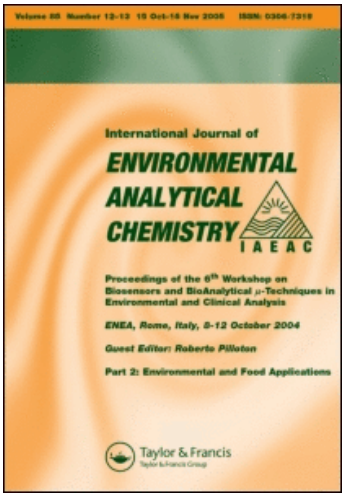

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Study on pesticide residues in apples, apple-based baby food, and their behaviour during processing using fast GC-MS multiresidue analysis

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Study on pesticide residues in apples, apple-based baby food, and their behaviour during processing using fast GC–MS multiresidue analysis

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Food-processing experiments using apples were conducted to obtain more knowledge on the behaviour of pesticides during apple-based baby-food production. The residues were determined in raw material (apples), in intermediate products at different steps of the processing procedure (baby food production) and in final products (apple purée) using a rapid GC–MS method in combination with two different sample-preparation approaches. During 2 years of a monitoring programme, 84 analyses of apple samples and 102 of baby food sample apple purée intermediate and final product samples from baby food production were performed. A pesticide-residue search revealed that residues in fresh apples do not exceed the maximum residue limit for the adult population, but there were some positive findings concerning apples as baby food. The maximal pesticide concentration (fluquinconazole) found in apples was 0.099 mg kg^{-1}. In the processed apple-based baby food the concentration of pesticide residues were mostly below 0.010 mg kg^{-1}.

Keywords: Fast GC–MS; Sample preparation technique; Baby food; Apples; Pesticide residues; Sample processing

1. Introduction

Baby food is any food that is made specifically for infants, roughly between the ages of 6 months and 2 years [1]. A common trait of the many different baby foods is that they are designed for ease of eating; either a soft, liquid paste or an easily chewed food. The term 'baby food' covers a wide range of different food: fruit and vegetable-based, meat/egg/cheese-based, and cereal-based baby food. Concerning pesticide-residue contamination (pesticides remaining on or in food and their metabolites), baby food is considered more strictly compared with food intended for adults, as infants may be especially vulnerable to toxic substances. Relative to their size, infants eat more food than adults. Because they also eat more of certain foods, any toxins in those foods would raise their relative exposure. Therefore, the European Union (EU) legislation

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put stringent requirements on the maximal acceptable concentrations of pesticide residues in baby food. In 1996, The Commission of the European Communities adopted the commission directive 96/5/EC [2], which first stated that processed cereal-based foods and baby foods shall not contain residues of individual pesticides at levels exceeding $0.01\,mg\,kg^{-1}$ (the maximum residue limit (MRL)), except for those substances for which specific levels have been set in Annex VII, in which case these specific levels shall apply. The directive was amended by directives 1999/39/EC [3], recently 2003/13/EC [4] and 2003/14/EC [5], which set even more stringent requirements for some specific pesticide residues.

One of the main requirements of the Slovak accession to the EU was approximation and harmonization of Slovak legislation to that of the EU (currently the requirements for food products used for special purposes including baby food are defined by Food Codex [6], 2nd part, chapter 7). In Slovakia, the most common raw material for processed baby food production is apples. Apples can be infested with fungal diseases as well as attacked by insects or mites. Consequently, intensive pesticide usage is necessary to protect the crop. Among 360 plant protection products currently approved for use in Slovakia, ca 60 of them are relevant for apple trees [7]. National organizations responsible for pesticide residues monitoring in Slovakia monitor food samples, but there is still no monitoring programme on pesticide residues in baby food at sufficiently low concentration levels satisfying EU baby food safety requirements.

