using QuEChERS technique takes <10 min per individual sample, or <1 h for the two chemists to prepare 32 pre-homogenized samples and <10 min LP-GC run time and <15 min cycle time allowed > 32 injections in 8 hrs for identification and quantification of 150 pesticides. Time requirements of QuEChERS and gel permeation chromatography (GPC) in combination with 7 min LP-GC-TOF-MS run time for separation of multiple pesticide residues were compared by Čajka et al., 2008, and the batch of 12 fruit samples with 6 matrix-matched standards were analyzed within 4 h with the use of QuEChERS in contrary to 20.5 h with the use of EtOAc extraction with GPC, thus time reduction by a factor of 5. However, GPC is considered as universal method for cleaning-up purposes of a wide range of matrices and multi-class pesticides, the time analysis and the cost is too high. According to Húšková et al., 2009, the batch of 6 samples in parallel is prepared within 46 min with the fast GC with narrow-bore column single run time 11.45 min.

QuEChERS technique is the most effective technique employing the clean-up step. If the extract does not contain co-extractants and also a lot of matrix components, avoiding clean-up step lead to decreasing the analysis time.

Other extraction techniques and particularly novel mikroextraction techniques belong to effective and fast techniques. They overcome the shortcomings of classical liquid-liquid extraction or solid-phase extraction. To have simple, fast and green procedures microextraction techniques are developed. Solid-phase microextraction (SPME), stir bar sorptive extraction (SBSE) and microextraction with packed sorbents (MEPS) are examples that are used for sample preparation of pesticide residues containing food matrices (Chen et al., 2010). It was shown by several authors (Ochiai et al., 2005, Barriada-Pereira et al., 2010), that using SBSE technique allows batch sample preparation, for example 60 samples on one stir-plate, (typically in minutes (up to 60 min)), high recovery and extremely low LODs at sub $ng.l^{-1}$. Whereas SPE and MSPD need a concentration step, SPME and SBSE allow carrying out the extraction and concentration step in a single step. SPME and SBSE are equilibrium processes, but SBSE enables a much higher capacity because of the large amount of polymeric phase (24-126 µl) compared to SPME (0.5 µl).

6. Selectivity enhancement by GC-NCI-MS approach

Over the past 10 years, there has been an increased interest in negative ion/molecule reactions as an ionization technique in MS detection (Liapis et al., 2003; Schulz, 2004; Húšková et al., *b*, 2010). In negative chemical ionization (NCI), a reagent gas at higher pressure is introduced into the ion source. The electron beam in the mass spectrometer collides with the reagent gas and the essence of the technique is based on the ionization through the capturing of a low energy electron by the analyte molecule. Compounds with sufficient electron affinity, such as chlorinated molecules, are very sensitive towards this mode of detection. NCI is a low energy process with limited fragmentation (easily identifiable molecular ion) and provides simple mass spectra in comparison to the EI technique. With this technique, usually a few ions of high abundance are observed in the relevant mass spectrum and this enhances analyte detectability. Summarily, advantages of the NCI ionization technique are chromatograms with less chance for the interferences from ions derived from the sample matrix; better S/N ratio; higher sensitivity and selectivity; analysis of organic compounds at the ultratrace concentration levels (ppt concentration) with low LODs and LOQs. Detection limits are usually two orders of magnitude lower than the corresponding EI-MS or positive chemical ionization methods.

