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Stability of pesticides in plant extracts used as calibrants in the gas chromatographic analysis of residues

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Abstract

The stability of commonly used pesticides in plant sample extracts was evaluated. Matrices differing in the character of coextracts were represented by wheat, oranges and white cabbage. After homogenisation with ethyl acetate and anhydrous sodium sulphate, spiked filtrates were stored for 60 days at 20°C or 40°C. The decrease of concentrations was observed at 20°C after 40 days for chlorothalonil and iprodione in cabbage extracts and some degradation was observed for most organophosphates, iprodione and pirimicarb in orange extracts. At increased temperature (40°C), degradation of most pesticides in the orange and cabbage extracts was observed. No decomposition was noticed for synthetic pyrethroids in all tested extracts. The stability of pesticides in wheat extracts was distinctly higher than that in other extracts. Most pesticides are stable enough to store plant sample extracts several weeks prior to further handling, or to use them as calibrants to avoid matrix-induced enhanced GC response. Some degradation of pesticides, in ''pure'' ethyl acetate solutions was noticed only for some organophosphates (mevinphos, methamidophos, dichlorvos, heptenophos, pirimiphos-methyl) after 60 days at 40°C.
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1. Introduction

Contrary to ''classic'' organochlorine pesticides such as DDT, aldrin etc., which are very persistent and relatively stable during analytical procedure, ''modern'' pesticides are significantly less stable; their degradation can be catalysed by many physico-chemical factors. Although common organic solvents themselves are not reactive, some decomposition of pesticides can occur, especially when traces of impurities are present.

In many multiresidue methods, ethyl acetate is used for the extraction of pesticide residues from grains, fruits and vegetables [1–6]. Filtered extracts are often stored for several days in this solvent prior to the further determinative step. Some testing laboratories entirely omit sample clean-up and this routine practice results in excessively high recoveries depending on analysed materials and concentration levels. The use of matrix-standards can be (in some instances) the cost-effective way to compensate for matrix effects. To compensate for matrix-induced-enhancement of recoveries, standard solutions in residue-free sample extracts are used for the gas chromatographic calibration in some testing laboratories [7,8].

Our study was aimed at the evaluation of pesticide stability in plant extracts in order to consider suitable

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conditions for their storage and handling in testing laboratories prior to gas chromatographic determination. To test the influence of coextractives on the pesticide stability, different types of matrices represented by wheat, oranges and cabbage were employed as important food commodities currently analysed for pesticide residues within Europe. Each of these matrices represents a broader group of commodities as to the content of moisture, lipids, pigments and many other components potentially influencing the stability of pesticides.

Samples were homogenised with ethyl acetate and anhydrous sodium sulphate and ''crude'' extracts were spiked with standard solution of pesticides mixture.

2. Experimental

2.1. Materials

Ethyl acetate, cyclohexane and toluene, all organic trace analysis grade SupraSolv, were supplied by Merck (Darmstadt, Germany). Sodium sulphate anhydrous (analytical grade) was obtained from Lachema Brno (Brno, Czech Republic) and heated 4 h at 600°C before use. Silanized 2-ml amber ampoules (Supelco, Bellefonte, PA, USA) were used for the storage of extracts.

All 38 pesticide standards with purity >95% were supplied by Dr. Ehrenstorfer (Germany). Two stock solutions were prepared in toluene (''ECD-mixture'' and ''NPD-mixture''); concentration of analytes in ''ECD-mixture'' ranged from 10.8 to 101 μg/ml and in ''NPD-mixture'' from 4.6 to 95.5 μg/ml, respectively.

2.2. Apparatus

A Waring HGB 550 laboratory mixer (Waring, USA), with steel beaker and coffee-mill (Braun, Germany) and a high-speed disperser Ultra-Turrax IKA T25 (IKA, Germany) were used.

The gas chromatograph was a Hewlett-Packard 6890 (Palo Alto, CA, USA) with automatic liquid sampler HP 7673, and ^{63}Ni electron-capture detection (ECD) and nitrogen–phosphorus detection (NPD) systems; a Büchi R-114 rotary vacuum evaporator (Switzerland) was used.

