PERGAMON

Chemosphere 41 (2000) 1313–1320

CHEMOSPHERE

Analytical method for the determination of *O*,*O*-diethyl phosphate and *O*,*O*-diethyl thiophosphate in faecal samples

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Received 17 November 1999; accepted 20 January 2000

Abstract

A residue analytical method was developed for the determination of the dialkylphosphate metabolites of parathion in faecal samples obtained from rabbits. The faecal pieces were homogenised in water and highly water-soluble *O*,*O*-diethyl phosphate (DEP) and *O*,*O*-diethyl thiophosphate (DETP) were subsequently alkylated to pentafluorobenzyl esters by a phase transfer reaction. Derivatisation yields depend on the reaction time. The recovery rates were determined over the complete procedure using authentic reference standards in matrix solution. The reference standards allow to observe an effect of the sample matrix on the area of signals while GC-FPD is used. The recoveries over the concentration range from 0.05 to 5 μg/g were 47–62% for *O*,*O*-diethyl phosphate and 92–106% for *O*,*O*-diethyl thiophosphate potassium salt with FPD.

Keywords: Dialkylphosphates; Faecal samples; GC-NPD; GC-FPD

1. Introduction

Thiophosphorus and dithiophosphorus compounds applied as insecticide have been suspected of causing sublethal and lethal toxic effects in wildlife (Joermann and Gemmeke, 1994). Exposure normally leads to the inhibition of various esterases. This fact is used for assessment of exposure, but it is also understood that the inhibition of esterases is also influenced by other factors and environmental impacts (Mineau, 1991). Today the real exposure of wildlife can be roughly estimated.

Examination of dialkylphosphate metabolites in faeces originating from organophosphate insecticides could be an alternative tool as noninvasive indicator of exposure in the environment. Analysis of the highly polar and water-soluble dialkylphosphates has been developed with different success since 1968. Table 1 gives a chronological overview of the essential methods described in the literature. The recovery rates given in these papers are only relative amounts from fortification reactions without usual primary, authentic reference standards. Reference standards were used only for the analysis of *O*,*O*-diethyl phosphate (DEP) and *O*,*O*-diethyl thiophosphate (DETP) in spinach (Archer, 1974). Weisskopf and Seiber (1989) estimated derivatisation yields by comparing molar phosphorus response with trimethyl phosphate standard, but the yield of dimethyl phosphate (DMP) could not be determined due to interferences. *O*,*S*,*S*-trimethyl phosphorothioate was only an internal standard for gas chromatography but not for the whole method (Drevenkar et al., 1994). Aprea et al. (1996) shows recovery rates limited at the stage of purification. In this study the pentafluorbenzyl (PFBz) ester of the parathion metabolites *O*,*O*-diethyl phosphate and *O*,*O*-diethyl thiophosphate were synthesised, isolated and characterised. An analytical method

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0045-6535/00/$ - see front matter
PII: S0045-6535(00)00020-5

Table 1
Overview of the residue analytical methods for dialkylphosphate metabolites of organophosphorus insecticides[a]

Matrix	Extraction		Derivatisation	Concentration (μg/g)	Recoveries (%)						Reference
	Solvents	Additives			DMP[b]	DEP[b]	DMTP[c]	DETP[c]	DMDTP[d]	DEDTP[d]	
Grapes, soil	Acetone, diethyl ether	NaOH, HCl	Diazomethan	0.1							St. John and Lisk (1968)
Urine	Acetonitrile, diethyl ether	NaCl, HCl	Diazopentane	0.1	98	98	96	100	99	100	Shafik et al. (1973)
Spinach	Isopropanol, benzene	HCl	Diazomethan	0.1–1		70–90		70–90			Archer (1974)
Urine	Ion exchange resin	$Ca(OH)_2$	Diazoethane	0.05–150	95						Blair and Roderick (1976)
Water, urine	Acetone, ion exchange resin	NaCl, HCl	Diazomethane	0.01–0.1	40–50	100	97	85			Daughton et al. (1976)
Urine	Acetone, ion exchange resin	HCl	Diazopentane	0.1–1	74–85	97–106	36–42	87–76			Lores and Bradway (1977)
Urine	Chloroform	Bitartrate	PNBTT[e]	0.01–1							Talade et al. (1979)
Urine, agar	Acetone, ion exchange resin	$Ca(OH)_2$, $HClO_4$	BTT[f]								Daughton et al. (1979)
Urine	Dichloromethane	TBA, THA	PFBzBr[g]	0.1							Bradway et al. (1981)
Urine	Acetonitrile		PFBzBr	0.8	91	96	92	99	98	102	Reid and Watts (1981)
Urine	Ethyl acetate	NaCl, HCl	TMAH[h]	0.011–11			61–97				Moody et al. (1985)
Water Urine	Ethyl acetate	NaCl HCl	TMAH	0.004–0.38				44 <38–105			Weisskopf et al. (1988)
Urine	SPE	$(NH_4)_2SO_4$, acetic acid	TMAH	0.002–0.2		n.n.–27	78–106	96–131	83–113	48–92	Weisskopf and Seiber (1989)

