

Long-term stability of pure standards and stock standard solutions for the determination of pesticide residues using gas chromatography

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Abstract

The regular replacement of pure standards used in pesticide residue analysis laboratories and frequent preparation of stock standard solutions, both required by many accreditation bodies, impose considerable demands on a laboratory's resources. In this study, pure standards for all but one (heptenophos) of 118 different pesticides amenable to analysis by GC, and stock standard solutions (1000 µg/ml) prepared from these in toluene, acetone or ethyl acetate have been shown to be stable at $\leq -20^{\circ}\text{C}$ over long periods: 4–13 and 2–8 years, respectively, for pure standards and solutions. Suitable solvents, containers and handling procedures are essential to avoid evaporation from solutions. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

The monitoring of pesticide residues in fruit and vegetables is essential to protect consumers, obtain data for risk assessment, check conformity to good agricultural practice and ensure fair trade practices. However, these analyses are expensive, partly because of the sophisticated analytical techniques required for trace analyses, but also because of the considerable demands imposed on the financial and personnel resources of a laboratory by the need to maintain a valid stock of pure standards (the certified pesticide standards purchased from suppliers) and stock standard solutions (the most concentrated solutions prepared directly from pure standards) for the large number of compounds to be screened and the cost of disposing of expired materials. Accreditation bodies frequently require that the expiry dates assigned by suppliers to pure standards be strictly adhered to.

Experience in several laboratories indicates that the large majority of pure standards and stock standard solutions used for gas chromatographic (GC) analyses are stable over long

periods of time, subject to the conditions under which they are stored [1–4]. Despite this, and often as a requirement of national accreditation bodies, most laboratories replace pure standards and stock standard solutions relatively frequently.

Certified pure pesticide standards are assigned an expiry date by the supplier that is typically from 2 to 5 or 6 years from the date of the last purity check or the date of manufacture, depending on the compound, supplier and prescribed storage conditions. The date of the last purity check may, in some cases, be several months prior to the date of purchase of the compound by the laboratory. The storage conditions recommended can vary from -20°C to room temperature, 20°C , appropriate conditions, etc. Table 1 compares the assigned lifetimes and stated storage conditions given by different suppliers for the same pure compound for some pesticides and demonstrates how variable these can be.

The purity of existing pure standards and stock standard solutions may be checked by preparing a new stock standard solution and comparing the detector responses obtained from freshly prepared dilutions of old and new stock standard solutions. According to the requirements laid down in the EU document "Quality Control Procedures for Pesticide Residues Analysis" [5], which laboratories participating in

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Table 1
A comparison of lifetimes and storage conditions applied by different suppliers to the same pesticide

Pesticide	Supplier	Purity (%)	Date received	Date certified	Lifetime ^a (years)	Storage conditions (°C)
Bifenthrin	A	98.0	May 1996	April 1996	3	4
	A	93.0	April 1998	October 1997	2	−18
Bromopropylate	A	99.3	May 1996	April 1996	4	Stable at 20
	A	99.3	April 1998	October 1997	2.5	20
Captan	D	99.8	November 1995	December 1994	5	5
	A	99	May 1996	September 1995	4	4
	A	98.4	April 1998	September 1996	4	20
Chlorothalonil	A	99.1	May 1996	February 1996	4	4
	A	98.5	April 1998	March 1998	6	20
Chlorpyrifos	A	98.7	May 1996	December 1995	4	4
	A	99.5	April 1998	November 1996	4	−18
Chlorpyrifos-methyl	A	98.8	May 1996	June 1995	4	4
	A	99.5	April 1998	November 1996	3.5	−18
Cypermethrin	D	92.3	November 1995	August 1991	5	Refrigerator
	H	95.7	July 1996	February 1996	2	Room temperature
	A	91	May 1996	June 1994	3	4
	A	91.5	April 1998	October 1996	3.5	20
Deltamethrin	I	99.5	August 1995	November 1994	2	2–8
	A	98.5	May 1996	December 1994	4	4
	A	98.0	April 1998	September 1997	6	20
Dichlofluanid	A	99.7	May 1996	March 1994	3.5	4
	A	98.2	April 1998	November 1997	3	4
Dimethoate	J	99.8	August 1995	April 1995	2	Freezer
	A	98.4	May 1996	June 1995	3	4
	A	99.5	April 1998	April 1997	3	−18
Endosulfan sulfate	A	97.8	May 1996	June 1995	6	4
	A	99.4	April 1998	June 1997	6	20
Fenthion	C	99.7	November 1995	August 1994	2	0–10 (or lower)
	C	99.1	August 1997	November 1996	2	0–10
Iprodione	E	99.5	March 1996	December 1995	10	In brown glass bottle at 4
	A	99	May 1996	March 1996	4	4
	A	95.0	April 1998	September 1996	4	20
Metalaxyl	A	99.9	May 1996	February 1996	6	4
	A	99.3	April 1998	August 1997	6	20
Methamidophos	A	99.5	July 1995	March 1995	2	4
	C	99.5	November 1995	Jan 1995	2	0–10
Omethoate	C	99.0	November 1995	July 1995	1	0–10
	A	95.5	April 1998	December 1997	3	4
Permethrin	D	99.4	November 1995	September 1993	5	Refrigerator
	H	95.2	July 1996	December 1995	1	Room temperature
	A	97	May 1996	December 1994	4	4
	A	97.5	April 1998	April 1997	6	20
Phosalone	E	99.5	March 1996	June 1995	10	In brown glass bottle at 4
	A	99.4	May 1996	February 1994	3.5	4
	A	98.5	April 1998	November 1996	4	−18
Pirimiphos-methyl	D	99.6	November 1995	March 1994	5	5
	A	94	May 1996	February 1996	4	4
Procymidone	C	99.5	November 1995	October 1991	4.5	Ambient temperature
	F	99.1	January 1999	January 1997	3	Proper storage conditions in originally closed package
Pyrazophos	G	99.8	September 1995	October 1992	4	−20
	F	99	January 1999	February 1994	7	Proper storage conditions in originally closed package

