

Monitoring of Pesticide Residues in Apples from Slovakia for Baby Food Production

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Abstract

DÖMÖTÖROVÁ M., HERCEGOVÁ A., MATISOVÁ E. (2006): **Monitoring of pesticide residues in apples from Slovakia for baby food production.** Czech J. Food Sci., 24: 84–92.

There is a basic lack of information about the presence of pesticide residues in apples obtained from farms in Slovakia collaborating with baby food producer. Residues of several pesticides (widely used for the protection on apple trees) have been determined in apples (a common raw material for the baby food production and baby food) from Slovakia (agricultural area in the South of Slovakia). The analysis of the pesticides was performed by gas chromatography on CP-Sil 5 CB (15 m long, 0.15 mm I.D., film thickness 0.15 μm) with normal bore retention gap (1 m long, 0.32 mm I.D.) using the subsequent determination with MS detector in SIM mode, after the acetonitrile extraction of the pesticide residues from apples, the clean-up and preconcentration steps of samples with SPE-NH₂. For the study pesticides belonging to various groups were selected, such as organophosphorus pesticides, oximinoacetates, anilinopyrimidines, triazoles, and triazines pyrethroids. The GC-MS analysis of pesticide residues in all samples searched showed that most of the detected and quantified residues were below 10 $\mu\text{g}/\text{kg}$ which corresponds to the maximum residual limit for pesticide residues in baby food.

Keywords: pesticides; apples; baby food; sample preparation; fast CG

Pesticides have been applied worldwide to a broad variety of crops both for the field and post-harvest protection. The use of chemical pesticides is known to have a significant positive impact on crop yields and, therefore these are used in increasing amounts. This is confirmed by the registered pesticide import statistics showing that traditional subsistence farmers apply increasing amounts of pesticides in their production systems (KAMMERBAUER & MONCADA 1998). But the effective pesticide use must be seen in a wider context than just the efficient pest control, and must take into account the effect of the pesticide accumulation in the environment, and the impact of pesticide residues on human health.

The increasing public concern in recent years about the possible health risk due to the pesticide residues in the diet has deeply modified the strategy for the crop protection, with emphasis on food quality and safety, and the widespread concern for the health of society led to the strict regulation of maximum residue limits (MRLs) of the pesticide residues in food commodities (SAFI *et al.* 2002).

The production of safe and healthy food is a key priority of EU and is valid also for Slovakia as a new member. The harmonisation with the requirements and regulations in the field of food quality and safety needs a strong scientific base for implementing the principles of sustainable

development and minimising health risks related to the food contamination.

The standard multiresidue procedures for fruits are described by many monitoring agencies in their screening programs and are officially accepted in many countries. The most suitable approaches in the determination of the pesticide residues contents in fresh and processed fruits (considered as non-fatty food samples) are chromatographic methods connected with various sample preparation methods (TORRES *et al.* 1996; SCHENCK *et al.* 2002; ANASTASSIADES *et al.* 2003). The combination of GC/mass spectrometry (MS) and LC/MS/MS can currently provide the most effective and efficient means to both quantify and identify hundreds of pesticide analytes in a variety of matrixes (LEHOTAY *et al.* 2005).

GC techniques analyse semivolatile and less polar analytes. Especially the fast GC techniques provide faster, cost-effective analytical answer (KORYTÁR *et al.* 2002; MATISOVÁ & DÖMÖTÖROVÁ 2003). The pesticide residues monitored were detected, identified and quantified using fast GC with MS detection in the selected ion monitoring (SIM) mode. For the sample preparation, a method based on acetonitrile extraction in combination with cell disruption by pulsed ultrasound and SPE-NH₂ clean-up was chosen. The objective of this study was to monitor and compare the pesticide residues in apples from the farms (South Slovakia) collaborating with the baby food producer.

MATERIALS AND METHODS

Reagents and materials. The standards of pesticides were obtained from various sources and were of purity > 95% – 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 (BASE, Germany), myclobutanil (Dow Agro Science, USA), pyrimethanil (Schering, Germany), tebuconazole, captan, cypermethrin, diazinon (Argovita), phosalone, chlorpyrifos-methyl (Dr. Ehrenstorfer, Germany).

