Loss of Paraoxon in Aqueous Acetonitrile Extractions

H. R. McLean, S. Futagaki, and J. T. Leffingwell
University of California
School of Public Health
Warren Hall
Berkeley, Calif.

INTRODUCTION

There are many methods available for the extraction of parathion from diverse substrates for residue analysis, among which is a method wherein the pesticide is partitioned from an acetonitrile extract after it has been diluted with water. Finley and co-workers (FINLEY and ROGILLIO, 1969, FINLEY, et al., 1974) have reported the extraction of cloth for parathion using this technique. Similarly GUNTHER, et al. (1973, 1974) have extracted leaf homogenates by this general procedure for pesticide residue analysis. It is easy to assume that this procedure works as well for the oxygen analog, paraoxon, as it does for the parent parathion. However, this is not the case and tests with this method yield paraoxon recoveries as low as 13%.

In the course of studies conducted by our group at the School of Public Health, University of California at Berkeley, wherein we were examining the effects of weathered foliar parathion residues on fieldworkers, it became necessary to measure residue penetration of clothing. This required the analysis for both parathion and paraoxon in cloth squares and matched gauze pads.

METHODS

The method used in our laboratory for the extraction of parathion and paraoxon from fabric consists simply of a benzene extraction. One ml of a solution containing 116 ppm of parathion and 200 ppm of paraoxon in benzene was applied to each of three shirt fabric samples (50% cotton, 50% polyester) and three gauze pad samples (100% cotton). Each sample consisted of three 58 cm^2 swatches (174 cm^2/sample). Two of each type of sample were extracted with 150 ml of benzene for 30 minutes, rinsed with 50 ml of benzene for 30 seconds and pressed out with a spatula in a funnel. The solvent volume was reduced to 1 ml on a rotary evaporator. The remaining samples (one of each kind) were extracted in an identical fashion using acetonitrile instead of benzene, and the solvent was converted to benzene for chromatographic analysis by three successive additions of 10 ml of benzene after reduction of the extract volume to ∿1.5 ml between each addition.

Bulletin of Environmental Contamination & Toxicology,
Vol. 18, No. 2 © 1977 by Springer-Verlag New York Inc.

To check the extraction procedures according to the methods published by FINLEY and ROGILLIO (1969) and GUNTHER, et al. (1973) wherein aqueous acetonitrile is back-extracted with hexane or petroleum ether, two 125 ml portions and two 40 ml portions of acetonitrile, respectively, were dosed with 1 ml of each of the pesticide stock solution. These simulated extracts were diluted with water and back-extracted according to their respective work-up schemes, after which they were evaporated to 1 ml and diluted to 10 ml with benzene.

The samples were analyzed for parathion and paraoxon using a Tracor MT-222 gas chromatograph equipped with a Melpar photometric detector operating in the phosphorous mode. A 180 x 0.35 cm glass U-shaped column packed with 10% DC-200 on 80/100 mesh Chromosorb W provided satisfactory separations. Nitorgen-carrier gas flow was 125 ml/min. Flame parameters were: Hydrogen 70 ml/min and oxygen 5 ml/min. Isothermal temperatures were set at: Oven 180°C, on column injector 220°C, and detector 210°C. The retention times for paraoxon and parathion were 163 and 213 sec, respectively. An Auto Lab model 6300 digital integrator was used to quantitate peaks.

RESULTS

The results of testing various extraction procedures are shown in Table I.

TABLE I

EXTRACTION EFFICIENCIES OF FOUR METHODS

Extraction Method	Sample Type	Recoveries (percent)			
		Paraoxon	Avg.	Parathion	Avg.
Benzene Extraction	shirt	101.7	98.3	98.3	95.5
	shirt	96.6		92.9	
	gauze	101.3		98.1	
	gauze	93.6		92.7	
Acetonitrile Extract	shirt	98.9	99.0	96.8	96.3
	gauze	99.0		95.7	
Finley Method	simulated extract	13.6	13.2	92.1	94.9
		12.7		97.6	
Gunther Method	simulated extract	22.3	22.2	90.6	93.2
		22.2		95.7	