Table 1 (Continued)

Pesticide	Supplier	Purity (%)	Date received	Date certified	Lifetime ^a (years)	Storage conditions (°C)
Tetradifon	K	>99.5	July 1995	July 1990	10	15–35 in original packing
	A	99.9	May 1996	December 1995	6	4
	A	99.5	April 1998	January 1998	6	20
Triazophos	G	41.7	September 1995	August 1994	3	–20
	A	87.0	April 1998	March 1998	3	4

^a From date of analysis or certification to expiry date given by supplier.

the EU monitoring programme of fruits and vegetables are recommended to follow, the mean measurements for two solutions should not normally differ by more than $\pm 5\%$ (or $\pm 10\%$ for problematic analytes if the number of replicate determinations required to distinguish a difference of $\pm 5\%$ is unacceptably large) in order to demonstrate that the standards have indistinguishable purities. This document recommends that the identity and purity of all newly purchased primary standards be checked against existing standards. Therefore, databases on the stability of both pure standards and stock standard solutions exist in individual laboratories as part of their quality control system, but these data are rarely published.

The aim of this study, which was carried out over the period July 2003 to May 2004, was to examine the long-term stability of both pure standards and stock standard solutions used for the determination of pesticide residues with GC and to make these data available to other pesticide residue laboratories. With the publication of stability data in the literature, it is hoped that laboratory management and accreditation bodies will accept the validity of assigning longer lifetimes to both pure standards and stock standard solutions, where appropriate, thereby contributing significantly to the cost-effectiveness of pesticide residues monitoring.

2. Experimental

2.1. Pure standards and stock standard solutions

Pure standards of pesticides were obtained from various suppliers between 1995 and 2000 and stored in the freezer at $\leq -20^\circ\text{C}$. A large number of the standards initially acquired when the laboratory was founded in 1995 were donated, free of charge, by various agrochemical companies and a certificate of analysis did not accompany a small number of these. Purities for all compounds ranged between 93 and 99.9% except cypermethrin (91.5%), etrimphos (65.4%), heptenophos (50.5%), oxyfluorfen (70.8%) and triazophos (87.0%). The pesticides tested included 73 compounds determined with nitrogen-phosphorus detection (NPD) (55 organophosphorus and 18 organonitrogen) and 50 compounds determined with electron-capture detection (ECD).

All stock standard solutions were prepared at a concentration of 1000 $\mu\text{g/ml}$ and stored in the freezer at $\leq -20^\circ\text{C}$.

From 1995 to 1997, 25 or 50 ml of each stock standard solution was prepared in acetone, or less frequently in toluene, and stored in 50 ml brown glass bottles with Teflon-lined, screw-topped caps. These standards were used relatively infrequently and were removed individually from the freezer when required. From 1998, 10 ml of each stock standard solution was prepared in toluene, or less frequently in ethyl acetate, and stored in 16 ml brown glass bottles (National Scientific Co., Lawrenceville, GA, USA), again with Teflon-lined, screw-topped caps. The bottles were stored in racks with 36 or 40 bottles per rack, and the whole rack was sometimes removed from the freezer and allowed to reach room temperature when any one solution was required.

For the purposes of this study, new stock standard solutions were prepared in toluene mostly within the 3-month period before testing.

2.2. Standard mixtures

2.2.1. Standard mixtures for testing stability

Standard mixtures (3 for ECD and 6 for NPD), containing up to 20 pesticides each, were prepared in 10 or 20 ml volumetric flasks using 1 ml glass bulb pipettes. The flask was weighed after each addition to check the reliability of the volume measurements and the mixture was made up to 20 ml with toluene where necessary. For gas chromatographic (GC) determination, the mixtures were diluted first with toluene and then to between 0.2 and 1 $\mu\text{g/ml}$, as appropriate, with matrix extract from cucumber or grape in toluene or ethyl acetate. For each mixture composition, 3–5 different mixtures were made containing stock standard solutions prepared (i) on different dates from the same pure standard and (ii) from different pure standards, where more than one was available. The same stock standard solution for at least one compound was added to all these mixtures as an internal standard.

2.2.2. Standard mixtures for the assessment of method reliability

As a test of the reliability of the method, the same stock standard solution was added to more than one different mixture of the same composition wherever the number of stock standard solutions to be tested for any given pesticide was fewer than the number of mixtures prepared. This is illustrated in Table 2, which gives the stock standard solutions added to the different mixtures prepared for one of the NPD pesticide mixture compositions.