The stock solution of pesticides in the concentration of 0.5 mg/ml was prepared by dissolving 5 mg of each compound in 10 ml of toluene (Suprasolv, Merck, Darmstad, Germany) and was stored at

–18°C. The pesticides and their chemical classes are listed in Table 1. The stock solution was diluted with acetone (Suprasolv, Merck, Darmstadt, Germany) to get the appropriate pesticide standard solutions for the preparation of spiked samples and matrix-matched standards.

Magnesium sulfate (anhydrous powder) was obtained from Lachema (Neratovice, Czech Republic). Acetonitrile (MeCN) was of gas chromatography grade (Suprasolv, Merck, Darmstadt, Germany). The sample was filtered through the glass fibre paper Z4 (Papírna Perštejn, Czech Republic). The SPE columns used were 500 mg of Bond Elut-NH₂ (IST Ltd., Mid Glamorgan, UK), 500 mg Supelclean ENVI-Carb (Supelco, Bellefonte, USA) and 1 g Mega BE-PSA (Varian Incorporated, Harbor City, USA).

Instrument GC-MS measurements were performed on an Agilent 6890N GC connected to 5973 MSD (Agilent Technologies, Avondale, USA) equipped with a programmed temperature vapouriser (PTV). A non-polar deactivated retention gap (1 m × 0.32 mm, Supelco, Bellefonte, USA) was coupled via a pressfit connector and sealed with a polyimide resin (Supelco, Bellefonte, USA) with a narrow-bore chromatographic column CP-Sil 5 Low-Bleed MS (15 m × 0.15 mm × 0.15 µm) (Varian, Middleburg, the Netherlands). Helium with the purity of 5.0 (Linde Technoplyn, Bratislava, Slovak Republic) was used as a carrier gas. PTV inlet was operated in cold splitless mode under the following conditions: temperature programme 120°C; hold 0 min; ramp 400°C/min to 300°C; hold 1.2 min; then the second temperature ramp 100°C/min to 350°C to release the less volatiles substances 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. An injection volume was 2 µl.

Chromatographic separation was performed under the following temperature programme: initial temperature 100°C; hold 1.5 min; ramp 30°C/min to 290°C; hold 5 min and a constant carrier gas flow 0.5 ml/min. MS with electron impact ionisation mode (70 eV) was operated in SIM mode. For each pesticide 2 ions were selected and sorted into groups, the dwell time used was set to 25 ms (except for the time window starting at 6.50 min – 10 ms) (KIRCHNER *et al.* 2005). The retention times, ions for SIM and group start times of 18 pesticides studied are listed in Table 1.

The standards were weighed on a Sartorius Analytic MC1 balance (Sartorius, Göttingen, Germany)

Table 1. List of pesticides used; retention times, and monitored ions in SIM mode

Compound	Chemical class	Retention time (min)	Monitored ions in SIM Target ion	SIM group start time (min)
Dimethoate	organophosphate	5.86	87, 125	3.00
Terbutylazine	triazine	6.02	214, 229	5.50
Diazinon	organophosphate	6.02	276, 304	
Pyrimethanil	anilinopyrimidine	6.11	198, 199	
Chlorpyrifos-methyl	organophosphate	6.41	286, 288	5.90
Fenitrothion	organophosphate	6.62	260, 277	
Chlorpyrifos	organophosphate	6.72	286, 314	6.30
Cyprodinyl	anilinopyrimidine	6.96	224, 225	6.50
Penconazole	triazole	7.00	248, 250	
Captan	phtalimide	7.13	79, 264	
Methidathion	organophosphate	7.18	145, 302	
Kresoxim-methyl	oximinoacetate	7.41	131, 132	6.85
Myclobutanil	triazole	7.43	179, 245	
Tebuconazole	triazole	8.03	250, 252	7.40
Phosalone	organophosphate	8.55	182, 367	
Bitertanol 1	triazole	9.07	168, 170	8.25
Bitertanol 2	triazole	9.14	168, 170	
Cypermethrin 1	pyrethroid	9.54	163, 181	8.70
Cypermethrin 2	pyrethroid	9.66	163, 181	
Cypermethrin 3	pyrethroid	9.73	163, 181	
Etofenprox	non-ester pyrethroid	9.85	163, 376	

with the precision of $\pm 10 \mu\text{g}$. The apples were homogenised with a blender Braun MX 2050 (Kronberg, Germany). To disrupt the cells of apples the sonication sonda of the pulsed ultrasonic cell disrupter VibraCell (Sonics and Materials Inc., Danbury, USA, CVX 400, frequency 20 kHz) was used. The flow rate of the elution solution, IST VacMaster (IST Ltd., MidGlamorgan, UK) was adjusted.