Urine	Acetonitrile	HCl	PFBzBr	1.5×10^3 2.5×10^3			120		70		Fenske and Leffingwell (1989)
Urine			PFBzBr	0.4–1	70	89	100	61	100	93.8	Li et al. (1991)
Liver	5% Ethanol in ethyl acetate	HCl	TBAH[i]	0.25	104	102	91	87	52	40	Richardson and Seiber (1993)
				0.5	88	111	74	89	93	30	
Kidney				0.5	89	101	94	102	99	39	
Blood	Diethyl ether	NaCl	Diazomethane	0.1–0.5		31					Drevenkar et al. (1994)
		HCl		0.7–1.7		51					
				1.9–2.4		97					
				0.2–2.8	36		92	97	79	71	
Urine	Acetonitrile azeotropic distillation		PFBzBr	0.062	100	88	86	99	90	101	Aprea et al. (1996)

[a] M – methyl, E – ethyl.
[b] Dialkylphosphates.
[c] Dialkylthiophosphates.
[d] Dialkyldithiophosphates.
[e] 1-(4-Nitrobenzyl)-3-(4-tolyl)triazene.
[f] 3-(Benzyl)-1-(4-tolyl)triazene.
[g] Pentafluorobenzyl bromide.
[h] Trimethylanilinium hydroxide.
[i] Tetrabutylammonium hydroxide.

containing a phase transfer reaction developed by Bradway et al. (1981) was improved and tested with faeces from rabbits.

2. Material

O,*O*-diethyl phosphate (DEP-K) and *O*,*O*-diethyl thiophosphate (DETP-K), both as potassium salt with a purity of about 98%, were produced by Studio Chimico Dr. M. Giuntini (Firenze, Italy). The stock solutions were prepared by dissolving 20 mg salt in 50 ml methanol. The working solutions were diluted with methanol. Pentafluorobenzyl bromide (PFBzBr) was purchased from Sigma.

The pentafluorobenzyl ester of *O*,*O*-diethyl phosphate (DEP-PFBz) was synthesised in boiling acetonitrile for 3 h with one equivalent 18-Crown-6 and 2.5 equivalent potassium carbonate. Correspondingly *O*,*O*-diethyl thiophosphate (DETP-PFBz) was prepared in acetone with a magnetic stirrer at room temperature. After the reactions the solvents were evaporated. Fifty ml water were added to the oily residue. The suspensions were extracted with hexane. The pentafluorobenzyl esters of DEP and DETP were obtained as colourless liquids by vacuum distillation. The stock solutions were made at 0.2 mg/ml in hexane. Working solutions in hexane for calibration curves in the range of 50–1500 pg/μl were prepared daily. Salts, esters and the stock solutions were stored at −20°C.

Tetrahexyl-ammonium hydrogen sulphate (THA) (Fluka) solution was made with 4.5 g salt in 100 ml 0.2 N hydrous sodium hydroxide (Roth) solution. The purification columns (15 mm i.d.) were packed with 5 g Florisil (60–100 mesh, Fluka, activated at 560°C for 6 h and conditioned with 10% water) slurred in hexane and topped with 1 cm anhydrous sodium sulphate (Roth). Solvents with the SupraSolv quality were obtained from Merck.