The most suitable approaches for the determination of the pesticide residues content in baby food matrices are chromatographic methods combined with various sample-preparation methods [8]. The appropriate multiresidue chromatographic analysis of pesticide residues at the concentration level of $\leq 0.01\,mg\,kg^{-1}$ in such complex matrices as apples expects sample preparation capable of sufficient removal of matrix components in simultaneous preservation of high recoveries and good precision. The possibility of pre-concentration is an additional benefit. Its requirement depends on the selected detection system in a quantitation method. Our recent research offers two sample preparation methods: the modifications of Schenck's method (introduced in 2002 [9]) based on acetonitrile extraction followed by a liquid–liquid partitioning step and SPE clean-up, and the QuEChERS method modified in the clean-up step (introduced by Anasstassiades *et al.* [10]) based on acetonitrile extraction and liquid–liquid partitioning in one step followed by SPE clean-up. First, Schenck's method was modified in terms of a reduction in the amount of solvent used and a simplification of the whole procedure [11]. The gain of the modification of the QuEChERS method was a cleaner final extract using cartridge-based SPE instead of dispersive SPE [12]. Both sample preparation methods were connected with a fast GC–MS (utilizing a quadrupole benchtop mass selective detector (MSD)) to obtain unquestionable benefits compared with conventional capillary GC such as a high sample throughput, low GC operating cost, higher sensitivity, and more reliable analytical results [13, 14] and were validated and compared.

The main objective of this monitoring project was to assess the pesticide-residue compliance status of baby food in Slovakia, checking compliance with the MRLs laid down by the EU. The quality of the raw materials—in this case, apples—is essential to guarantee the safety of a high-quality apple-based baby food. Therefore, pesticide residues in apples intended directly for baby food production were also monitored in this work.

During 2 years of the monitoring programme (2004–2005), samples of fresh apples and apple-based baby food were collected and analysed, employing a validated multiresidue analytical method that enabled a reliable control of a wide range of GC amenable pesticides at levels 0.01 of $mg\,kg^{-1}$ and lower. To gain more insight into the behaviour of residues during apple processing, the effects of individual technological operations were evaluated on the basis of residue content determined in fresh apples, apple pureé intermediate products, and final product.

2. Experimental

2.1 *Monitoring and processing*

Apples were selected as the commodity, given the fact that apple production is of great economic importance for Slovakia, and both fresh and processed apples are used in baby food. The pesticides to be studied were selected according to testing on the basis of a survey of plant protection products applied by apple producers in south Slovakia, who deliver their raw material to baby food producer (Novofruct s.r.o., Nové Zámky).

2.1.1 Sampling of apples. The monitoring programme was carried out in collaboration with a baby food producing company located in the south Slovakia. Monitoring in two agricultural seasons 2004 and 2005 was performed. In 2004 three farmers localities in south Slovakia (8 cultivars) were selected, in 2005 another three localities (3 cultivars). In total, 62 samples of apples and apple purées were collected during the monitoring programme (2004–05). Apples (Golden Delicious, Idared, Topaz, Rubinola, Jonagold, Gloster, Sampion, Selena varieties), which are the basic raw material for baby food production, were of local origin. After harvest, apples were collected into paper bags (weight of a batch 30–40 kg). Upon arrival into the laboratory the samples were homogenized with a blender Braun MX 2050 (Krönberg, Germany) and frozen at $-18^{\circ}C$.

2.1.2 Field experiments. The experiments were carried out in an orchard of the school farm near the village Vištuk. Pesticide was applied on one triad of neighbouring trees in one row. One triad was left without treatment for control samples. The field treatments of apples with selected pesticide myclobutanil (Systane 20 EW, applied on Jonatan and Golden Delicius cultivar) were performed according to EPPO guidelines in spring-summer 2003. Field experiments were performed under the conditions of the registration experiments to evaluate the efficiency of the used formulation.

Sampling was selected in the common harvesting season (as the raw material for simulation of the technological processing of baby food), approximately 60 days after last spraying. One field sample 30–40 kg was composed by fruits collected from all three replicate plots (each plot comprised 3 trees). Apples were also picked from untreated trees to be used as control samples. Upon arrival into the laboratory the samples were homogenized and frozen at $-18^{\circ}C$.