Sampling. Approximately 2–3 kg of apples from the harvest of 2004 were used in this study. They were homogenised with peel and stored in a freezer at -18°C in a refrigerator. 25 g of the homogenised sample were taken for the analysis in order to achieve a representative sample.

Sample preparation. An apple sample with peel (25 g) was extracted with 50 ml of acetonitrile using the sonication sonda (an efficient release of the pesticide residues from the apple sample),

filtered through a coarse filter paper, and the filtrate was transferred into an Erlenmayer flask with a tap. NaCl was added (2.5 g) and the mixture was shaken for 1 min. The phases were allowed to separate for 15 min. The upper acetonitrile phase was transferred into an Erlenmayer flask, anhydrous magnesium sulfate (2 g) was added and the content was shaken for 1 min. 25 ml of the dried extract were evaporated to a volume smaller than 1 ml in a vacuum evaporator and transferred into SPE-NH₂ column. Magnesium sulfate (1 cm layer) was always added onto the top of SPE column; the column was conditioned with acetone. The elution solvent for SPE-NH₂ column was acetone. Vacuum was adjusted at the flow rate of 1–2 drops/s. The eluates were collected into 20 ml vials. The analytes were eluted with 15 ml of acetone and the eluates were evaporated to dryness with the aid of nitrogen stream. The

final volumes of the extracts were adjusted with toluene to 5 ml and analysed by GC-MS.

Fruit samples free of pesticides coming from field experiments (NATO project Sfp – 977983, 2003) were used for the preparation of a blank matrix standard. Blank samples were first analysed by GC-MS before spiking and none of the selected ions was found at the corresponding retention times of the pesticides selected (Table 1).

The solutions of matrix-matched standards were prepared by adding the appropriate volume of the pesticide stock solution to the extract of the blank apple sample prepared by the SPE method.

RESULTS AND DISCUSSION

Fresh and processed apples are used mostly as baby food in Slovakia. The apples used for the research (Idared, Golden Delicious, Topaz, Rubinola, Jonagold, Gloster, Šampion, Selena) were treated according to the recommendations of the producers of the pesticide formulations (Tables 2–4). The pesticides to be studied were chosen on the basis of certain criteria. The basic criterion was their importance for the local market. The second criterion was the performed statistical evaluation of the pesticides applied on the chosen commodity in South Slovakia. Farmers of this region delivered the raw material to the producer of baby food in the harvest season of 2004. The pesticides studied also represent those of a wide range of polarity and other physico-chemical properties. The model mixture of 18 pesticides belonging to the variety groups (anilinopyrimidins, organophosphorus pesticides, triazines, oximinoacetate, triazol) of pesticides in apples was studied in the first stage of the method development. According to the presently valid MRLs (10 µg/kg for processed cereal-based and baby food for infants and young children) as established by Codex Alimentarius Commission of FAO/WHO (Directive 1999/29/EC), the level of concentration of pesticide residues in apples was checked in real samples.

Method development

The method of fast GC/MS for the pesticide residues analysis in apples was developed and validated (HERCEGOVÁ *et al.* 2005). The sample preparation based on acetonitrile extraction and SPE-NH₂ cleaning was modified, combined with the cell disruption, and optimisation of several