For automated gel permeation chromatography (GPC), we applied a HP 1090 liquid chromatograph with fraction collector Retriever II (ISCO) and a stainless steel column (600 mm×7.5 mm I.D.) packed with 10 μm PL gel (PL Labs., UK).

2.3. Sample preparation

Approximately 200 g of the whole orange was sliced by knife and mixed for 5 min in the Waring blender. The same procedure was used for white cabbage (outer leaves were removed before homogenisation). About 200 g of wheat was milled (20–30 s) using the coffee-mill.

Fifty grams of homogenised sample (orange, cabbage) or 50 g of milled wheat were weighed in a 600-ml beaker and extracted for 10 min with 250 ml ethyl acetate and 100 g anhydrous sodium sulphate using the Ultra-Turrax. Crude extract was filtered through sodium sulphate into a 500-ml round-bottom flask, the filter was washed with 2×50 ml of ethyl acetate and the solvent was evaporated using the rotary vacuum evaporator (water bath at 35°C) to approximately 30–40 ml.

The concentrated solution was transferred into a 50-ml volumetric flask, spiked with the respective standard mixture of pesticides and the volume was made-up by ethyl acetate. Spiking levels expressed as mg/kg in the original plant material are listed in Table 1. Aliquots (2.5 ml) of the extract solution were then transferred into 4-ml amber ampoules which were heat-sealed using an oxy-acetylene blow torch. Ampoules were stored for 60 days at 20±2°C and 40±1°C, and analysed in duplicate after 10, 20, 40 and 60 days.

The content of each ampoule (2.5 ml) was transferred to a 5-ml volumetric flask and made-up by cyclohexane. Two ml of this solution was cleaned-up by GPC on the PL gel column (10 μm; 600 mm×7.5 mm), mobile phase cyclohexane–ethyl acetate (1:1, v/v). The eluate fraction (16–35 ml) was concentrated to 0.5 ml using the rotary vacuum evaporator (water bath 30°C), and solvents were removed by a gentle stream of dry nitrogen. The residue was

Table 1
Recoveries and repeatability of analysis (calculated from five replicates) in pure solvent and matrix extracts

Pesticide	Spike (mg/kg)	Detection method	Recovery (%)				R.S.D. (%)			
			Solvent	Wheat	Orange	Cabbage	Solvent	Wheat	Orange	Cabbage
Bromopropylate	0.28	ECD	92	101	96	83	7	5	11	7
Bupirimate	3.18	NPD	90	86	85	62	6	8	4	8
Captan	0.53	ECD	86	126	81	106	7	6	4	7
Chlorfenvinphos	0.49	NPD	96	96	89	86	5	7	3	5
Chlorothalonil	0.11	ECD	84	107	75	69	8	8	11	16
Chlorpropham	3.70	NPD	93	89	97	82	6	10	6	3
Chlorpyrifos	0.22	NPD	88	88	94	82	5	7	4	3
Chlorpyrifos-methyl	0.25	NPD	92	94	109	84	6	11	5	5
λ-Cyhalothrin[a]	0.59	ECD	37	33[a]	33[a]	39[a]	8	8	22	6
Cypermethrin[a]	0.92	ECD	74	93	58	45[a]	8	3	5	10
Deltamethrin	0.50	ECD	81	93	97	57	7	6	6	12
Diazinon	0.22	NPD	92	86	87	80	5	7	6	6
Dichlofluanid	0.58	ECD	103	98	87	92	5	5	6	7
Dichlorvos	0.25	NPD	56	64	78	59	7	17	12	10
Endosulfan I	0.29	ECD	90	86	86	90	6	8	8	
Endosulfan II	0.21	ECD	92	89	88	80	5	4	7	7
Endosulfan-sulphate	0.23	ECD	89	101	91	82	5	5	8	6
Ethion	0.23	NPD	93	92	97	82	5	6	3	9
Fenitrothion	0.18	NPD	93	83	121	84	5	9	6	7
Fenvalerate	0.82	ECD	81	96	79	51	7	4	4	12
Heptenophos	0.15	NPD	98	93	98	92	8	12	6	8
Imazalil[a]	3.82	NPD	41	65	15[a]	35[a]	10	8	13	15
Iprodione	0.34	ECD	87	96	92	59	10	15	10	9
Lindane	0.14	ECD	91	84	79	73	4	6	6	8
Metalaxyl	3.28	NPD	96	92	81	75	5	8	5	6
Methamidophos	1.98	NPD	90	95	82	79	6	11	8	3
Methidathion	0.17	NPD	89	105	101	88	5	6	4	4
cis-Mevinphos	0.27	NPD	94	81	94	75	7	14	8	5
trans-Mevinphos	0.21	NPD	89	86	97	84	6	12	5	7
Parathion	0.20	NPD	91	92	91	79	4	8	5	4
Parathion-methyl	0.26	NPD	102	95	99	87	4	11	5	2
Permethrin	1.01	ECD	86	94	67	73	6	3	5	12
Phosalone	0.96	NPD	88	96	108	77	7	5	6	8
Pirimicarb	1.21	NPD	80	89	64	57	9	11	11	6
Pirimiphos-methyl	0.25	NPD	100	90	97	80	5	6	5	2
Procymidone	0.20	ECD	92	90	94	73	7	7	6	4
Tolylfluanid	0.25	ECD	97	101	91	77	6	6	3	9
Vinclozolin	0.17	ECD	104	93	94	79	5	6	3	6

