

Simultaneous Determinations of Azinphos Ethyl, Azinphos Methyl and its Oxygen Analog by Gas Liquid Chromatography

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Azinphos methyl¹, an organophosphorous insecticide, is formulated for application as a mixture of azinphos methyl (0,0-Dimethyl S-(4-oxo-1,2,3-benzotriazin-3(4H)-ylmethyl) phosphorodithioate) and the ethyl homolog (0,0-Diethyl S-(4-oxo-1,2,3-benzotriazin-3 (4H)-ylmethyl)phosphorodithioate).

Several methods of analysis have been published for residue studies for these two compounds and the metabolite of azinphos methyl, its oxygen analog, in treated crops, milk and tissue (1, 2, 3, 4, 5, 6). Two of these methods are capable of quantitating all three compounds; however, separate determinations are required, which is time-consuming and costly. Therefore, a simultaneous method of analysis applicable to routine analysis for all three compounds was developed and is presented.

Experimental

Apparatus

Gas Chromatograph: Micro Tek 2000R equipped with a flame ionization detector. Conditions were as follows: column 265°C, injection port 280°C, detector 285°C, nitrogen flow rate approximately 50 ml/min, negative polarity and attenuation 0.1X16.

Column: Stainless steel 5' x 1/8" O.D. packed with 5% Silicone substrate (SE-30) on chromosorb W(80/100 mesh) high purity, acid washed, and DMCS treated. The column was conditioned at 280°C for 48 hours before use.

Reagents: Insecticide standards were prepared in carbon disulfide from analytical grade azinphos methyl (99.5%), technical azinphos ethyl (98.4%) and oxygen analog.

Procedure: The extraction procedure of Adams and Anderson (1) was modified slightly to extract all three compounds simultaneously from milk. Previously this procedure had only been used to extract azinphos methyl and the oxygen analog.

¹Azinphos methyl and other test materials used in this study were furnished by Chemagro Corporation, Kansas City, Missouri, as Guthion^R, Ethyl Guthion^R (ethyl homolog) and Gutoxon^R (oxygen analog).