Application of fast GC set-up using narrow-bore column (0.15 mm I.D.) in combination with MS detector in NCI mode was introduced and compared to fast GC-MS with electron ionization by Húšková et al., 2009. Multi-residue method of 25 pesticides belonging to different groups (organochlorines, organophosphates, pyrethroids, dicarboximides, 2,6-dinitroaniline, triazinone, substituted urea, phthalamide, cyclodiene, triazole, imidazole), varying in polarity, volatility and other physicochemical properties from non-fatty fruit and vegetable matrices based on fast GC with quadrupole NCI-MS was developed and verification of the method was realized. Blank apple sample extracts were used for the preparation of matrix-matched standards. The illustrative chromatograms of target ions of endocrine disrupting pesticides in matrix-matched standard solution using both ionization techniques are presented in Fig. 6. The concentration level corresponding to 10 $µg.kg^{-1}$ in fruit matrix was below or far below the MRL values of all pesticide/commodity combinations and it was selected with intention to show the potential of the method for utilizing in ultratrace analysis that is essential in the analysis of endocrine disruptors. EDCs are compounds that are expected even in minute amounts to be able to disrupt the

endocrine system and cause cancer, harm to male and female reproductive systems, and other adverse effects. Chromatogram obtained in the NCI mode (Fig. 6 A) with the very high response of detector, lower background disturbances and better S/N ratio in comparison to the EI mode (Fig. 6 B) at the same concentration level can be seen. Matrix-matched standard solutions were analyzed to determine the linear response range of the MS detection in the NCI and EI mode, repeatability of the peak area measurement, and to compare the overall performance of NCI vs. EI. The selected EDCs pesticides were analyzed in 11.45 min. Linearity of calibration curves constructed from absolute peak areas (A_i), expressed as coefficient of determination (R^2), was in the range of 0.9936 – 1.000 in the NCI mode and 0.9820 – 0.9999 in the EI mode. Repeatability of calculated R^2, expressed as relative standard deviations (RSDs), for both absolute and normalized peak areas was ≤ 1.1 %. NCI is more sensitive, resulting in up to 100-fold decrease in the lowest calibration levels (LCLs, Table 4). For the majority of EDCs pesticides the LCLs were 0.01 and 0.05 ng.ml^{-1} (0.01 and 0.05 µg.kg^{-1}) for fast GC-NCI-MS and 1 ng.ml^{-1} (1 µg.kg^{-1}) for fast GC-EI-MS. Instrument LODs, LOQs and further validation parameters are listed in Table 4.