[a] Unacceptable low recovery (<50%), and/or high R.S.D. (>15%).

redissolved in 1 ml toluene, transferred into a GC autosampler vial and sealed.

The stability of some pesticides in pure ethyl acetate solutions (concentration levels were equal to that in crude extracts) was tested in the same way both at 20°C and 60°C by the same procedure but without GPC clean-up (direct injection into GC system).

2.4. Gas chromatography

Gas chromatography was performed on DB-5 MS fused-silica capillary column (60 m×0.25 mm, film thickness 0.25 μm; J&W Scientific, Folsom, CA, USA). The following conditions were used: carrier gas: helium (0.8 ml/min, constant flow); splitless injection (1 μl). Oven temperature programme: (1)

''ECD-compounds'': 90°C (2 min), then 10°C/min to 200°C, and 2.5°C/min to 280°C (20 min). Injector temperature: 250°C, detector temperature (ECD): 300°C. (2) ''NPD-compounds'': 90°C (2 min), then 3°C/min to 270°C (8 min). Injector temperature: 220°C, detector temperature (NPD): 300°C.

Standard (working) solutions were prepared at the same concentrations as samples. They were kept at −20°C and used as calibrants.

3. Results and discussion

A modified analytical method according to the European standard prEN 12393 (method ''P'') was used [6]. As a part of the intra-laboratory method validation, both recovery and repeatability for relevant pesticides/matrices were determined for sample extracts spiked at concentration levels corresponding to those used in further stability study. Data in Table 1 illustrate the performance characteristics of the employed multiresidual method. Recoveries were evaluated for all residues on spiked sample extracts analysed immediately after their spiking by pesticide standards. It was decided that recoveries <50% are considered as unacceptable. Higher values were accepted, providing that the relative standard deviation (under repeatability conditions) was ≤15%.

Low recoveries for some pesticides (e.g., synthetic pyrethroids) are due to the analytical procedure itself and we assumed that this method recovery is constant during the stability study because the fortification of freshly prepared ethyl acetate extracts give the same method recoveries as the fortification of blank extracts stored before at 40°C. Results obtained in the further stability study were not corrected for recoveries because only relative changes were followed during storage of extracts.

The stability of pesticides listed in Table 2 is expressed as time (days), at which the concentration of analyte decreased below 80% of original value (i.e., that at ''zero'' time). The expanded uncertainty of the analysis is relatively high (see R.S.D. in Table 1) and this is the reason why only concentration decrease below 80% of the original value is considered as ''degradation'' whereas higher values are within the uncertainty of the determination.

The decrease of pesticide concentrations during stability tests at 40°C are given in Table 3. Interpolated results expressed as days without significant decomposition are presented in Table 2 for all tested pesticides both at 20 and 40°C.