Table 2
Stock standard solutions (1 ml each) added to different mixtures for one NPD mixture composition

Pure standard ^a	Date of stock standard solution preparation			
	Mixture A	Mixture B	Mixture C	Mixture D
Acephate I	21.3.96	26.6.03		12.10.98
Acephate II			26.6.03	
Bromophos-methyl	2.3.00 ^b	14.7.03 ^b	2.3.00 ^b	14.7.03 ^b
Carbophenothion	16.2.00 ^b	14.7.03 ^b	16.2.00 ^b	14.7.03 ^b
Chlormephos (I.S.)	26.4.96 ^b	26.4.96 ^b	26.4.96 ^b	26.4.96 ^b
Chlorpyrifos-me I	15.2.96	27.6.03		
Chlorpyrifos-me II			5.4.99	26.6.03
Coumaphos	22.2.00 ^b	14.7.03 ^b	22.2.00 ^b	14.7.03 ^b
Diazinon I		1.7.03		
Diazinon II	20.5.99		30.10.00	20.7.03
Dichlorvos	5.3.96	14.7.03	11.5.99	6.3.01
Disulfoton	25.4.96 ^b	26.6.03	25.4.96 ^b	26.5.99
Ditalimphos	16.2.00 ^b	14.7.03 ^b	14.7.03 ^b	16.2.00 ^b
Ethoprop (I.S.)	22.2.00 ^b	22.2.00 ^b	22.2.00 ^b	22.2.00 ^b
Leptophos	16.2.00 ^b	14.7.03 ^b	14.7.03 ^b	16.2.00 ^b
Parathion-ethyl I	17.4.96	30.6.03		
Parathion-ethyl II			11.5.99	14.7.03
Phenthoate	3.11.99 ^b	14.7.03 ^b	3.11.99 ^b	14.7.03 ^b
Phorate	13.5.96 ^b	26.6.03	13.5.96 ^b	26.5.99
Phosmet	17.4.96 ^b	11.4.03	9.10.98	17.4.96 ^b
Pirimiphos-methyl I	11.1.96	2.7.03	9.10.98	
Pirimiphos-methyl II				14.4.03
Pyrazophos I	12.10.98	2.7.03		
Pyrazophos II			20.5.99	15.4.03

I.S.—internal standard.

^a Different pure standards denoted by I and II.

^b Same stock standard solution in two or more mixtures.

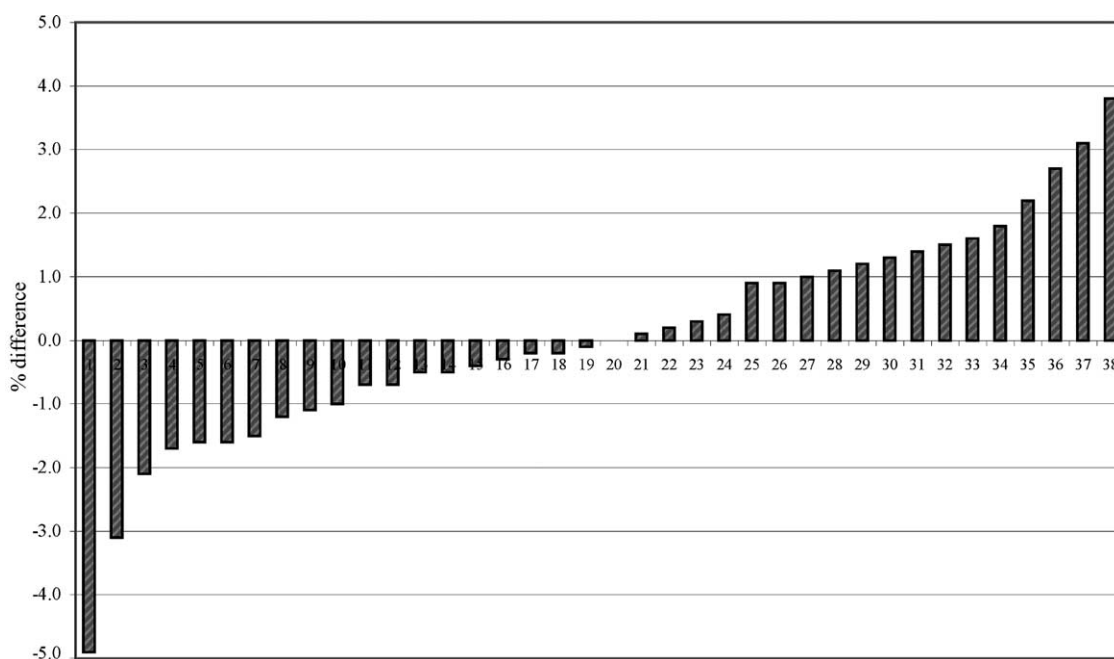


Fig. 1. Percentage differences determined when the same stock standard solution was added to two different mixtures of the same composition. 1 = Coumaphos, 2 = leptophos, 3 = phorate sulfoxide, 4 = ethion, 5 = carbophenothion, 6 = coumaphos, 7 = ditalimphos, 8 = bromophos-methyl, 9 = mephospholan, 10 = azinphos-ethyl, 11 = carbophenothion, 12 = fluvalinate, 13 = leptophos, 14 = phorate, 15 = disulfoton, 16 = bromophos-methyl, 17 = mevinphos, 18 = phenthoate, 19 = ditalimphos, 20 = etrimphos, 21 = a-endosulfan, 22 = b-endosulfan, 23 = phenthoate, 24 = etrimphos, 25 = fenclorphos, 26 = lambda-cyhalothrin, 27 = dieldrin, 28 = dicotophos, 29 = kresoxim-methyl, 30 = tolylfluanid, 31 = fenvalerate, 32 = azinphos-ethyl, 33 = cypermethrin, 34 = phosmet, 35 = phorate sulfoxide, 36 = mephospholan, 37 = mevinphos, 38 = paraoxon.