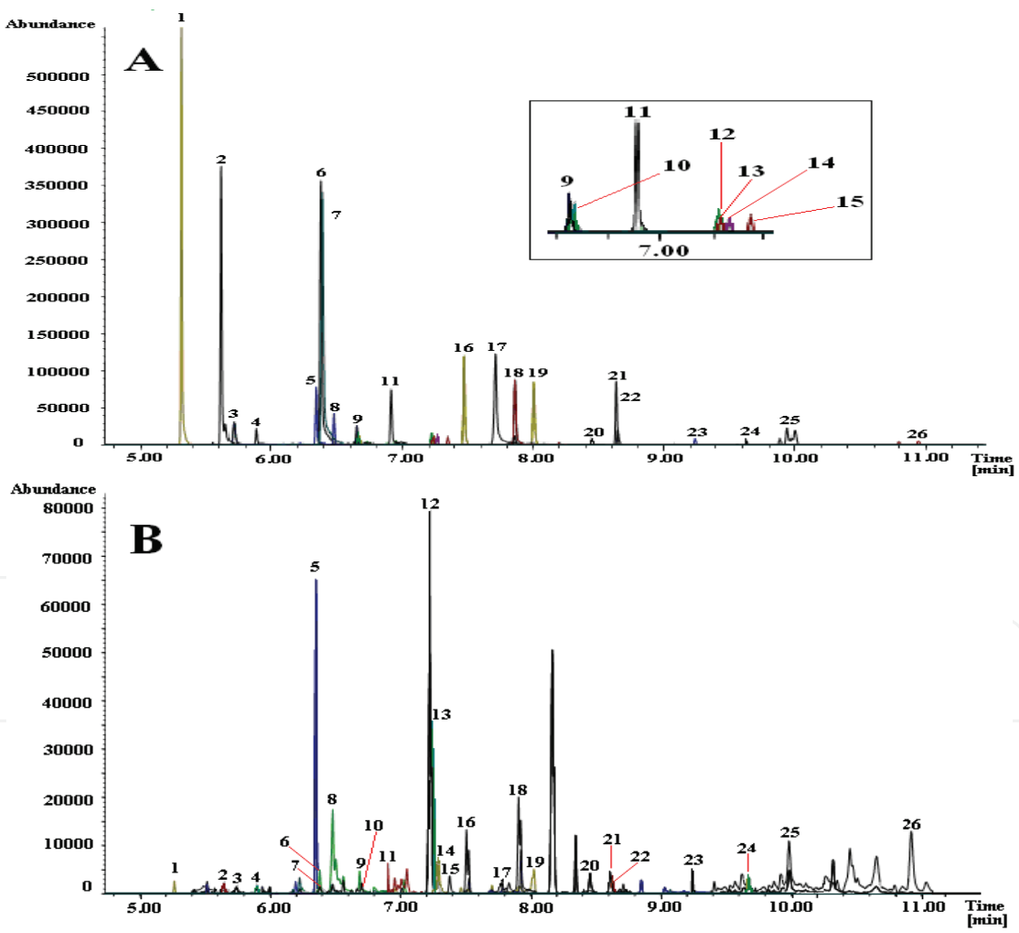


Fig. 6. Chromatograms of target ions of pesticides in matrix–matched standard solutions analyzed by fast GC–MS in SIM mode at the concentration level of 10 ng.ml^{-1} (corresponding to 10 µg.kg^{-1}): A – **NCI** mode; B - **EI** mode. Numbering of peaks is identical with the number of compounds given in the Table 4. (Húšková et al., 2009).

No	Pesticide	R^2		LCL (ng.ml^{-1})		RSD_{Ai} (%)		LC (pg.ml^{-1})
		NCI	EI	NCI	EI	NCI	EI	NCI
1	trifluralin	0.9998	0.9980	0.01	1.00	4.3	6.9	0.15
2	hexachlorobenzen	0.9996	0.9995	0.01	1.00	5.1	7.9	0.85
3	dimethoate	0.9997	0.9984	0.05	1.00	5.3	8.2	33.1
4	lindane	0.9996	0.9992	0.05	1.00	3.7	7.3	3.7
5	chlorpyrifos-methyl	0.9999	0.9990	0.05	1.00	4.9	8.6	33.8
6	metribuzin	0.9998	0.9986	0.05	1.00	4.8	8.8	8.8
7	vinclozolin	0.9990	0.9991	0.01	1.00	4.9	9.9	1.1
8	heptachlor	internal standard						
9	malathion	0.9998	0.9995	0.05	1.00	3.4	11	38.8
10	linuron	0.9936	0.9868	1.00	10.00	3.9	7.6	281
11	dicofol	0.9964	0.9820	0.10	10.00	4.1	6.9	30.4
12	procymidone	0.9999	0.9998	0.10	1.00	4.5	9.5	30.9
13	diazinon	0.9989	0.9988	0.10	1.00	4.0	8.1	55.1
14	folpet	0.9988	0.9984	0.50	10.00	15	9.0	430
15	chlordane	0.9995	0.9995	0.01	1.00	5.5	9.6	1.2
16	endosulfan-alfa	0.9995	0.9993	0.01	1.00	5.7	11	1.1
17	myclobutanil	0.9998	0.9990	0.01	1.00	2.9	9.9	3.0
18	nitrofen	0.9992	0.9939	0.01	5.00	4.9	8.2	2.7
19	endosulfan-beta	0.9995	0.9998	0.01	1.00	4.8	7.7	2.2
20	chlordecone	0.9998	0.9895	5.00	10.00	3.5	7.2	113
21	iprodione	1.0000	0.9999	0.01	1.00	4.2	11	2.3
22	bifenthrin	0.9998	0.9997	0.01	1.00	5.1	10	3.3
23	mirex	1.0000	0.9999	0.10	1.00	2.5	9.9	89
24	prochloraz	0.9992	0.9987	1.00	10.00	2.8	5.3	619
25	cypermethrin	0.9994	0.9993	0.50	5.00	5.6	11	127
26	deltamethrin	0.9991	0.9982	0.10	1.00	4.1	11	331