The decrease of concentrations was observed at 20°C after 40 days for chlorothalonil and iprodione in cabbage extracts and some degradation was observed for most organophosphates (e.g., mevinphos, methidathion, methamidophos, heptenophos, dichlorvos), iprodione and pirimicarb in orange extracts, presumably due to their hydrolysis. Concentrations of these compounds decreased slightly below 80% of original values after 60 days at 20°C.

At increased temperature (see Table 3), decomposition was recorded for bupirimate, chlorothalonil, chlorpyrifos-methyl, cyhalothrin, dichlofluanid, dichlorvos, endosulfan, endosulfan-sulphate, heptenophos and tolyfluanid in cabbage extracts stored at 40°C. The stability of all pesticides in wheat extracts was significantly higher than in the other plant extracts (with exception of captan). The most stable pesticides in all extracts seem to be synthetic pyrethroids (permethrin, cypermethrin, deltamethrin and fenvalerate). Their low recovery is due to the GPC conditions, where the clean-up effect is compromised with recovery of early eluting analytes.

Degradation of pesticide standards in the ''pure'' ethyl acetate solution was studied under the same conditions as in the case of plant extracts. Concentrations of dichlorvos, methamidophos and pirimiphos-methyl decreased slightly after 60 days at 40°C. These results correspond with those reported recently by Reynolds [9], who observed some degradation of pirimiphos-methyl, chlorpyrifos, chlorpyrifos-methyl, dimethoate, phosalone and triazophos after a four week storage in ethyl acetate at 60°C (UV light), whereas most of other pesticides were stable under these conditions.

The stability of most pesticides in the ''pure'' ethyl acetate seems to be comparable with that in wheat extracts. Nevertheless, the moisture together with basic impurities that could be present in wheat extracts could probably influence the stability of some pesticides sensitive to the hydrolysis (e.g., organophosphates) significantly.

For the extrapolation of measured stability to common temperatures used for the storage of pes-

Table 2
Stability of pesticides in plant sample extracts[a]

Pesticide	Solvent		Wheat		Orange		Cabbage	
	20°C	40°C	20°C	40°C	20°C	40°C	20°C	40°C
Bromopropylate	>	>	>	>	>	>	>	>
Bupirimate	>	>	>	>	>	14	>	42
Captan	>	28	>	10	>	>	>	>
Chlorfenvinphos	>	>	>	>	>	50	>	>
Chlorothalonil	>	>	>	>	>	>	8	5
Chlorpropham	>	>	>	>	>	>	>	>
Chlorpyrifos	>	>	>	>	>	9	>	58
Chlorpyrifos-methyl	>	>	>	50	>	7	>	52
λ-Cyhalothrin[b]	>[b]	>[b]	>[b]	>[b]	>[b]	>[b]	15[b]	10[b]
Cypermethrin[b]	>	>	>	>	>	>	>[b]	>[b]
Deltamethrin	>	>	>	>	>	>	>	>
Diazinon	>	>	>	54	>	10	>	9
Dichlofluanid	>	>	>	>	>	>	>	10
Dichlorvos	>	50	>	>	42	15	>	8
Endosulfan I	>	>	>	>	>	>	>	15
Endosulfan II	>	>	>	>	>	>	>	20
Endosulfan-sulphate	>	>	>	>	>	>	>	8
Ethion	>	>	>	58	>	42	>	>
Fenitrothion	>	>	>	52	>	9	>	8
Fenvalerate	>	>	>	>	>	>	>	>
Heptenophos	>	58	>	52	50	8	>	5
Imazalil[b]	>[b]	>[b]	>	48	15[b]	4[b]	45[b]	30[b]
Iprodione	>	>	>	>	>	>	15	12
Lindane	>	>	>	>	>	>	>	>
Metalaxyl	>	>	>	52	>	50	>	8
Methamidophos	>	55	>	55	40	8	>	>
Methidathion	>	>	>	50	55	10	>	8
cis-Mevinphos	>	55	>	45	45	10	>	55
trans-Mevinphos	>	>	>	55	42	10	>	55
Parathion	>	>	>	50	>	10	>	58
Parathion-methyl	>	>	>	57	>	9	>	>
Permethrin	>	>	>	>	>	>	>	>
Phosalone	>	>	>	52	>	42	>	50
Pirimicarb	>	>	>	58	8	8	>	>
Pirimiphos-methyl	>	58	>	>	>	15	>	5
Procymidone	>	>	>	>	>	>	>	>
Tolylfluanid	>	>	>	>	>	>	>	40
Vinclozolin	>	>	>	>	>	>	>	25