2.3. Follow-up test mixtures

Additional tests were carried out whenever a difference of >5% (or >10% for difficult compounds) was measured between different stock standard solutions for any given pesticide. These fell into two categories. (i) Where initial results showed that an old stock standard solution had a higher concentration than a freshly prepared one, this was retested using an aliquot of the solution, referred to below as a reference solution, that had been set aside in a weighed 2 ml bottle and stored separately from the bulk of the solution used routinely in the laboratory. (ii) In the few cases where no reference solution existed, a new pure standard was purchased. New mixtures were prepared as above for these tests, except that only 0.1 ml of each stock standard solution was taken because of the smaller volumes available.

2.4. Gas chromatography

The GC analyses with NPD were performed using a Varian (Walnut Creek, PA, USA) CP 3800 gas chromatograph with a Varian CP 8200 autosampler, TSD (300 °C), split-splitless injector operated in the splitless mode (240 °C, 60 s, 1 µL) and a 50% phenylmethylpolysiloxane capillary column (HP50) with oven temperature programme 75 °C, hold 2 min; 12 °C/min to 170 °C; 1.5 °C/min to 200 °C; 15 °C/min to 260 °C, hold 20 min. Analyses with ECD were performed using two Hewlett-Packard gas chromatographs (Avondale, PA, USA): a model 5890 Series II fitted with a 50% phenylmethylpolysiloxane capillary column (Rtx-50) and a model 6890 fitted with a 5% phenylmethylpolysiloxane capillary column (HP5-MS). Both had ECD detection systems operated at 300 °C, Hewlett-Packard 7673 autosamplers, split-

Table 3

Percentage difference between old stock standard solutions in toluene and new stock standards (from the same pure standard) and the time for which the old stock standard has been shown to be stable

Pesticide	Storage period		Percentage difference ^a	Pesticide	Storage period		Percentage difference ^a
	Years	Months			Years	Months	
Acephate	4	8	-1.7	Fenarimol	3	1	0.0
Alachlor	3	5	-0.9	Fenchlorphos	3	1	0.5
Aldrin	4	0	-1.0	Fenpropathrin	3	9	0.1
Atrazine	3	10	0.5	Fluvalinate	3	9	1.5
Azinphos-ethyl	4	7	0.1	Heptachlor	3	0	0.9
Azinphos-methyl	4	8	-0.7	Heptenophos	4	9	-10.7
Azoxystrobin	4	6	-4.2	Hexachlorobenzene	5	5	-2.6
Bendiocarb	7	5	1.5	Kresoxim-methyl	3	0	0.7
Bifenthrin	4	6	0.1	Lindane	4	6	-2.3
Binapacryl	4	0	-4.2	Malathion	4	9	-3.1
Bitertanol	3	6	1.7	Mecarbam	4	2	-6.2
Buprofezin	7	7	3.7	Metalaxyl	3	6	-0.2
Chlorfenvinphos	4	10	-0.2	Methamidophos	4	8	-1.8
Chlorothalonil	4	6	0.3	Methidathion	4	1	-1.2
Chlorpropham	3	6	-1.9	Metribuzin	2	9	-2.7
Chlorpyrifos-ethyl	4	4	-2.3	Paraoxon	3	11	2.0
Chlorpyrifos-methyl	4	2	0.1	Parathion-ethyl	4	2	2.4
Chlzolinate	6	0	-0.8	Parathion-methyl	4	6	3.4
2,4'-DDD	3	0	-3.4	Penconazole	5	1	-0.9
2,4'-DDE	3	0	-0.5	Pentachloraniline	5	5	-5.0
2,4'-DDT	3	2	-3.0	Permethrin	2	9	3.6
4,4'-DDD	3	0	0.2	Phenthoate	3	8	-4.6
4,4'-DDE	3	0	0.5	Phorate	4	1	0.4
4,4'-DDT	3	2	1.2	Phosmet	4	6	3.7
Diazinon	4	2	-0.1	Pirimiphos-methyl	4	9	-1.4
Dibrom	3	7	-1.6	Procymidone	4	0	-3.0
Dichlobenil	3	7	-0.6	Promecarb	4	6	-2.4
Dichlofluaniid	2	9	-1.9	Propham	5	2	-3.9
Dichlorvos	4	2	-2.1	Propiconazole	7	7	5.1
Dicloran	5	5	3.3	Pyrazophos	4	9	3.3
Dicrotophos	3	1	-3.2	Quintozene	3	9	-1.0
Dinobuton	3	2	-3.5	Terbufos	5	0	-1.6
Diphenylamine	3	9	2.7	Tetradifon	4	6	-0.3
Disulfoton	4	1	-0.3	Tolylfluaniid	4	9	-3.2
Endosulfan sulfate	2	10	-1.0	Triadimefon	4	6	-2.0
Ethion	4	9	-2.2	Triazophos	4	9	-2.0
Etridiazole	3	6	-4.7	Vamidothion	5	0	-2.8

^a Percentage differences greater than ±5% are given in bold type.

splitless injectors operated in the splitless mode (220 °C, 60 s, 1 µL) and an oven temperature programme 80 °C, hold 1 min; 15 °C/min to 190 °C, hold 1 min; 3 °C/min to 280 °C hold 30 min. All columns had dimensions 30 m × 0.250 mm I.D., 0.25 µm film thickness and the carrier and make-up gases were helium and nitrogen, respectively. For each mixture composition, individual mixtures were injected in turn and this injection sequence was repeated at least five times.