2.1.3 Processing studies. Simulation studies and real technological processing studies of baby food production were performed. In both cases, the behaviour of pesticides during the whole processing was exaimed. The five steps of the simulation are presented below:

(1) Approximately 1 kg of the homogenously mixed apple sample was placed into a 1-L beaker, then warmed up to 60°C for 15 min; the pH was then checked (with the addition of citric acid to pH < 4).
(2) The sample was heated to 80°C for 30 min.
(3) The sample was heated to 90°C.
(4) L-Ascorbic acid (70 mg kg^{-1}) was added.
(5) Sterilization was carried out at 98°C for 40 min.

The heating process was performed in the liquid bath in a closed beaker. A portion of the mixture was sampled for the analysis after each step.

The steps were identical for the technological processing, except for the quantity of raw material. The sample collections from individual steps of the technological process of baby food production were accomplished in autumn 2004 (eight samples) and in 2005 (24 samples). Samples were collected directly from the baby food manufacturer and stored in glass bottles at −18°C, originally used for baby food distribution.

2.2 *Pesticide standards, chemicals, and materials*

The pesticides studied also represent those of a wide range of polarity and other physico-chemical properties. Pesticides belonging to a variety of groups (anilinopyrimidins-pyrimethanil, cyprodinyl, organophosphorus pesticides—dimethoate, diazinon, chlorpyrifos-methyl, fenitrothion, chlorpyrifos, methydathion, phosalone, triazine-terbuthylazine, oximinoacetate-kresoxim-methyl, triazol-penconazole, myclobutanil, tebuconazole, bitertanol, pyrethroids-cypermethrin, etofenprox) were used in our studies.

Pesticides were obtained from various sources and were of >95% purity (bitertanol (Bayer, Germany), cyprodinyl, methidathion, penconazole, terbuthylazine (Ciba-Geigy, Basel, Switzerland), dimethoate (Cheminova Agro, Denmark), etofenprox (Mitsui Toatsu Chemicals, Japan), fenitrothion (Sumimoto Chemical Co., Japan), chlorpyrifos (Dow Chemical Company, USA), kresoxim-methyl (BASF, Germany), myclobutanil (Dow Agro Science, USA), pyrimethanil (Schering, Germany), tebuconazole, captan, cypermethrin, diazinon, phosalone, chlorpyrifos-methyl (Dr. Ehrenstorfer, Germany). A stock solution of pesticides with concentration of 0.5 mg mL^{-1} was prepared by dissolving 5 mg of each compound in 10 mL of toluene (Suprasolv, Merck, Darmstadt, Germany) and was stored at −18°C. The stock solution was diluted with acetone (Suprasolv, Merck, Darmstadt, Germany) to obtain the appropriate pesticide standard solutions for preparation of spiked samples and matrix-matched standards. Acetonitrile (MeCN) and acetone used were of gas-chromatography grade (Suprasolv, Merck, Darmstadt, Germany). Magnesium sulfate (anhydrous powder) and NaCl p.a. were from Lachema (Neratovice, Czech Republic). For filtration purposes, glass fibre paper (Papírna Perštejn, Czech Republic) was used. The SPE columns used were 500 mg of Bond-Elut—NH_2, (1ST Ltd, Mid Glamorgan, UK) and 1 g of Mega BE-PSA

(Varian Incorporated, Harbor City, USA). Standards were weighted on Sartorius AnalyticMCI balances (Sartorius, Götingen, Germany) with a precision of ±10 μg.