[a] The stability is expressed as time (days), at which the concentration of analyte decreased below 80% of original value (i.e., at ''zero'' time).
[b] Unacceptable low recovery (<50%).
> Stable more than 60 days.

ticide solutions in laboratory practice, the following equation can be employed [10]:

$$t_s = t_t 2^n \quad \text{where } n = (T_t - T_s)/10$$

where t_s = predicted time (days) of stability at the temperature T_s; t_t = time of stability (days) at the testing temperature T_t, i.e., time, where test results exceeded 80% of the initial concentration (found in time = 0); T_t = temperature of test (i.e., 40°C) and T_s = temperature to which is the result extrapolated.

Values measured at 40°C and extrapolated to 20°C (Table 4) are in good agreement with experimental data measured at this temperature (Table 2). This

Table 3
Degradation of pesticides – % of original concentration after 10, 20, 40 and 60 days of storage at 40°C

Storage	Detection	Solvent (ethyl acetate)				Wheat extract				Orange extract				Cabbage extract			
		10 days	20 days	40 days	60 days	10 days	20 days	40 days	60 days	10 days	20 days	40 days	60 days	10 days	20 days	40 days	60 days
Bromopropylate	ECD	89.8	93.2	94.0	95.5	94.8	93.0	90.6	95.6	126.8	118.0	140.8	119.1	85.0	71.8	81.6	81.2
Bupirimate	NPD	101.0	97.4	98.2	90.4	99.0	96.8	102.9	87.4	84.1	73.7	73.9	54.6	61.7	78.3	81.3	73.3
Captan	ECD	88.8	95.3	90.1	80.5	77.1	68.2	66.1	65.2	131.3	127.2	138.9	131.1	94.1	91.2	79.2	81.9
Chlorfenvinphos	NPD	100.2	96.6	99.4	91.2	99.0	90.1	100.6	84.6	90.0	87.4	90.6	82.1	88.9	85.8	84.1	86.6
Chlorothalonil	ECD	92.9	96.0	97.6	94.0	107.6	89.7	99.6	93.8	128.1	119.1	126.3	128.0	68.7	54.7	52.6	49.3
Chlorpropham	NPD	98.7	92.3	98.7	87.2	102.6	96.2	104.5	79.3	87.5	84.6	85.8	78.0	83.1	80.1	92.4	80.3
Chlorpyrifos	NPD	98.5	102.2	103.1	104.8	100.8	95.8	108.6	85.3	76.1	78.1	75.9	65.8	82.3	81.5	93.5	78.4
Chlorpyrifos-methyl	NPD	100.6	97.0	88.6	80.1	96.4	89.5	92.7	68.8	68.9	60.0	58.7	55.5	82.7	83.5	89.2	74.1
λ-Cyhalothrin[a]	ECD	90.0	96.5	98.4	97.1	105.8	101.5	105.3	97.3	92.4	100.5	115.7	104.6	78.3	71.2	62.6	74.7
Cypermethrin[a]	ECD	98.9	95.3	98.1	90.0	101.1	102.4	105.5	99.5	90.7	84.8	96.0	75.0	101.9	105.0	105.3	113.4
Deltamethrin	ECD	99.9	103.2	104.9	101.1	98.3	97.4	98.4	102.7	107.1	93.5	110.4	111.2	99.0	96.6	93.1	93.4
Diazinon	NPD	100.7	94.1	96.7	87.8	90.1	88.2	91.4	73.8	79.9	76.5	77.3	69.3	76.6	77.2	84.4	75.7
Dichlofluanid	ECD	101.9	105.3	107.1	102.2	97.8	90.3	97.1	95.5	109.8	104.4	111.8	103.1	80.1	70.5	71.8	70.7