2.5. Calculations

Areas for the response of each pesticide in each mixture were calculated from the mean of five consecutive injections, after adjustment for the internal standard area. These were compared using the formula:

$$\text{percentage difference} = 100 \times \frac{\text{area of newer standard} - \text{area of older standard}}{\text{area of older standard}}$$

Where the solutions being compared were the same, this was adjusted to:

$$\text{percentage difference} = 100 \times \frac{\text{area of first mixture injected} - \text{area of second mixture injected}}{\text{area of second mixture injected}}$$

3. Results and discussion

3.1. Measurements on stock standard solutions from the same pure standard

3.1.1. Validity of the approach for testing standard stability

Fig. 1 shows percentage differences calculated for mixtures containing the same stock standard solution of a given pesticide. These all lie within the ±5% range (−4.9% to 3.8%) assigned by the method as indicating no measurable

Table 4

Percentage difference between old stock standard solution in acetone and new stock standard (from the same pure standard) and the time for which the old stock standard has been shown to be stable

Pesticide	Storage period		Percentage difference ^a	Pesticide	Storage period		Percentage difference ^a
	Years	Months			Years	Months	
Acephate	7	3	−6.8	Fenthion sulfone	7	6	1.1
Azinphos-ethyl	7	2	−1.1	Fenthion sulfoxide	7	6	−1.0
Azinphos-methyl	7	2	−0.3	Fenvalerate	7	3	−4.1
Bitertanol	7	2	−5.6	Flucythrinate	7	3	−2.6
Bromopropylate	7	5	2.3	Heptachlor	7	7	−0.4
Captan	7	7	−0.9	Heptenophos	7	3	−15.8
Chlorfenvinphos	7	3	−3.6	Iprodione	7	5	−2.7
Chlorpropham	8	1	0.7	Lambda-cyhalothrin	7	4	−0.5
Chlorpyrifos-methyl	7	4	−0.9	Malathion	7	3	−2.7
Cyfluthrin	8	0	−4.8	Methamidophos	7	3	5.8
2,4'-DDD	7	7	−1.2	Methidathion	7	4	−3.3
2,4'-DDE	7	7	−0.5	Monocrotophos	7	3	−1.7
2,4'-DDT	7	7	−2.7	Omethoate	7	5	−2.7
4,4'-DDD	7	7	−0.2	Oxyfluorfen	8	1	−0.5
4,4'-DDE	7	7	2.2	Parathion-ethyl	7	2	−3.3
4,4'-DDT	7	7	2.0	Parathion-methyl	7	1	−0.5
Dichlofluanid	7	8	−3.4	Penconazole	7	8	−3.5
Dichlorvos	7	4	−4.1	Permethrin	7	7	3.5
Dieldrin	7	6	−3.1	Phorate	7	1	−4.1
Dimethoate	7	5	1.0	Phorate sulfone	7	10	−2.4
Disulfoton	7	2	−3.0	Phorate sulfoxide	7	2	−2.6
a-Endosulfan	7	3	−2.0	Phosalone	7	0	−4.9
b-Endosulfan	7	3	−0.8	Phosmet	7	0	−1.2
Endosulfan sulfate	7	7	−1.0	Pirimicarb	7	3	−6.6
Ethion	7	2	−4.1	Pirimiphos-methyl	7	6	−1.0
Fenamiphos	7	8	2.0	Procymidone	7	7	−1.3
Fenitrothion	7	2	−2.0	Profenophos	7	3	−2.6
Fenoxon	6	0	1.0	Propham	8	1	−4.8
Fenoxon sulfone	5	5	−4.4	Propyzamide	6	7	1.7
Fenoxon sulfoxide	5	5	−1.0	Vinclozolin	4	7	−0.5
Fenthion	7	6	−2.1				

^a Percentage differences greater than ±5% are given in bold type.

Table 5

Percentage difference between old stock standard solution in ethyl acetate and new stock standard (from the same pure standard) and the time for which the old stock standard has been shown to be stable

Pesticide	Storage period		Percentage difference	Pesticide	Storage period		Percentage difference
	Years	Months			Years	Months	
Bromophos-methyl	3	4	-4.0	Hexaconazole	4	3	1.0
Carbophenothion	3	5	-3.6	Leptophos	3	5	-4.5
Chlorpyrifos-ethyl	2	0	-3.1	Mephospholan	3	5	-2.8
Coumaphos	3	5	-1.9	Metribuzin	3	6	1.4
Demeton- <i>O</i> -me	3	6	-0.4	Mevinphos	4	2	-0.3
Demeton- <i>S</i> -me	3	6	-1.9	Pirimiphos-ethyl	3	6	-4.7
Dichlorvos	2	4	0.2	Profenophos	3	5	-2.4
Dimethoate	2	3	1.2	Quinalphos	4	3	-2.9
Ditalimphos	3	5	2.1	Tebuconazole	4	3	0.4
Etrimphos	3	5	-4.6	Tebuconazole	4	2	3.6
Fenamiphos	2	6	1.6				

difference in purity between two solutions, and 82% lie within $\pm 2\%$. These results indicate the magnitude of the combined uncertainty from volume measurements, mass measurements and GC analysis and demonstrate the validity of the approach for testing standard stability.