parameters in the whole sample preparation procedure was performed. The separation of pesticides from the matrix components was presented in the extracted ion chromatogram of 18 pesticides. The unit resolution quadrupole mass analyser together with the increased separation power reached by utilisation of the narrow-bore column provide a good resolution also under fast temperature programming. The ions were carefully selected with regard to the background noise and S/N ratio of a blank apple matrix extract compared to the spiked samples at the lowest concentration studied (0.0125 ng/µl) (KIRCHNER *et al.* 2004). Good recoveries (≥ 90%) were obtained, which is in agreement with the directives laid down by the European Commission (at the concentration five times the limit of determination, the pesticide recoveries should be in 70–110% range with relative standard deviations < 20%) (Council Directives 94/43/EC 1994). The concentration levels investigated correspond to the ultra-trace concentrations of pesticides in apples that are also covering the MRLs of pesticides in baby food. LOQs less than 5 µg/kg were reached with all pesticides studied (LOQ_{fenitrothion} = 0.37 µg/kg, LOQ_{penconazole} = 0.54 µg/kg, LOQ_{etofenprox} = 0.51 µg/kg and LOQ_{cypermethrin} = 1.6 µg/kg – LOQs of relevant pesticides in this monitoring study).

Reduction of the matrix effects

In the pesticide residue analysis, the injected sample contains large amounts of the unavoidably present co-extractives which are responsible for the matrix effects occurring on the injector (causing changes in peak responses), the column (changes in peak responses and separation efficiency), and/or the detector side (false positive or negative results) (HAJŠLOVÁ & ZROSTLÍKOVÁ 2003). Several ways leading to the reduction of the matrix effects were practiced: (a) in order to decrease the matrix effects on the detector site, narrow-bore column was employed to increase the separation power; utilisation of (b) pre-column and (c) prolonged final isothermal part of the temperature program to protect the analytical column from an excessive contamination, and (d) PTV injection in the split vent mode (used after injection period) to eliminate the less volatile compounds entering into the column. The changes in the peak response with a number of injections were also eliminated by injections in sequences,

Table 2. GC-MS pesticide residues on apples locality Nové Zámky

Pesticide applied	Formulation	Date of crop treatment (2004) (concentration*, kg/ha)	MRL (µg/kg)	GC amenable	Supplied to baby food producer			Not supplied to baby food producer						
					Golden Delicious average concentration (µg/kg)	u _c (%)	average concentration (µg/kg)	Idared average concentration (µg/kg)	u _c (%)	average concentration (µg/kg)	Topaz average concentration (µg/kg)	u _c (%)	Rubinola average concentration (µg/kg)	u _c (%)
Acetamiprid	Mospilan	5/15 (0.05)	-	+	/	/	/	/	/	/	/	/	/	/
Captan	Merpan	5/24 ^a , 6/6 ^a , 6/29 ^a , 7/9 ^a (1.00)	3000	+	-	-	-	-	-	-	-	-	-	-
Dinocap	Karathane	7/17 (0.35)	-	+	/	/	/	/	/	/	/	/	/	/
Dithianon	Delan	6/14 ^a (0.53)	-	+	-	-	-	+	+	-	-	-	-	+
Etofenprox	Trebon	6/29 (0.15)	-	+	3.09	15.1	11.3	14.1	14.1	19.6	4.6	3.38	5.7	5.7
Folpet	Shavit	5/4 (1.40)	3000	+	-	-	-	-	-	-	-	-	-	-
Kresoxim-methyl	Discus	5/15, 5/24 (0.10)	200	+	-	-	-	-	-	-	-	-	-	-
Mancozeb	Dithan	7/17 ^a , (2.00)	3000	-	-	-	-	-	-	-	-	-	-	-
Novaluron	Rimon	5/24, 7/9 (0.05)	-	+	/	/	/	/	/	/	/	/	/	/
Pyridaben	Sanmite	6/14, (0.15)	-	+	/	/	/	/	/	/	/	/	/	/
Pyrimethanil	Mythos	4/23 (0.23), 5/2 ^a (0.3)	-	+	-	-	-	-	-	-	-	-	-	-
Teflubenzuron	Nomolt	4/23, (0.11)	-	-	-	-	-	-	-	-	-	-	-	-
Tetraconazole	Domark 10 EC	4/23 (0.03)	-	+	+	+	+	+	+	+	+	+	+	+
Thiacloprid	Calypso	6/6 (0.12)	-	-	-	-	-	-	-	-	-	-	-	-
Triadimenol	Shavit	5/4 (0.03)	-	+	-	-	-	-	-	-	-	-	-	-
Triazamate	Aztec	4/23 (0.14)	-	-	-	-	-	-	-	-	-	-	-	-

u_c = combined standard uncertainties calculated in accordance with ISO 21748:2004 (ŠTĚPÁN *et al.* 2004), *n* = 2