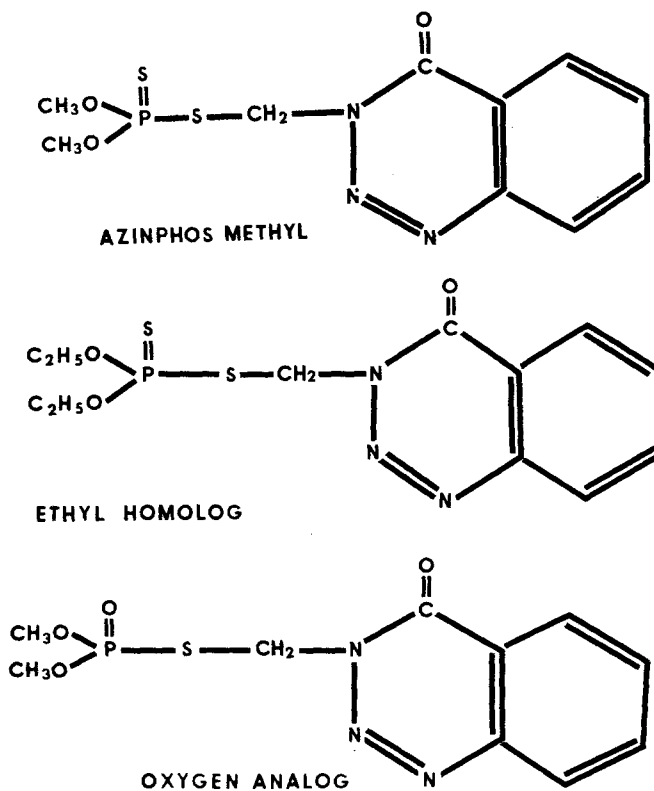


Figure 1

RESPONSE CURVES SHOWING SENSITIVITY RANGE OF AZINPHOS METHYL, OXYGEN ANALOG AND

METHYL HOMOLOG

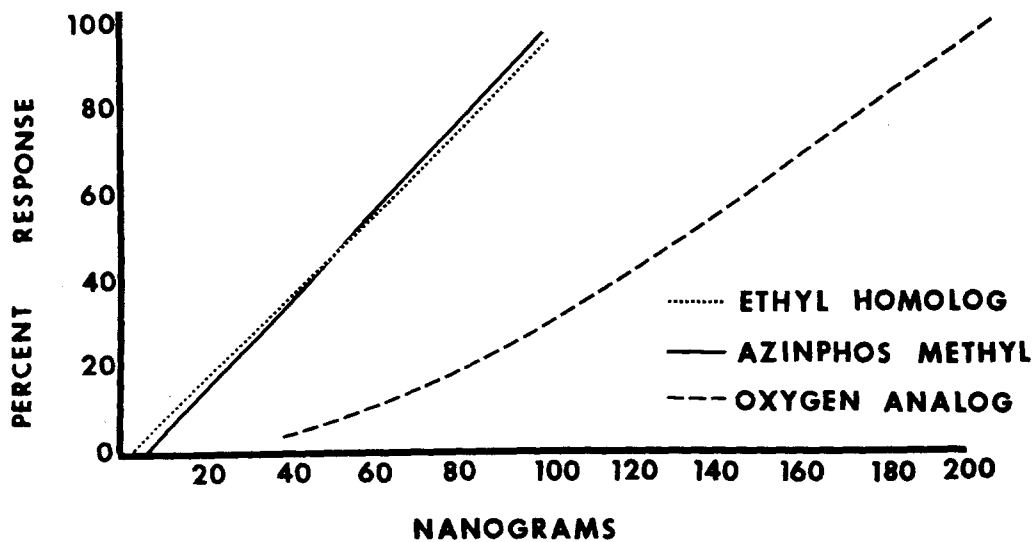
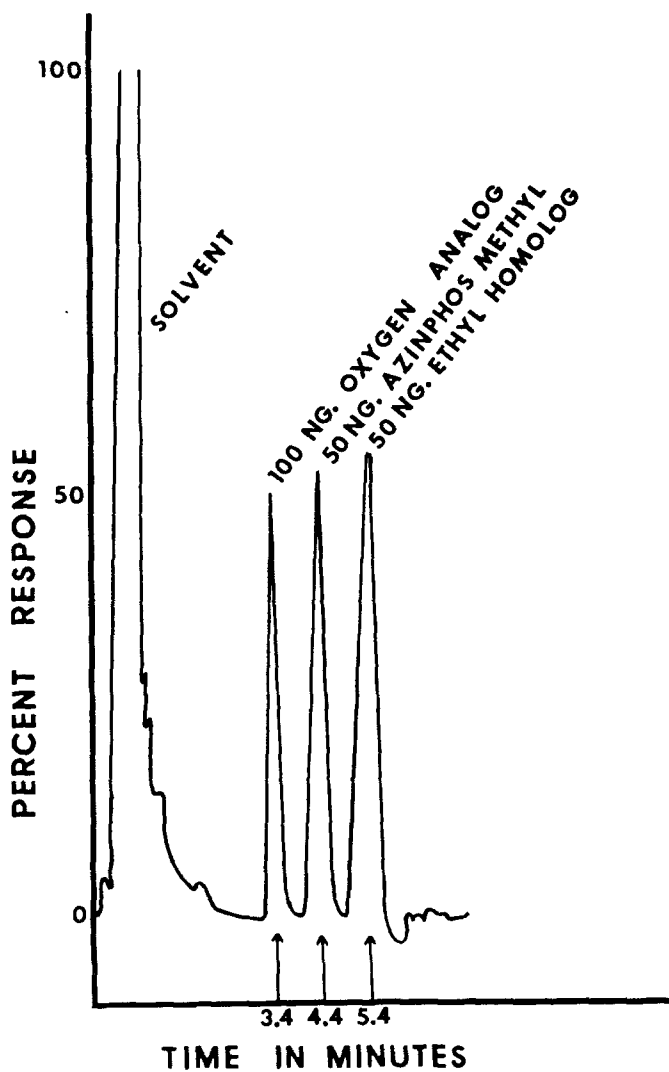