3.1.2. Measurements on different stock standard solutions from the same pure standard

Tables 3–5 give the results, after all tests had been completed, for the percentage differences calculated between the oldest and newest stock standard solutions prepared from the same pure standard and the times over which stock standard solutions have been shown to be stable, i.e. the time between the preparation of the old and new stock standard solutions. The results are divided according to the solvent used to prepare the solution, with results for toluene presented in Table 3, those for acetone in Table 4 and those for ethyl acetate in Table 5. According to the method used to calculate the results, a negative percentage difference may indicate degradation of the pure standard or evaporation of solvent from the old stock standard solution, while a posi-

tive percentage difference may indicate degradation or loss by adsorption onto the glass of pesticide in the older stock standard solution. For all of the 156 stock standard solutions tested (with the possible exception of heptenophos), the solutions were stable with no degradation over the 3–8 years storage period (2–4 years for ethyl acetate solutions). Of the 125 pure standards from which these were prepared, representing 118 different pesticides, only heptenophos, with an assigned expiry date of 30 days from the date of analysis and purity of 50.5%, degraded slowly (15%) within the storage period of 8 years.

The above data all refer to final results after carrying out any retests that were necessary. Initial measurements that gave percentage differences $>5\%$ (or $>10\%$ for difficult compounds) are shown in Table 6. Subsequent tests using reference solutions made it possible to ascertain that these higher values were due to evaporation from the stock standard solution rather than degradation of the pure standard, and indicate the importance of guarding against solvent evaporation during the storage and routine use of stock standard solutions. This is most effectively done by making up stock

Table 6

Details of initial measurements with high percentage differences

Solvent	Pesticide	Percentage difference	Storage period	
			Years	Months
Acetone	Chlorpyrifos-ethyl	-5.5	7	2
Toluene	Mecarbam	-8.7	4	2
	Phosalone	-8.8	4	7
	Pirimicarb	-15.3	5	0
	Dicrotophos	-20.3	3	1
Ethyl acetate	Mevinphos	-14.4	3	2
	Mephospholan	-7.4	3	5
	Pirimiphos-ethyl	-16.9	3	7
	Demeton- <i>O</i> and <i>S</i> -methyl	-9.8	3	6
	Ditalimphos	-15.4	3	5
	Leptophos	-7.2	3	5
	Quinalphos	-14.4	3	2
	Profenophos	-12.4	3	2
	Fenitrothion	-9.8	3	4

Table 7
Summary of stability data for stock standard solutions in different solvents

	Solvent			Same stock standard solution in different mixture
	Toluene ^a	Acetone ^a	Ethyl acetate	
Number of solutions tested	73	60	21	38
Median of % differences	−0.85	−1.50	−1.90	−0.05
Mean of % differences	−0.71	−1.63	−1.22	0.06
SD of % differences	2.40	2.44	2.50	1.70
Number of solutions showing evaporation in first test	4	1	9	

^a Omitting heptenophos.

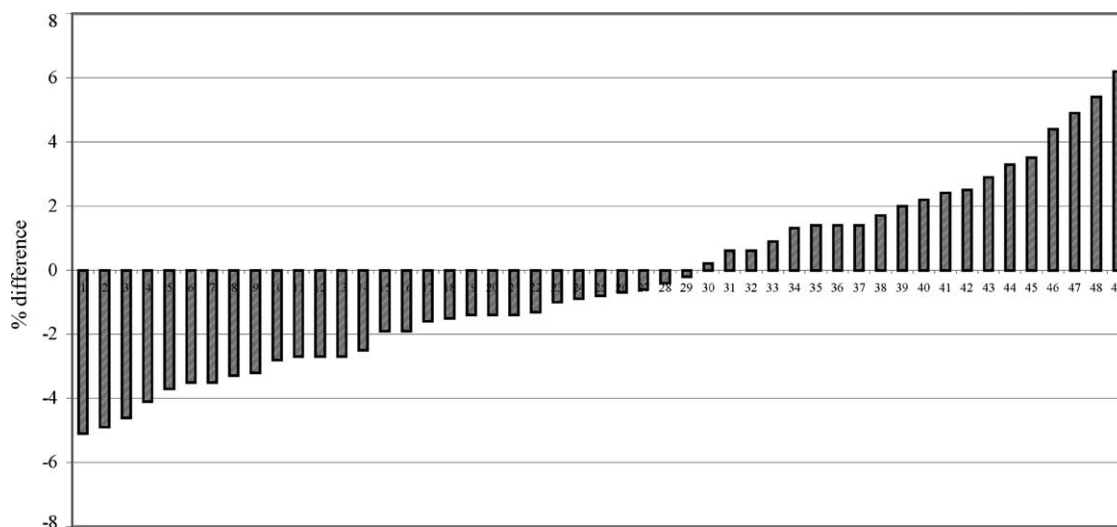


Fig. 2. Percentage differences determined between new stock standard solutions prepared from different pure standards of the same pesticide.

Table 8
Suppliers' expiry dates for different pure standards of the same pesticide