Dichlorvos	NPD	98.3	91.9	88.3	76.7	81.8	95.6	102.3	83.0	94.1	64.2	54.6	13.4	74.8	78.6	79.9	63.3
Endosulfan I	ECD	99.8	103.6	104.5	106.1	102.2	98.4	100.2	101.2	118.3	102.0	114.7	101.2	84.1	75.8	75.0	70.1
Endosulfan II	ECD	93.3	95.7	96.5	88.9	102.4	101.1	99.5	102.2	113.7	103.3	108.7	100.5	85.6	79.6	73.1	78.4
Endosulfan-sulphate	ECD	96.7	103.8	105.7	104.4	104.7	95.5	102.6	98.7	113.0	111.0	117.3	101.4	75.1	74.6	69.3	70.9
Ethion	NPD	100.9	97.3	100.1	90.7	100.7	91.7	99.1	76.9	81.6	83.1	81.8	74.0	80.4	84.8	89.3	81.2
Fenitrothion	NPD	98.3	91.1	88.3	85.7	88.2	82.0	88.2	76.5	77.9	68.9	68.9	59.8	75.2	77.4	87.7	75.5
Fenvalerate	ECD	98.1	101.8	102.7	104.3	96.3	97.2	94.6	93.9	110.4	113.6	112.3	104.0	107.4	105.3	110.3	107.4
Heptenophos	NPD	101.9	98.3	89.8	79.1	97.5	84.0	91.1	74.5	70.9	75.0	70.3	53.4	58.3	53.6	65.5	51.4
Imazalil	NPD	88.8	85.3	77.1	75.9	100.5	94.9	102.0	45.1	40.4	18.8	22.1	19.1	94.2	96.5	104.7	0.0
Iprodione[a]	ECD	106.3	102.5	105.5	96.8	109.8	88.3	114.0	110.8	118.7	98.7	120.3	111.8	82.6	61.7	51.2	63.7
Lindane	ECD	101.9	104.3	97.0	103.1	105.5	95.0	104.2	99.2	116.9	111.6	113.2	98.4	87.5	83.7	87.5	78.8
Metalaxyl	NPD	93.7	95.9	88.4	76.2	92.9	87.8	91.0	71.7	94.4	92.3	89.3	73.5	72.4	71.0	86.3	75.4
Methamidophos	NPD	102.4	96.5	91.0	79.0	100.9	93.5	101.4	69.5	68.3	77.1	64.8	21.2	86.5	85.8	93.2	80.0
Methidathion	NPD	96.3	101.4	86.2	71.0	94.3	88.3	89.6	68.9	79.3	86.1	85.5	64.5	73.5	69.9	88.2	79.0
cis-Mevinphos	NPD	102.2	98.5	94.2	75.1	90.5	76.2	85.4	62.5	78.6	77.4	46.8	39.1	88.3	86.8	92.0	75.5
trans-Mevinphos	NPD	97.0	89.9	87.2	80.6	98.0	94.6	105.1	73.0	79.0	77.3	54.0	36.0	85.5	85.8	91.3	77.7
Parathion	NPD	105.5	101.5	107.4	93.5	97.3	86.5	97.3	68.1	80.7	77.6	77.1	73.2	81.5	81.3	93.9	78.0
Parathion-methyl	NPD	103.9	100.2	91.5	80.7	97.8	92.3	98.6	74.3	76.5	75.5	67.7	63.8	79.9	83.0	89.8	80.1
Permethrin	ECD	98.7	103.2	105.5	101.0	97.4	92.0	94.1	94.6	95.0	86.3	90.9	80.1	99.5	97.4	86.6	85.8
Phosalone	NPD	96.2	89.3	86.0	81.5	95.6	88.5	98.4	69.6	85.3	83.3	79.3	80.0	75.5	78.4	84.7	75.5
Pirimicarb	NPD	102.6	101.8	96.4	88.9	100.0	94.8	105.9	75.4	73.9	70.6	75.2	24.5	82.6	81.3	89.6	87.4
Pirimiphos-methyl	NPD	97.3	102.2	94.9	79.6	100.2	94.4	105.8	83.2	83.6	78.2	75.9	51.2	82.0	81.5	92.8	82.0
Procymidone	ECD	90.3	88.2	87.8	84.1	93.7	83.4	81.1	83.7	97.3	95.1	102.7	84.8	90.8	90.8	90.4	85.9
Tolylfluanid	ECD	99.6	102.3	91.0	88.4	96.6	87.3	94.2	90.4	107.5	103.1	111.0	104.8	88.0	87.5	78.6	75.0
Vinclozolin	ECD	101.0	97.5	93.9	100.8	99.7	92.9	97.1	98.1	106.5	101.3	105.2	96.1	87.8	82.4	72.5	72.6