+ = identified, not quantified; - = unidentified; / = not monitored

* concentration of active substance/one spraying

^ano spraying of Topaz and Rubinola

MRL – maximum residual limit for commodity apple (Council Directives 76/895/EEC)

Table 3. GC-MS pesticide residues on apples locality Dvory nad Žitavou

Pesticide applied	Formulation	MRL (µg/kg)	GC amenable	Supplied to baby food producer			Not supplied to baby food producer		
				Golden Delicious	Jonagold	Gloster	Idared	Šampion	
				average concentration (µg/kg)	u _c (%)	average concentration (µg/kg)	u _c (%)	average concentration (µg/kg)	u _c (%)
Captan	Merpan	3000	+	–	–	–	–	–	–
Diflubenzuron	Dimilin	–	–	–	–	–	–	–	–
Dodine	Efuzin	–	–	–	–	–	–	–	–
Fenitrothion	Sumithion Super	500	+	–	–	–	–	18.50	–
Kresoxim-methyl	Discus	200	+	–	–	–	–	–	–
Metiram	Polyram	3000	–	–	–	–	–	–	–
Novaluron	Rimon	–	+	/	/	/	/	/	/
Penconazole	Topas	200	+	–	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Quinalphos	Oleokalux	50	+	–	–	–	–	–	–
Thiacloprid	Calypso	–	–	–	–	–	–	–	–

u_c = combined standard uncertainties calculated in accordance with ISO 21748:2004 (ŠTĚPÁN *et al.* 2004), *n* = 2

+ = identified, not quantified; – = unidentified; / = not monitored

MRL – maximum residual limit for commodity apple (Council Directives 76/895/EEC)

Table 4. GC-MS pesticide residues on apples locality Nová Trstená

Pesticide applied	Formulation	MRL ($\mu\text{g}/\text{kg}$)	GC amenable	Selena (supplied to baby food producer)		Golden Delicious (not supplied to baby food producer)	
				average concentration ($\mu\text{g}/\text{kg}$)	u_c (%)	average concentration, ($\mu\text{g}/\text{kg}$)	u_c (%)
Diflubenzuron	Dimilin	–	–				
Fenarimol	Rubigan	300	+	+		+	
Fenitrothion	Sumithion Super	50	+	–		–	
Chlorpyrifos	Oleoeko	500	+	–		–	
Kresoxim-methyl	Discus	200	+	–		–	
Teflubenzuron	Nomolt	–	–				
Tetraconazole	Domark 10 EC	–	+	–		–	
Thiacloprid	Calypso	–	–				
Cypermethrin	Fury	1000	+	6.5	18.4	–	

u_c = combined standard uncertainties calculated in accordance with ISO 21748:2004 (ŠTĚPÁN *et al.* 2004), $n = 2$

+ = identified, not quantified; – = unidentified; / = not monitored

MRL = maximum residual limit for commodity apple (Council Directives 76/895/EEC)

where after 3 injections of the blank matrix sample (in order to occupy the active sites in the liner and to stabilise the conditions of an inlet) the alternation of spiked samples and real samples (resp. matrix matched samples) follows (HERCEGOVÁ *et al.* 2005). For the determination of the concentration levels of pesticide residues in real samples, the subsequent sequence was used: 3–5 \times blank matrix standard, 2 parallel real sample extracts, 1 \times matrix matched standard, 2 parallel real sample extracts, 1 \times matrix matched standard, 2 parallel real sample extracts, 1 \times matrix matched standard.

Real samples analysis

The fast GC-MS analysis of the pesticide residues in various cultivars of apples (from three different localities of South Slovakia) was carried out and the data are presented in Tables 2–4. The apple samples from the locality Nové Zámky (Table 2) showed a relatively high level of etofenprox in the cultivar Topaz. The concentration 19.6 $\mu\text{g}/\text{kg}$ of etofenprox exceeded MRL (10 $\mu\text{g}/\text{kg}$) almost twice and the cultivar was not supplied for the baby-food production. The level of etofenprox in the cultivar Idared (11.3 $\mu\text{g}/\text{kg}$) very slightly exceeded MRL for the pesticide residues in baby food. The detected pesticide residues of etofenprox

in Golden Delicious and Rubinola were quantified and were below the MRL.