R^2 – coefficients of determination, LCL- the lowest calibration level, RSD_{Ai} – relative standard deviation (6 replicates), LOD – limit of detection calculated as 3:1 S/N ratio from calibration measurements, LOQ – limit of determination calculated as 10:1 S/N ratio from calibration measurements.

Table 4. Verification parameters of the GC-NCI-MS and GC-EI-MS analytical methods.

In the NCI mode, LODs were in the range of 0.15 – 88.82 pg.ml^{-1} (0.00015 – 0.089 μg.kg^{-1} in real sample) and LOQs were in the range of 0.52 – 291.35 pg.ml^{-1} (0.00052 – 0.291 μg.kg^{-1} in real sample) for the majority of analytes under the study. Linuron, folpet, chlordecone, prochloraz, cypermethrin and deltamethrin have the LOD values > 100 pg.ml^{-1} and LOQ values > 300 pg.ml^{-1}. LODs and LOQs obtained in EI mode are at the level of ng.ml^{-1}. For all analytes except linuron, dicofol and prochloraz, the LOQs were below 10 μg.kg^{-1}, which is the MRL required for the pesticide residues in baby-food. The NCI mode provided significantly higher selectivity and sensitivity. Better results for the NCI mode were obtained as a consequence of minimizing the background interferences and a better S/N ratio. The method LOQs, determined from recovery studies, was 5 μg.kg^{-1} in EI mode (except for folpet, chlordecone, endosulfan-alfa and endosulfan-beta). NCI-MS detection allowed 5 times to even 50 times for some pesticides lower method LOQs. The developed GC-NCI-MS method fulfilled the EU criterion concerning recovery rates and RSDs at the concentration of 1, 5 and 150 μg.kg^{-1} for all compounds under study.

The main advantage of the GC-NCI-MS measurement procedure was the increase of the selectivity, e.g., the differentiation between the target component and the accompanying sample matrix coextractants. As the universal detection by MS in EI mode is changed to selective detection by the process of chemical ionization (CI), the selectivity is increased, and the measured sensitivity of the selected analytes is enhanced for a variety of active endocrine disrupting pesticides with adverse effect on human endocrine system. For the proper balance it is necessary to mention the disadvantages of NCI, unavailability of library spectra for analytes and the requirement for an analyte to be active in NCI mode, e.g. to contain halogen elements are the most weighty.

7. Real-life samples analysis

The most important application of fast GC is in situations, where the results of analysis are needed close to where the answer is needed (e.g. process control, on-site environmental and industrial hygiene applications) to obtain increased laboratory throughput. Practicality of fast GC is a function of a sample preparation step and the matrix interferences, so, for those applications, where the GC separation is the bottleneck using fast GC is indeed a significant contribution. Several real-life analyses usually follow the method validation or the developed method is applied to a screening or monitoring. Examples of real-life samples analysis employing the fast GC with the narrow-bore columns and resistive heating approach as an analytical technique for pesticide residues determination were summarised in Table 2.

Cunha et al., 2009 applied the fast LP-GC-MS method for the determination of multiple pesticides in grapes, musts and wines, 8 min time analysis for fast GC versus 24 min using conventional approach was obtained. Total analysis time including QuEChERs sample preparation technique was less than 20 min. LP-GC-MS-MS was applied to the analysis of 65 pesticide residues in fat fruit matrices such as avocado (Moreno et al., 2006), pesticides in tomato samples (Walorczyk & Gnusowski, 2006), determination of pesticides residues in tropical fruit (Vidal et al., 2007), analysis time reduction in half was obtained by Arrebola et al., 2003 for 71 pesticides in fresh vegetables matrices. Koesukwiwat et al., 2010 evaluated method ruggedness and matrix effects in LP-GC-TOF-MS analysis of 150 pesticides in fruit and vegetables.