[a] Unacceptable low recovery (<50%).

Table 4
Stability of pesticides at 20°C – values extrapolated from measurements at 40°C[a]

	Solvent	Wheat	Orange	Cabbage
Bromopropylate	240	240	240	240
Bupirimate	240	240	56	168
Captan	112	40	240	240
Chlorfenvinphos	240	240	200	240
Chlorothalonil	240	240	240	20
Chlorpropham	240	240	240	240
Chlorpyrifos	240	240	36	232
Chlorpyrifos-methyl	240	200	28	208
λ-Cyhalothrin[b]	[b]	[b]	[b]	[b]
Cypermethrin[b]	240	240	240	[b]
Deltamethrin	240	240	240	240
Diazinon	240	216	40	36
Dichlofluanid	240	240	240	40
Dichlorvos	200	240	60	32
Endosulfan I	240	240	240	60
Endosulfan II	240	240	240	80
Endosulfan-sulphate	240	240	240	32
Ethion	240	232	168	240
Fenitrothion	240	208	36	32
Fenvalerate	240	240	240	240
Heptenophos	232	208	32	20
Imazalil[b]	[b]	192	[b]	[b]
Iprodione	240	240	240	48
Lindane	240	240	240	240
Metalaxyl	240	208	200	32
Methamidophos	220	220	32	240
Methidathion	240	200	40	32
cis-Mevinphos	220	180	40	220
trans-Mevinphos	240	220	40	220
Parathion	240	200	40	232
Parathion-methyl	240	228	36	240
Permethrin	240	240	240	240
Phosalone	240	208	168	200
Pirimicarb	240	232	32	240
Pirimiphos-methyl	232	240	60	20
Procymidone	240	240	240	240
Tolylfluanid	240	240	240	160
Vinclozolin	240	240	240	100

[a] The stability is expressed as time (days), at which the concentration of analyte decreased below 80% of original value (i.e., at ''zero'' time).
[b] Unacceptable low recovery (<50%).

supports our assumption, that the stability of most pesticides is acceptable to store plant sample extracts several days at laboratory temperature (18–22°C) or few weeks in the refrigerator (4–8°C) and to use them as calibrants to compensate for matrix effects which can usually influence GC quantitation.

It should be noticed that the question ''if pesticide is stable or not'' can be rather complicated. We should take into account the uncertainty of the analytical method and then decide if the concentration changes after storage are proved or not. The expanded uncertainty of the calculated stability is relatively high: about ±20–30%.

In general, problems with the precision mostly result from either the degradation of some pesticides in the injector (captan, dichlofluanid) or poor NPD performance (relative response fluctuations, tailing of organophosphates). In addition to these phenomena,

''matrix effects'' may influence the precision of the routine GC analysis of real samples.

4. Conclusions

Most of the examined pesticides were stable in ethyl acetate plant extracts at least 40 days if stored at temperatures below 20°C. No degradation of synthetic pyrethroids was observed even at 40°C, whereas decomposition of most organophosphates in orange or cabbage extracts become significant at elevated temperatures. If stored at a sufficiently low temperature, the stability of all pesticides in wheat extracts is comparable with that in pure extraction solvent. Pesticide standard solutions prepared in plant extracts are stable enough (at least 20 days at 20°C) to be used as GC calibrants to compensate for matrix effects in GC analysis. General guidelines for the preparation and use of matrix-standard calibration solutions are given by Erney et al. [11].

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