The situation concerning apples in the locality Dvory nad Žitavou (Table 3) showed that only fenitrothion levels of 18.5 $\mu\text{g}/\text{kg}$ were higher than the required MRL. Out of the other pesticides, only penconazole was detected on a very low concentration level in the cultivar Šampion, Idared, Gloster, and Jonagold. Table 4 shows that in the apple samples from the locality Nová Trstená the only residue quantified was cypermethrin residue which did not exceed 10 $\mu\text{g}/\text{kg}$. Figure 1 shows examples of the extracted ion chromatograms of two pesticides found.

The measurement of uncertainty is a quantitative indicator of the confidence, when the analytical data are to be compared with legal limits (SANCO/10476/2003). The combined standard uncertainty associated with the results presented in Tables 2–4 is based on the experimental evaluation of uncertainty sources represented by repeatability of analysis of spiked samples (expressed as relative standard deviation for individual analytes ($n = 2$)), and uncertainty of recovery derived from rectangular distribution (according to ISO 21748:2004 – ŠTĚPÁN *et al.* 2004).

The data presented show in general that the majority of the residues monitored are supposed

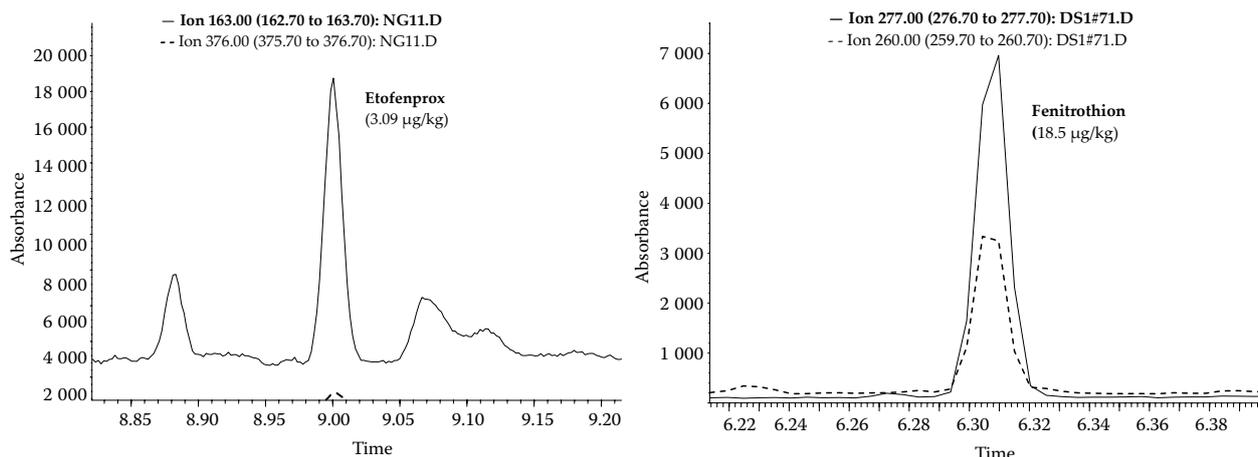


Figure 1. Extracted ion chromatograms of target and qualifier ions of pesticides etofenprox (Golden Delicious, Nové Zámky) and fenitrothion (Šampion, Dvory nad Žitavou)

to be in the concentrations below LOD. Only in three cases the concentration of the pesticide residues exceeded MRL (not more than twice) from which only one cultivar was supplied for baby food production, slightly exceeding the MRL of pesticide etofenprox. The pesticide residues that are not among the standards of the mixture studied are denominated in tables as “identified”. These were proved by software AMDIS (Nist, Gaithersburg, 1997) evaluating 8–10 the most intensive and typical ions selected from the library spectra, which were measured in SIM mode and were at very low concentrations.

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Received for publication April 25, 2005

Accepted after corrections September 8, 2005

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