No.	Pesticide	First	Second	No.	Pesticide	First	Second
1	Cyfluthrin	February 1997	March 2006	26	Chlorpyrifos-methyl	November 1995 ^a	June 1999
2	Pyrazophos	October 1996	December 2000	27	Aldrin	May 1995 ^a	August 1999
3	Chlozolinate	February 1997	February 1999	28	Endosulfan sulfate	June 1998	June 2003
4	Monocrotophos	November 1995	February 2001	29	Parathion-ethyl	November 1996	July 2002
5	a-Endosulfan	September 2001	March 2003	30	Fenthion	August 1996	November 1998
6	b-Endosulfan	November 2001	November 2003	31	Fenvalerate	April 1996 ^a	December 2005
7	Triazophos	August 1997	March 2001	32	Lindane	August 1999	June 2001
8	Parathion-methyl	August 1997	November 1999	33	Bifenthrin	April 1999	October 1999
9	Procymidone	June 1996	December 2000	34	Cypermethrin	August 1996	May 2000
10	Atrazine	July 1996	April 2001	35	Chlorothalanil	November 1995 ^a	March 2004
11	Fenthion sulfoxide	May 1997	April 1999	36	Deltamethrin	November 1996	September 2003
12	Permethrin	March 1998	April 2003	37	Metribuzin	December 2001	May 1997
13	Tetradifon	July 1995	Jan 2004	38	Dichlofluanid	September 1996	November 2000
14	Dimethoate	May 1997	June 1998	39	Metalaxyl	February 2002	August 2003
15	Fenitrothion	April 1996 ^a	June 2000	40	Thiabendazole	February 2002	February 2002
16	Mecarbam	December 1996 ^a	June 1999	41	Methamidophos	January 1997	March 1997
17	Chlorpyrifos-ethyl	November 1995 ^a	November 1999	42	Iprodione	December 2005	September 2002
18	Chlorfenvinphos	November 1999	November 1998	43	Simazine	December 1996	August 2002
19	Methidathion	November 1995	November 2001	44	Tolyfluanid	May 1999	June 1999
20	Triadimenol	July 1996	May 2007	45	Phosalone	June 2005	November 1997
21	Bromopropylate	October 1996	April 2000	46	Fenthion sulfone	May 2000	May 2000
22	Profenophos	November 1995	August 2000	47	Omethoate	August 1996	December 2000
23	Quinalphos	August 2003	April 2005	48	Captan	December 1999	September 2000
24	Pirimiphos-methyl	March 1999	February 2000	49	Acephate	July 1996	July 1996
25	Diazinon	December 1995	October 2001				

^a Date of purchase.

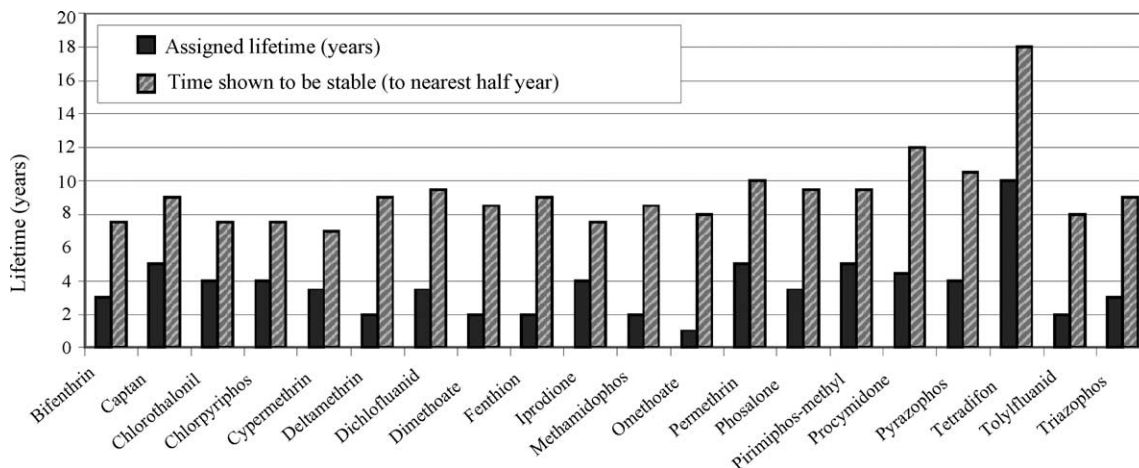


Fig. 3. Comparison for 20 of the oldest pure standards of the lifetime assigned by the supplier and the time that the pure standard has been shown to be stable.

standard solutions in a relatively high boiling point solvent such as toluene. Recording the masses of stock standard solutions before and after each use would enable any isolated cases where evaporation occurred from toluene solutions to be identified. Clearly the conditions used for the handling of stock standard solutions in ethyl acetate in our laboratory were unsatisfactory. Laboratory staff notes that insufficient care taken in closing bottles tightly after use and the un-

essarily long time standard solutions were sometimes left outside the freezer were the most likely causes of solvent evaporation. The older standards in acetone were used less frequently and by one member of staff only. Table 7 summarises data for standard solutions in each solvent, including the median and mean of the percentage differences. The fact that these are slightly negative is likely to indicate very small losses of solvent from the solutions over time.