In this sub-chapter the example of real sample analysis by narrow-bore fast GC-NCI-MS method combined with QuEChERS sample preparation developed by our group is presented. The selected positive findings of pesticide residues in different real fruit and vegetable samples are shown in Table 5.

Matrix	Pesticide	NCI		EI	
		c_i [µg.kg^{-1}]	RSD [%]	c_i [µg.kg^{-1}]	RSD [%]
orange	malathion	50.1	0.52	52.5	3.5
lettuce	iprodione	40.1	1.2	42.0	3.0
pear$_A$	iprodione	40.1	1.2	41.3	3.4
pear$_B$	bifenthrin	69.0	5.2	64.8	4.1
	myclobutanil	0.07	6.8	n.d.	-
kohlrabi	metribuzin	0.06	3.0	n.d.	-
	vinclozolin	0.15	2.1	n.d	-
	myclobutanil	0.25	3.6	n.d.	-
plum	iprodione	234.3	0.31	241.1	2.8
strawberry	iprodione	40.9	1.2	41.3	3.4
pepper	myclobutanil	24.3	6.3	30.4	4.2
	cypermethrin	47.2	2.2	54.9	6.0

Table 5. Concentration c_i (µg.kg^{-1}) of pesticide residues in real samples and repeatability of measurements expressed as relative standard deviation RSD (%) of parallel extractions; n. d. – not detected.

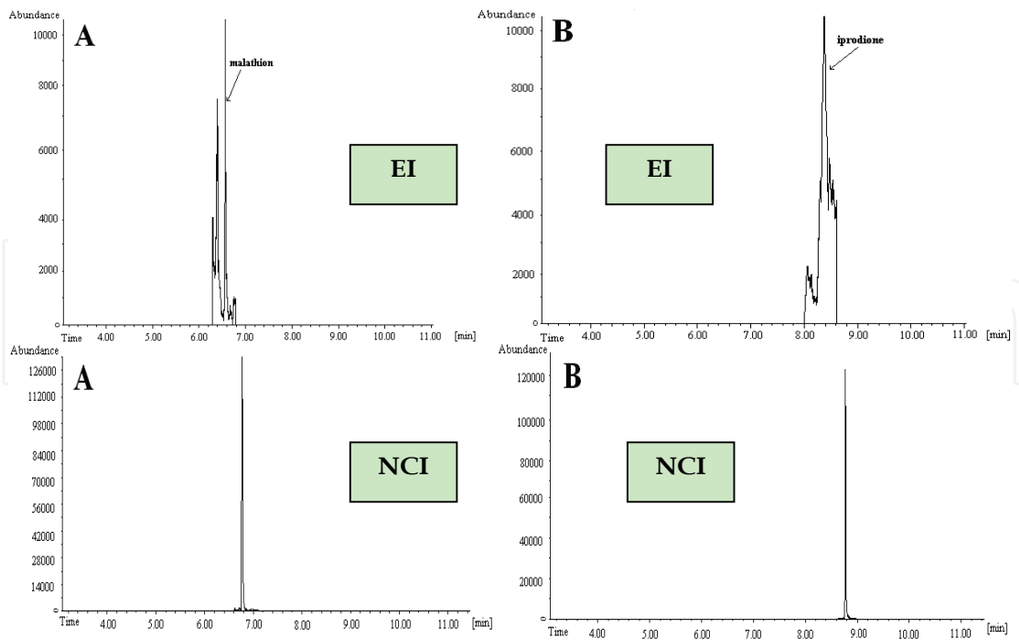


Fig. 7. Chromatogram of target ions of EDCs pesticides analyzed by fast GC-MS in SIM in EI (upper figures) and NCI mode (bottom figures) in real samples A - orange (malathion), B - lettuce (iprodione).