DISCUSSION

The extraction of parathion from cloth followed by the partitioning procedure as described by Finley and co-workers (FINLEY and ROGILLIO, 1969, FINLEY, et al., 1974) was performed with four replicate extractions on five fabric types. Although they reported no statistical analysis of their data, recoveries were reported that ranged from a high of 88.0% to a low of 33.6%, from which we derived the following values: $n = 20$, $\bar{x} = 65.5\%$, $s = 11.2$, and $\bar{v} = 17.1\%$ ($\bar{v} = 100s/\bar{x}$). The reproducibility of the benzene extraction procedure was calculated: $n = 4$; Parathion: $\bar{x} = 95.5\%$, $s = 3.12$, $\bar{v} = 3.27\%$; Paraoxon: $\bar{x} = 98.3\%$, $s = 3.90$, $\bar{v} = 3.96\%$. This method provides reasonable efficiency, reproducibility and ease of execution. The direct acetonitrile extraction is quantitative for both compounds but when the residue is partitioned into hexane after the addition of water, only the parathion is recovered in high yield. The number of serial extractions required to partition 99% of the oxon from aqueous acetonitrile into hexane was calculated by the method of MORRISON and FREISER (1957) to be 31.5 and 18.3 for the procedures of FINLEY (1969) and GUNTHER, et al. (1973), respectively; thus, the method appears unworkable for samples containing paraoxon. This difference in extraction behavior results from the fact that paraoxon has a relatively high water solubility (2400 mg/l) compared to parathion (20-25 mg/l) (WILLIAMS, 1951). If the acetonitrile is first stripped from the aqueous extract before the hexane or petroleum ether partitioning (GETZ, 1962, KADOUM, 1968), the migration of the paraoxon into the hexane might be improved. However, that technique was deemed impractical for the purposes of the work in this laboratory and has not been tested here. Alternatively, Klein extracted parathion from soils with acetonitrile, and rather than adding water and back-extracting with hexane, removed the acetonitrile on a rotary evaporator and substituted benzene as the solvent for chromatographic analysis (KLEIN, et al., 1974).

Studies by Spear and co-workers have shown appreciable deposits of paraoxon on citrus foliage, with concomitant residues of the toxicant in the clothing of field workers exposed to that foliage (SPEAR, et al., 1974, 1975). Likewise SPENCER, et al. (1975) have found substantial quantities of parathion and its oxygen analog in soils in parathion-treated groves. Thus, the presence of paraoxon can well be suspected in environmental samples containing parathion. To avoid erroneous results and improper conclusions, care must be taken to avoid extraction procedures utilizing the partitioning of the extracted residues between aqueous acetonitrile and a hydrocarbon solvent, such as hexane or petroleum ether.

REFERENCES

FINLEY, E.L. and J.R.B. ROGILLIO: Bull. Environ. Contam. Toxicol., 4, 343 (1969).

FINLEY, E.L., G.I. METCALFE, F.G. McDERMOTT, J.B. GRAVES, P.E. SCHILLING and F.L. BONNER: Bull. Environ. Contam. Toxicol., 12, 268 (1974).

GETZ, M.E.: J. Ass. Offic. Agr. Chem., 45, 393 (1962).

GUNTHER, F.A., W.E. WESTLAKE, I.H. BARKLEY, W. WINTERLIN and L. LANGBEHN: Bull. Environ. Contam. Toxicol., 9, 243 (1973).

GUNTHER, F.A., I.H. BARKLEY and W.E. WESTLAKE: Bull. Environ. Contam. Toxicol., 12, 641 (1974).

KADOUM, A.M.: Bull. Environ. Contam. Toxicol., 3, 247 (1968).

KLEIN, S.A., D. JENKINS, R.J. WAGENET, J.W. BIGGAR and M.S. YANG: An Evaluation of the Accumulation, Translocation and Degradation of Pesticides at Land Wastewater Disposal Sites, SERL Report No. 74-4, Sanitary Engineering Research Laboratory, College of Engineering and School of Public Health, Univ. of Calif., Berkeley, Calif. (1974).

MORISON, G.H. and H. FREISER: Solvent Extraction in Analytical Chemistry, John Wiley & Sons, Inc., New York, N.Y., p. 81, (1957).

SPEAR, R.C., T.H. MILBY, J.T. LEFFINGWELL and W.J. POPENDORF: Abstracts, 167th ACS Meeting, Los Angeles, Calif., (April 1974).

SPEAR, R.C., W.J. POPENDORF, J.T. LEFFINGWELL and D. JENKINS: J. Agric. Food Chem., 23, 4, 808 (1975).

SPENCER, W.T., M.M. CLIATH, H.R. DAVIS, R.C. SPEAR and W.J. POPENDORF: Bull. Environ. Contam. Toxicol., 14, 265, (1975).

WILLIAMS, E.F.: Ind. Eng. Chem., 43, 950 (1951).