3. Analytical method

3.1. Extraction and clean-up

Five g faeces (f.w.) was dissolved in 30 ml distilled water and homogenised for 1 h on a rotary shaker (Heidolph). Eighty ml dichloromethane, 10 ml THA-solution and 250 μl PFBzBr were added to this suspension. For the derivatisation the Erlenmeyer flask was shaken only 10 min at room temperature. The solution was filtrated through glass wool in a separation funnel. The residue and the funnel were rinsed with 40 ml dichloromethane. The combined organic layer was dried over anhydrous sodium sulphate and evaporated to dryness with a rotary evaporator (Büchi) in a 30°C water bath. Three ml hexane was added to the sample, sonicated to redissolve the residue and transferred to the purification column. The mobile phase was hexane–acetone (v/v = 95/5). The first 25 ml of eluant was discarded. DEP-PFBz and DETP-PFBz were eluted with the other 275 ml. The solvent was evaporated to dryness as described above. The residue was refilled with a certain volume hexane. Aliquots were transferred into autosampler vials for quantification by gas chromatography with different detectors. The vials were stored at −20°C until measurement.

3.2. Gas chromatography

The analysis was performed using a gas chromatograph HP 5890 equipped with an NPD; injection port: 250°C, split/splitless injection (0.5 min splitless), 1 μl injected volume; column: 30 m DB–Wax (J&W Scientific) 0.252 mm i.d., film thickness 0.25 μm; column temperature program: 60°C (1 min) – 20°C/min – 150°C (15 min) – 30°C/min – 180°C (10 min) – 30°C/min – 250°C (10 min); flow rates: nitrogen 2.4 ml/min, make up 24.1 ml/min, hydrogen 3.5 ml/min, air 78 ml/min; detector: 280°C.

Gas chromatograph HP 5890 series II equipped with an FPD and phosphorus filter (525 nm), injection port: 200°C, split/splitless injection (0.75 min splitless), 1 μl injected volume; columns: 15 m SE-54 0.259 mm i.d., film thickness 0.25 μm; column temperature program: 90°C (1 min) – 5°C/min – 250°C (5 min); flow rates: helium 100 kPa, nitrogen 34 ml/min, hydrogen 103 ml/min, air 73 ml/min; detector: 200°C. 30 m HP-5 0.32 mm i.d., film thickness 0.25 μm; column temperature program: 90°C (1 min) – 10°C/min – 200°C – 30°C/min – 300°C (1 min); flow rates: helium 100 kPa, nitrogen 34 ml/min, hydrogen 103 ml/min, air 73 ml/min; detector: 200°C.

Mass spectral analysis was made using a GCQ, Finnigan MAT. The electron impact ionisation mass spectra were obtained at 70 eV, with mass range scanned from 50 to 650 amu. A 30 m DB–XLB 0.25 mm i.d., film thickness 0.25 μm was used for confirmation analysis.

4. Results and discussion

4.1. Standard compounds

The authentication of gas chromatographic standard compounds is summarised in Table 2. The fragmentation in the mass spectra and the shift and methylene coupling constants in the NMR-spectra characterised DETP-PFBz as the thiolate in accordance with the results found by Li et al. (1991).

Table 2
Characterisation of gas chromatographic standards[a]

	DEP-PFBz	DETP-PFBz
Boiling point, $bp_{(8)}$ (°C)	141	145
^{1}H-NMR (ppm) δ(Me_4Si) (in $CDCl_3$)		
–OCH_2CH_3	1.34 (*t*, 6H, *J* = 7 Hz)	1.36 (*t*, 6H, *J* = 7 Hz)
–OCH_2CH_3	4.14 (*m*, 4H, *J* = 7 Hz)	4.18 (*m*, 4H, *J* = 7 Hz)
–XCH_2–C_6F_5	5.14 (*d*, 2H, *J* = 7.5 Hz)	4.09 (*d*, 2H, *J* = 12 Hz)
GC–MS EI (*m/z*) (in %)	*Important masses*	
$(C_2H_5O)_2P(O)XCH_2C_6F_5$	334 (11%)	350 (14%)
H–$XCH_2C_6F_5$	198 (20%)	214 (5%)
H–$CH_2C_6F_5$	182 (100%)	182 (40%)
$(C_2H_5O)_2P(O)X$–H	154 (53%)	170 (100%)
$(C_2H_5O)(HO)P(O)X$	125 (82%)	141 (17%)

[a] X = O (DEP), S (DETP).