Average pesticide concentration (calculated from triplicate analysis of two parallel samples) obtained from absolute peak areas and relative standard deviations (RSDs < 6.8 %) for parallel samples are presented in Table 5. Determined pesticide residues concentrations were in the range of 0.06 – 241.1 $\mu g.kg^{-1}$. The concentrations of pesticide residues determined by fast GC-MS in the NCI and EI mode were in a good agreement. The example of $pear_B$ and kohlrabi shows the ability of the NCI-MS method for the pesticide residue analysis at low concentration level. For illustration the chromatograms of the target ions of the pesticides analyzed by fast GC-MS in the SIM mode in the real sample extracts, in NCI and EI ionization modes, are given in Fig. 7 (Húšková et al., 2009). It is evident from the chromatograms that there are interferences in EI mode which are dependent on the matrix (orange, lettuce), whereas in NCI mode very "clean" chromatograms with high responses of analytes without influence from the matrices were obtained.

8. Conclusions

For pesticide residues analysis ultrasensitive analytical methods are required and there is still the need to improve the performance and ruggedness of analyses. Despite the tremendous developments and improvements in the analytical instrumentation, for most of substances there is continuous need to employ the extraction and preconcentration steps. Speeding-up analysis in gas chromatography is the unavoidable way in routine analytical laboratories requiring higher throughput and reduced costs of performed analyses. The use of narrow-bore capillary columns with the enhanced separation efficiency and the use of short wide-bore column for low-pressure GC are the most promising ways and an additional research in these areas is expected. The advances obtained in the study of fast GC are a base of knowledge for comprehensive gas chromatography where the fast GC takes a place.

Nowadays fast GC can be performed on commercial gas chromatographs with standard equipment for high-speed injection, electronic pressure control, rapid oven heating/cooling and fast detection. The main stress of this contribution was given to the advances and achievements in the area of narrow-bore approach of speeding the GC analysis up, as there is the significant contribution of our research group to the study of possibilities and limitations and to the search on ruggedness of fast GC with narrow-bore columns for pesticide residues analysis at ultratrace concentration level. It was shown, that not only time-of-flight, but also in laboratories widely used quadrupole MS detector was shown to broaden its ability to detect the narrow peaks without the loss of sensitivity. Multiresidual fast GC methods for analysis of pesticide residues in different non-fatty fruit and vegetable samples employing MS in electron ionization and negative chemical ionization modes were developed. The use of negative chemical ionization was demonstrated as a tool for sensitivity enhancement for selected analytes and matrices. Applicability of the methods was demonstrated on real samples. The special emphasise was given to the analysis of samples contaminated by endocrine disrupting pesticides with the aim to obtain LOQs significantly lower in comparison to MRL values.

9. Acknowledgement

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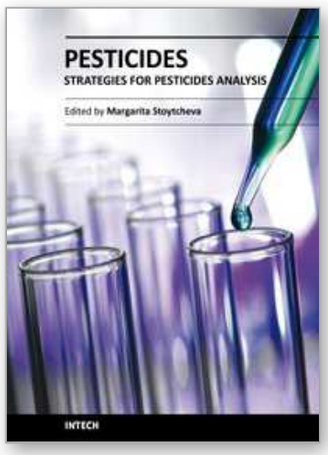

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This book provides recent information on various analytical procedures and techniques, representing strategies for reliability, specificity, selectivity and sensitivity improvements in pesticides analysis. The volume covers three main topics: current trends in sample preparation, selective and sensitive chromatographic detection and determination of pesticide residues in food and environmental samples, and the application of biological (immunoassays-and biosensors-based) methods in pesticides analysis as an alternative to the chromatographic methods for "in situ" and "on line" pesticides quantification. Intended as electronic edition, providing immediate "open access" to its content, the book is easy to follow and will be of interest to professionals involved in pesticides analysis.

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