2.3 *Analytical methods*

2.3.1 Sample preparation. The original Schenck method [9] was modified: 25 g of the apple sample was extracted with 50 mL of acetonitrile using the pulsed ultrasonic cell disrupter VibraCell (Sonics and Materials Inc., Danbury, CT; CVX 400, frequency 20 kHz). The ultrasonic pulses at 80% amplitude with a duration of 3 s paused for 3 s were applied for 3 min. The extract was filtered through glass-fibre paper (Papírna Perštejn, Czech Republic), and the filtrate was transferred into an Erlenmeyer flask with a tap. NaCl (2.5 g) was added, and the mixture was shaken for 1 min. Phases were allowed to separate for 15 min. The upper acetonitrile phase was transferred into an Erlenmeyer flask, anhydrous magnesium sulfate (2 g) was added, and the mixture was shaken for 1 min. A small quantity (25 mL) of the dried extract was evaporated to less than 1 mL in a vacuum evaporator and transferred into SPE-NH_2 column utilizing apparatus IST VacMaster (IST Ltd, MidGlamorgan, UK). Magnesium sulfate (1 cm layer) was always added to the top of SPE column; the column was previously conditioned with acetone. The eluates were collected into 20-mL. Analytes were eluted with 15 mL of acetone, and eluates were evaporated to dryness under a stream of nitrogen. The final volumes of the extracts were adjusted with toluene to 5 mL and analysed by GC–MS. The preconcentration factor in this method is 2.5.

The original QuEChERS method [10] was modified in a clean-up step: 10 g of apple sample weighed into the 40 mL centrifuge tube was extracted with 10 mL of acetonitrile using an Ultra-Turrax (IKA, Germany) homogenizer at 19,000 rpm for 3 min. Then, liquid–liquid partitioning (LLP) followed: 1 g of NaCl and 4 g of $MgSO_4$ were added, and the mixture was shaken by hand for 1 min. The mixture was then centrifuged at 3000 rpm for 5 min. A portion of the upper layer was transferred into a 10-mL centrifuge tube containing 25 mg of PSA sorbent and 125 mg of $MgSO_4$ per 1 mL of the cleaned extract. The mixture was shaken by hand for 1 min, then centrifuged for 5 min at 3000 rpm to separate solids from the solution. A 5 mL extract of the upper layer was transferred on an SPE column filled with acetone conditioned (0.5 g), NH_2 sorbent covered with 1 cm layer of $MgSO_4$. The SPE column was eluted with 10 mL of acetone. The cleaned extract was evaporated under N_2 to dryness, and the solvent exchange to 2 mL of toluene was performed. The preconcentration factor of the method is 2.5.

2.3.2 Chromatographic instrumentation and conditions. GC–MS measurements were performed on an Agilent 6890N GC coupled to 5973 MSD (Agilent Technologies, Little Falls, DE) equipped with PTV and an Agilent 7683 autoinjector. 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; the dwell time used was 10 ms. The PTV inlet was operated in cold splitless mode. The injection volume was 2 μL. Helium with a purity of 5.0 (Linde Technoplyn, Bratislava, Slovak Republic) was used as the carrier gas.

A non-polar deactivated retention gap (1 m × 0.32 mm, Supelco, Bellefonte, PA) was coupled via a pressfit connector and sealed with a polyimide resin (Supelco, Bellefonte, PA) with a narrow-bore chromatographic column CP-Sil 5 Low-Bleed MS (15 m × 0.15 mm × 0.15 μm) (Varian, Middleburg, Netherlands). Chromatographic separation was performed under a temperature programme, 130°C (1.13 min), 27.25°C min^{-1}, 290°C (6 min). PTV conditions: temperature programme, 150°C, 400°C min^{-1}, 300°C (2 min), 400°C min^{-1}, 350°C (5 min); split vent open time 1.13 min; flow rate 160 mL min^{-1}.