The purity of DEP-PFBz and DETP-PFBz was determined by the peak areas in the gas chromatograms as being about 95%.

4.2. Extraction

The properties of dialkylphosphates required consideration of the pH-value (Lores and Bradway, 1977; Weisskopf and Seiber, 1989) and of the variability of the medium. Problems lie in the choice of the best extraction solvents, the relation between solvent and analysed matrix (Lores and Bradway, 1977; Richardson and Seiber, 1993) and in the choice of additives to produce a saturated solution (Daughton et al., 1976; Weisskopf and Seiber, 1989). Drevenkar et al. (1994) found the best recoveries by diluting plasma with deionised water. In contrast to the samples with a high water content (Table 1) faeces produced by rabbits are a relatively compact matter. The pieces were shaken in distilled water for 1 h to form a homogeneous pap so that the dialkylphosphates were better available for short derivatisation. The pH-value of the faeces–water suspension was about 9–10. Both higher (pH = 13) and lower (pH = 3) pH-values led to decreasing yields of DEP-PFBz.

4.3. Derivatisation

From the beginning of dealing with ultratrace detection of the dialkyl phospates it was clear that a gas chromatographic method would be successful. The injector block derivatisation developed by Moody et al. (1985) and Weisskopf and Seiber (1988) could not be realised with our equipment. Additionally, this derivatisation of DETP was strongly influenced by the urine concentration. Problems with the analytical quality for DETP were assumed with a complex matrix like faeces. The recoveries for DEP were exceptionally low compared to the other metabolites (Weisskopf and Seiber, 1989). So, derivatisation with pentafluorobenzyl bromide mentioned by Aprea et al. (1996) was found most suitable. Bradway et al. (1981) developed a method with a phase-transfer catalyst. Quaternary ammonium salt extracts the anions of DEP and DETP into dichloromethane, where they react with PFBzBr (Rabinovitz et al., 1986). The procedure is short versus the separate reactions with different temperature and purifications performed by Aprea et al. (1996).

Firstly, the method was tested with the individual extraction each of the dialkylphosphates from water (Fig. 1). For DETP-K the highest rates were obtained at

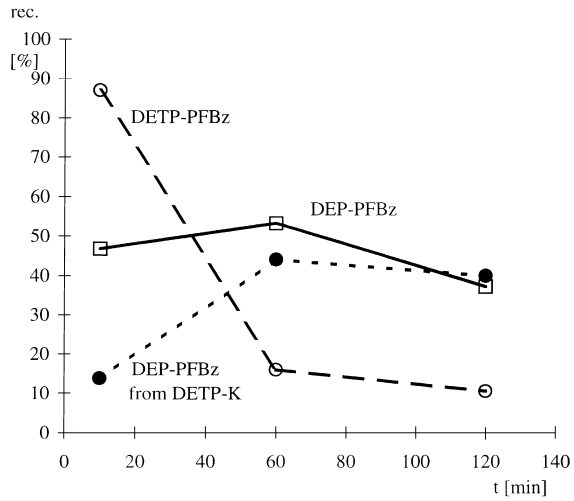

Fig. 1. Recovery rates for the derivatisation of DEP-K (—, □) and DETP-K (– – –, ○) and the transformation from DETP to DEP (- - -, ●) in water as a function of the reaction time measured with authentic reference standards (2.5 and 5 μg K-salts in 10 ml water).

10 min. The derivatisation carried out by Bradway et al. (1981) takes 25–30 min, more than the double time. With the authentic reference standard, it was shown that in this way only 60% DETP-K can be recovered as DETP-PFBz. The yield of the derivatisation of DEP-K was hardly influenced by the reaction time, with a maximum amount of about 50% for 1 h. These form a contrast to the recovery rates for DETP (80%) and DEP (10%) obtained by Bardarov and Mitewa (1989) with different ion-pair reagents after 1 h. Fig. 1 suggests the possibility of side-reactions to more than one alkylation with PFBzBr. Surprisingly DEP-PFBz was observed to develop from DETP-K. In accordance with the decreasing yields of DETP-PFBz, formation of DEP-PFBz from DETP-K increased with longer reaction times. A transformation has been known in the case of DMTP during the reaction with PFBzBr but only at higher temperatures (Reid and Watts, 1981). The analysis of faeces was carried out with a derivatisation time of 10 min.