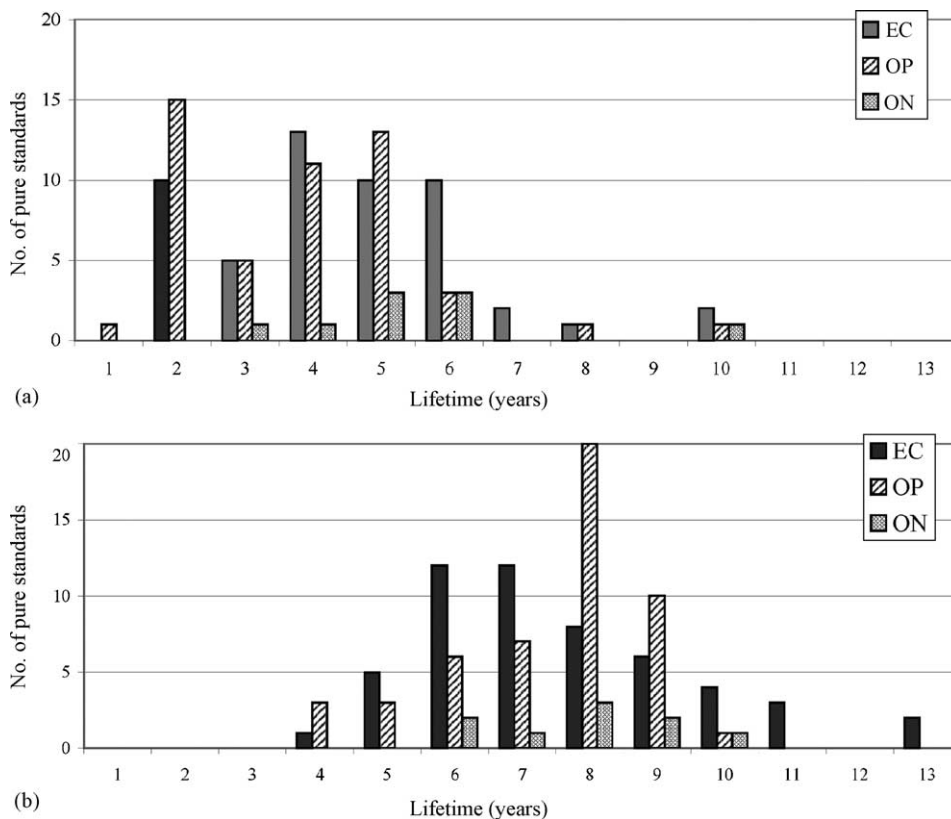


Fig. 4. Comparison of (a) the lifetime assigned by the supplier and (b) the time the pure standard has been shown to be stable for all pure standards supplied with a date of analysis.

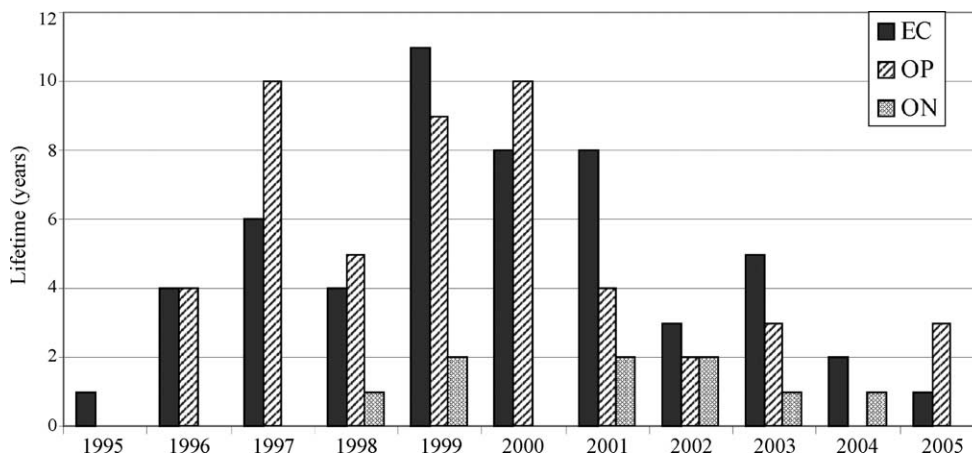


Fig. 5. Year in which pesticides should have been removed from use according to the supplier's expiry date.

3.2. Measurements on stock standard solutions from different pure standards of the same pesticide

Fig. 2 presents the results of a comparison of new stock standard solutions prepared from different pure standards of 49 pesticides. These pesticides are identified by their number in the histogram in Table 8, which also gives the suppliers' expiry dates for the pure standards tested. These had been previously extended on the basis of stability tests carried out in the laboratory in 1998–2000. In only three cases were differences greater than $\pm 5\%$ found: cyfluthrin -5.1% , captan 5.4% and acephate 6.2% . These were considered to be acceptable ($<10\%$) to show agreement for these particular pesticides.

3.3. Comparison of lifetimes assigned by the supplier and the times that pure standards have been shown to be stable

Fig. 3 gives a direct comparison for twenty of the oldest pure standards of the lifetime assigned by the supplier and the much longer time that the pure standard has been shown to be stable. Data for all the pure standards tested for which the supplier gave a date of analysis are shown in Fig. 4. The supplier's lifetime was calculated as the time between the date of analysis and the assigned expiry date, while the time for which the standard has been shown to be stable was calculated as the time between the date of analysis and the date the most recent stock standard solution was prepared and tested. These data have been separated into three categories, according to the type of pesticide. Fig. 5 shows the years in which these pesticides should have been removed from use according to the supplier's expiry date, although all were still stable at the time of testing.

4. Conclusions

Stock standard solutions in toluene, acetone and ethyl acetate of a wide range of pesticides amenable to analy-

sis by GC have been shown to be stable over several years (2–8 years) when stored in the freezer at $\leq -20^\circ\text{C}$. However, solvent evaporation was found to be a problem for stock standard solutions in ethyl acetate, probably due to inappropriate handling procedures during use rather than inadequate storage conditions. Generally, care must be taken through the use of suitable containers, storage conditions and handling procedures to avoid or allow for (through recording of the mass) solvent evaporation, if stock standard solutions are to be retained and used for several years. The use of a less volatile solvent such as toluene is preferable to minimise the risk of solvent evaporation.

Pure standards for GC pesticide residue analysis retain their purity over long periods of time when stored in the freezer at $\leq -20^\circ\text{C}$ with the exclusion of light and moisture. The data presented indicate that the expiry date assigned by the manufacturer may be extended by several years for the vast majority of compounds. The acceptance by accreditation bodies of the validity of tests carried out to extend the lifetime of pure standards and the assignment of more realistic expiry dates on the basis of published data would allow laboratories to significantly reduce the resources they presently allocate to the purchase and preparation of standards and the disposal of expired materials.

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