3. Results and discussion

3.1 *Method development*

Fruit samples free of pesticides were used for the preparation of a blank matrix standard. Blank samples were first analysed by GC–MS before being spiked, and none of the selected ions were found at the corresponding retention times of selected pesticides. The linearity of response of GC–MS in SIM mode was checked with calibration-matrix matched standards in blank extract in a range of concentrations from 0.0125 ng μL^{-1} (0.005 mg kg^{-1} in original apples) to 2.5 ng μL^{-1} (1 mg kg^{-1} in original apples). The number of replicates for all concentrations levels was 5. A regression analysis was performed to generate the linear equation of the calibration curve, and the coefficients of determination R^2 were in the range of 0.9994–1, except for captan ($R^2 = 0.9945$) and cypermethrin ($R^2 = 0.9771$). The repeatability of peak areas for all pesticides expressed as the relative standard deviation (RSD) ($n = 5$) was in the range of 0.5–11%, except for cypermethrin (20%) at a concentration of 5 μg kg^{-1} and captan, which might indicate some problems during GC analysis. Cypermethrin has four isomer forms [15]. During the chromatographic analysis, there might be partial conversion of one form to the other. Decomposition of pesticide captan in the inlet was mentioned by Maštovská *et al.* [16] and Kirchner *et al.* [14]. For real sample measurements, an external calibration method was used, utilizing bracketing [11, 12]. Recovery data were validated at concentration levels of 5, 10, and 100 μg kg^{-1}. At the concentration of five times the limit of determination, pesticide recoveries should be in the range of 70–110%, with relative standard deviations <20% [17]. Satisfactory recoveries (>90%) using GC–MS were obtained from spiked apples at the given concentration levels except for captan (46.1%) and dimethoate (77.7%) [11]. Unstable pesticides such as captan and dimethoate might be decomposed in apples by the reaction between apple components and pesticides. Both methods used reached the requirements of EU legislation on LOQs and for pesticides, which shall not be used in agricultural production intended for the production of processed cereal-based foods and baby foods [18]. The LOQ values are summarized in table 1.

3.2 *Processing studies*

Pesticide residues in food are influenced by storage and processing, which occurs between harvesting of raw commodities and consumption of prepared foodstuffs. Procedures used in food processing have been shown to have considerable effects on

Table 1. Limits of quantification[a] (LOQs) (mg kg^{-1}) $\times 10^3$.

Pesticide	Modified Schenck method	Modified QuEChERS method
Dimethoate	0.38	0.30
Terbuthylazine	0.17	0.16
Diazinon	0.50	0.32
Pyrimethanil	0.07	0.07
Chlorpyrifos-methyl	0.18	0.08
Fenitrothion	0.33	0.22
Chlorpyrifos	0.46	0.34
Cyprodinyl	0.11	0.18
Penconazole	0.17	0.22
Methidathion	0.15	1.01
Kresoxim-methyl	0.22	0.65
Myclobutanil	0.14	1.44
Tebuconazole	0.29	0.43
Phosalone	0.73	1.20
Bitertanol 1	0.60	0.21
Bitertanol 2	1.44	1.02
Cypermethrin 1	0.08	2.33
Cypermethrin 2	0.38	1.31
Cypermethrin 3	0.17	3.43
Etofenprox	0.50	0.69

[a]Determined by fast GC–MS in SIM mode.

residues levels [19]. The extent and direction of the pesticide changes during processing depend on physico-chemical properties of the chemicals, type and conditions of the processes, and nature of the crops [20].

The simulation of the technological process of baby food production (apple purée) was performed to study the behaviour of myclobutanil (apples from field experiments) after each step of the simulation. A modified Schenck method was used as the sample preparation technique with subsequent rapid GC–MS determination. The results for both cultivars Jonathan and Golden Delicious are presented in table 2. No addition of citric acid was necessary, because the pH was <3.4 in both cases. Thermal processing (cooking, sterilization) may widely affect the concentration of pesticide residues in apple samples. The concentration of myclobutanil decreased after the first heating step. The increase in myclobutanil concentration in the last steps of the technological process was probably caused by the pre-concentration effect of the sample (water from samples was evaporated).

In autumn 2004, the behaviour of pesticides during the real technological process of baby food production was traced (apples were from the locality of Nové Zámky). Two pesticides, fenitrothion and pyrimethanil, were detected and quantified after each step of the technological process of baby food production from Novofruct, s.r.o. and also in raw apples used for baby food production. The results are presented in table 3. The concentration of both pesticide residues decreases after the first step, the differences in residue content after next steps are not significant, and the concentration values were near the LOQs (0.36×10^{-3} mg kg^{-1} for fenitrothion and 0.48×10^{-3} mg kg^{-1} of pyrimethanil).