4.4. Gas chromatography

Analytical results were verified using two GC-systems with different capillary columns and detectors. The NPD and FPD responses to injections ranging from 50 to 1500 pg were linear for both esters. The minimal detectable quantities (noise-signal-ratio:1/10) of DEP-PFBz and DETP-PFBz were 25 pg/μl. Matrix effects were assessed by comparing the peak area from the esters spiked in untreated faecal samples before the injection to that of the standards in hexane. Using NPD, interferences from the matrix occurring in some untreated samples influenced the results in the low concentration range (80 pg/μl), in particular for DEP-PFBz. The more selective FPD leads to an increased response of the analytes in the spiked matrix (c_M) in relation to the hexane standard (c_S). The increased response can be calculated over the described concentration range with the equation $c_M = a\,c_S^b$ (DEP-PFBz:$a = 2.3419$; $b = 0.9483$; $r^2 = 0.9999$/ DETP-PFBz:$a = 1.4151$; $b = 0.9801$; $r^2 = 1$).

4.5. Recovery

The faecal samples were fortified with an appropriate amount of both K-salts together in methanol and was kept at room temperature for 3 h until the analysis started with dilution. The recovery rates obtained are more realistic than the fortification of diluted samples, which suppresses the interaction of dialkylphosphates with the sample (Drevenkar et al., 1994).

Table 3 shows the recovery rates over the complete procedure from control faeces fortified in the range from 0.05 to 5 μg/g and measured by a primary, authentic reference standard. The results of recoveries listed in the table were obtained over half a year as a routine check during the analysis of a feeding study. So, they also reflect the robustness of the method. Neither of the hydrolytical metabolites was found when faecal samples were spiked with parathion at the beginning of analytical procedure.

It seems that an all-round method does not exist for all six metabolites listed in Table 1. The recovery rates of these methods were calculated with standards obtained by the same analytical procedure with fortified untreated samples or with fortified solvents. This is basically not comparable with the results developed using authentic reference standards, as described in this paper (Table 3).

The method from Bradway et al. (1981) is suitable to determine the concentration of DETP and DEP as metabolites of parathion. Observance of the reaction time will enhance the validity of the results. This method was adapted to faecal samples. In particular for DEP recovery rates at the low level of 0.05 μg/g with coefficients of variation below 20% were achieved. The decomposition of the polar metabolites in faeces was investigated under field condition over 4–8 days. The concentrations for DEP were in the range between 1 and 0.2 μg/g and for DETP from 2 to 0.5 μg/g (Schenke and Gemmeke, 1999).

4.6. Stability

The stock solutions of the salts and of the esters were prepared freshly after three months. The stability of the

Table 3
Average recoveries (REC) and coefficients of variation (CV) of DEP and DETP from fortified rabbit faeces by the complete procedure

K-salt	Concentration (μg/g)	Number	FPD (%)		NPD (%)	
			REC	CV	REC	CV
DEP-K	0.05	7	62	13	79	68
	0.5	8	47	11	68	14
	5	4	51	11	47	7
DETP-K	0.05	7	104	18	98	29
	0.5	8	92	10	81	11
	5	4	106	16	76	11

Table 4
Stability of DEP-K and DETP-K in faeces at −20°C (calculated with respect to recoveries (FPD))

Days after fortification	DEP-K (%)	DETP-K (%)
0	–	–
220	79	89
291	97	86
314	116	95
340	75	93

stock solution of DEP-K and DETP-K was shown by consistent recoveries carried out over this time. The stability of the esters tested with atrazine as references showed no deterioration. Table 4 shows the stability of DEP-K and DETP-K in untreated faeces samples stored at −20°C over nearly 1 year.

Acknowledgements

I cordially thank B. Kunde for her experimental assistance. Thanks also to B. Pusch and also H. Nowak and G. Reese-Stähler (both BBA – Institute of Ecological Chemistry, Berlin) for GC-measurements. I thank Dr. Heydenreich, University Potsdam, for the NMR spectra of reference substances.

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