Several collections of apples (raw material directly from baby food producer) together with samples from individual steps of the technological process of baby food production (24 samples) were accomplished also in autumn 2005. An example in the

Table 2. Myclobutanil content determined[a] after each step of simulation of technological process of baby food—apple purée production.

	Cultivar					
	Jonatan			Golden delicious		
Simulation step	Average concentration ($mg\,kg^{-1}$) $\times 10^3$	RSD_{PA}% ($n=2$)	RSD_{GC}% ($n=3$)	Average concentration ($mg\,kg^{-1}$) $\times 10^3$	RSD_{PA}% ($n=2$)	RSD_{GC}% ($n=3$)
0[b]	9.4	1.8	3.2	16.4	0.3	1.1
1	8.6	2	1.3	18.8	1.4	2.6
2	9.4	0.3	1	19.1	0.2	4
3	9.4	3.2	3.7	18.9	0.2	3
4	11.1	6.3	1.6	18.8	0.7	3.4
5	12.1	3.1	3.9	20.9	0.4	2.5

[a]By the modified Schenck method connected with rapid GC–MS; locality: Nové Zámky.
[b]Sampled before the simulation process; RSD_{GC}: relative SD of GC–MS measurements, $n=3$/sample extraction (the highest is given); RSD_{PA} – relative SD of analysis of two parallel sample extractions, calculated by Eckschlager [21] for $n=2$.

Table 3. Pyrimethanil and fenitrothion content determined[a] after each step of technological process of baby food production.

	Traced pesticide					
	Pyrimethanil			Fenitrothion		
Step of the technological process	Average concentration ($mg\,kg^{-1}$) $\times 10^3$	RSD_{PA}% ($n=2$)	RSD_{GC}% ($n=3$)	Average concentration ($mg\,kg^{-1}$) $\times 10^3$	RSD_{PA}% ($n=2$)	RSD_{GC}% ($n=3$)
0	1.13	35.8	2.2	6.77	4.5	3.2
1	0.72	8.0	4.7	1.68	6.7	1.8
2	0.67	8.0	4.7	1.56	10.8	6.2
3	0.59	11.0	3.8	1.53	9.4	4.8
4	0.80	2.3	5.1	1.47	4.3	6.1

[a]By the modified QuEChERS method connected with rapid GC–MS; step (0) raw apples; locality Nové Zámky (2004); RSD_{GC}: relative SD of GC–MS measurements, $n=3$/sample extraction (the highest is given); RSD_{PA}: relative SD of analysis of two parallel sample extractions, calculated by Eckschlager [21] for $n=2$.

determination of pesticide residue content in apples (locality Zemné) and after each step of the technological process of apple pureé production is given in table 4. Positive findings of pesticide residues in apples from two other localities and their behaviour during processing are shown in figure 1. Several studied pesticides underwent a significant reduction of residues after the first step.

3.3 *Monitoring*

Information on residues in fresh apples from farmers localities is summarized in table 5 (monitoring studies in 2004 and 2005). Only those pesticides for which the GC method is amenable and for which analytical methods were validated were quantified. In total, 28 apple samples were analysed (with three repetitive GC analyses plus matrix matched standards analysis). Twenty-four pesticide residues in 16 apple samples presented positive findings. Some pesticides exceeded the concentration of $0.01\,mg\,kg^{-1}$ (table 5).

Table 4. Pesticide residues content determined[a] after each step of the technological process of baby food production.

Applied pesticides	GC amenable	0. step		1. step		2. step		3. step		4. step	
		Average concentration[b] (10^{-3} mg kg^{-1})	u_c (%)	Average concentration[b] (10^{-3} mg kg^{-1})	u_c (%)	Average concentration[b] (10^{-3} mg kg^{-1})	u_c (%)	Average concentration[b] (10^{-3} mg kg^{-1})	u_c (%)	Average concentration[b] (10^{-3} mg kg^{-1})	u_c (%)
Acetamiprid	+	/		/		/		/		/	
Diflubenzuron	−										
Fenitrothion	+	–		–		–		–		–	
Fluquinconazole	+	10.2	16.3	1.7	2.8	1.7	2.6	1.1	110.7	0.4	–
Chlorpyrifos	+	–		–		–		–		–	
Luferunon	−										
Metiram	−										
Pyrimethanil	+	2.2	3.9	1.2	17.1	1.4	1	1.4	6.1	1.4	–
Tebuconazole	+	–		–		–		–		–	
Tetraconazole	+	1.6	17.3	0.8	12.5	0.9	1.2	0.8	2.6	0.7	1.2
Thiacloprid	−										
Tolylfluanid	+	7.5	10.3	0.9	12.1	0.5	12.9	0.6	–	–	

[a]By the modified QuEChERS connected with fast GC–MS; raw apple (0); locality Zemné; – unidentified; / not monitored.
[b]Average concentration of pesticide residue ($n = 2$); u_c: combined standard uncertainties calculated in accordance with ISO 21748:2004.

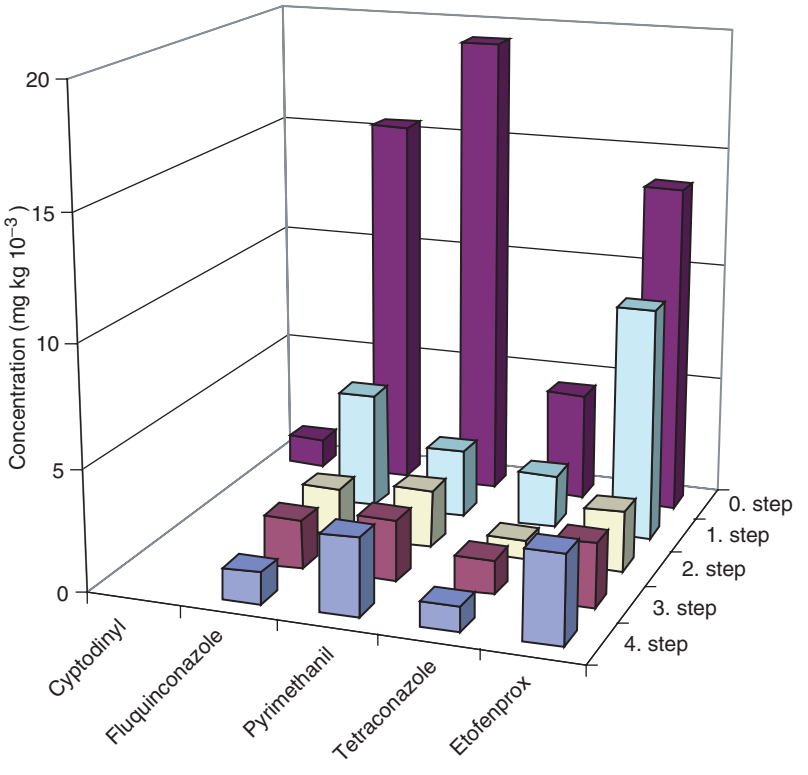

Figure 1. Results of positive findings of pesticide residues in apples, and steps in the processing procedure for apple purée; locality Nové Zámky, Komoča (2005).

Several pesticides leaving residues only in the lowest concentration range (≪LOQ) were identified. The maximal concentration found in apples was $0.099\,mg\,kg^{-1}$ (fluquinconazole).

In the autumn of 2004 and 2005, pesticide residues in the final product of apple purée were monitored (figure 2). Most of the detected and quantified residues were at a concentration below $0.01\,mg\,kg^{-1}$. The maximal concentration found was $0.0235\,mg\,kg^{-1}$ of fluquiconazole.

4. Conclusion

Effective sample preparation techniques (the modified Shenck's and QuEChERS method) in combination with fast GC–MS were shown to be sufficiently robust for processing and monitoring studies of pesticide residues at ultratrace concentration levels. Processing of raw materials can lead to concentration or losses of pesticide residues. Processing studies of the technological process of baby food production indicated that the technological process of baby food production in Slovakia affects the concentration of some pesticide residues under study (as fenitrothion, fluquinconazole, pyrimethanil, and tolylfluanid). Processing studies can help producers to tune the

Table 5. Results of pesticide residues content in apples.[a]

Supplier	Cultivar	Pesticide	Etofenprox	Tetraconazole	Penconazole	Fenitrothion	Cypermethrin	Pyrimethanil	Fluquinconazole	Tolylfluanid	Cyprodinyl
2004											
Nové Zámky	Golden delicius	c (mg kg^{-1}) × 10^3	3.1								
		u_c (%)	15.1								
	Idared	c (mg kg^{-1}) × 10^3	11.3								
		u_c (%)	14.1								
	Topaz	c (mg kg^{-1}) × 10^3	19.6								
		u_c (%)	4.6								
	Rubinola	c (mg kg^{-1}) × 10^3	3.4								
		u_c (%)	5.7								
Dvory nad Žitavou	Jonagold	c (mg kg^{-1}) × 10^3			<LOQ						
	Gloster	c (mg kg^{-1}) × 10^3			<LOQ						
	Idared	c (mg kg^{-1}) × 10^3			<LOQ						
	Sampion	c (mg kg^{-1}) × 10^3			<LOQ	18.5					
		u_c (%)				16.3					
Nová Trstená	Selena	c (mg kg^{-1}) × 10^3					6.5				
		u_c (%)					18.4				
	Golden delicius	c (mg kg^{-1}) × 10^3									
		u_c (%)									
2005											
Nové Zámky	Idared	c (mg kg^{-1}) × 10^3	13.7	4.5				0.4	98.9		
		u_c (%)	16.6	16.1				16.3	20.1		
Komoča	Golden delicius	c (mg kg^{-1}) × 10^3				17.0		19.3	15.5		1.2
		u_c (%)				17.7		9.3	6.3		7.6
Zemné	Selena	c (mg kg^{-1}) × 10^3		1.6				2.2	10.2	7.5	
		u_c (%)		17.3				3.9	16.3	10.3	

[a]Determined by modified QuEChERS connected with fast GC\MS in apples from suppliers of raw material for baby food production; c: average concentration of pesticide residue ($n = 2$); u_c: combined standard uncertainties calculated in accordance with ISO 21748:2004.

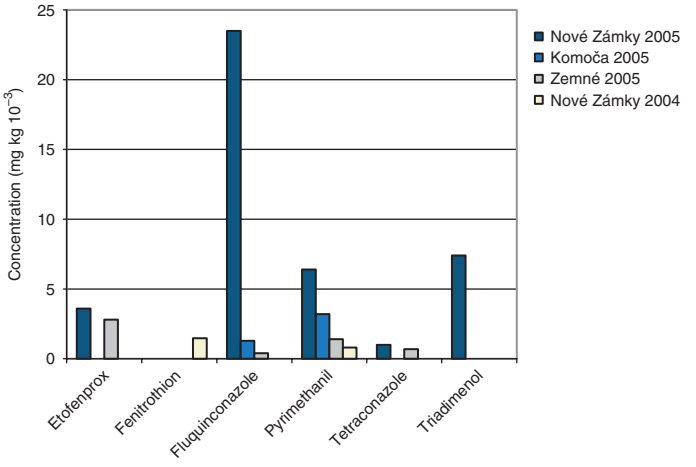

Figure 2. Positive findings of pesticide residues in apple purée (monitoring 2004, 2005).

technological parameters to avoid contamination problems. The changes in pesticide residues concentration levels during processing depend on the nature of the chemicals. The preliminary monitoring studies on fresh apples and the final product of baby food production indicate that apple trees were treated in accordance with principles of good agricultural practice. There were not any residual values exceeding MRLs for the adult population, but there were some exceeding findings for apples to be used for baby food (MRLs = 0.01 mg kg^{-1}). Concerning EU directives on pesticide residues in processed foods for infants and young children, there were no positive findings in the final product of baby food production (apple purée), or the content of most of the searched residues decreased to the value $\leq$0.01 mg kg^{-1}, with one exception (0.0235 mg kg^{-1} of fluquinconazole).

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