Figure 2

GAS CHROMATOGRAPHS OF AZINPHOS METHYL, OXYGEN ANALOG, AND ETHYL
HOMOLOG



Results and Discussion

Increments of three insecticidal compounds in carbon disulfide solution were injected into the gas chromatograph. The range of these injections were between 10 and 200 nanograms. The linear range of each compound is shown in Figure 1. The gas chromatograph column requires periodic priming with oxygen analog, approximately 200 ng at 2-hour intervals, in order to maintain maximum sensitivity. Retention time for the oxygen analog was 3.4 minutes, azinphos methyl 4.4 minutes, and the ethyl homolog 5.4 minutes (Figure 2).

Analyses were made on raw milk samples by fortifying 200 ml of raw milk with each of the three compounds. The samples were allowed to sit at room temperature for 1 hour before extracting. (The time of incubation was found not to be significant.) All three of the insecticidal compounds--azinphos methyl, the ethyl homolog, and the oxygen analog--can be separated and quantitated in one milk sample extract. The efficiency of the extraction procedure is indicated in Table I.

TABLE I

RECOVERY OF KNOWN QUANTITIES OF AZINPHOS METHYL, THE ETHYL HOMOLOG
AND THE OXYGEN ANALOG ADDED TO MILK

	P.P.M.	P.P.M.	Amount detected	
Materials	added	recovered	in ng.	% Recovery
Ethyl homolog	1.25	1.11	50	89
	0.60	0.50	24	83
Azinphos methyl	1.25	1.11	50	89
	0.60	0.49	24	82
Oxygen analog	2.50	1.50	100	60
	1.25	0.65	50	52

The recoveries are an average of duplicate extractions at two fortified levels. The recoveries of azinphos methyl and the ethyl homolog from fortified milk samples were comparable in range as described by Adams and Anderson, 82-89% (1). The recovery for the oxygen analog ranged from 52-60%.

The sensitivity of this method in analyzing milk samples for azinphos methyl and the ethyl homolog is about 0.038 ppm and that for the oxygen analog is 0.06 ppm. The sensitivity of this method, as with most determinations, is limited only by the cleanup procedure employed.

Summary

A simple gas liquid chromatographic method for simultaneous determinations of azinphos methyl, the ethyl homolog, and the oxygen analog is described. The procedure can detect, quantitatively by gas chromatography, azinphos methyl and the ethyl homolog residues in milk at 0.038 ppm. The oxygen analog can be detected and quantitated at 0.06 ppm.

References

1. ADAMS, J.M. and ANDERSON, C.A. J. Agr. Food Chem. 14, 53 (1966).
2. EVERETT, L.J., ANDERSON, C.A. and MAC DOUGALL, D. J. Agr. Food Chem. 14, 47 (1966).
3. LOEFFLER, W.W., JR., TRIMBERGER, G.W., FOX, F.H., RIDGEWAY, R.L., LISK, D.J. and GYRISCO, G.G. J. Agr. Food Chem. 14, 46 (1966).
4. MEAGHER, W.R., ADAMS, J.M., ANDERSON, C.A. and MAC DOUGALL, D. J. Agr. Food Chem. 8, 282 (1960).
5. COHEN, C.J., BETKER, W.R., WASLESKI, D.M. and CAVAGNOL, J.C. J. Agr. Food Chem. 14, 315 (1966).
6. GIANG, P.A. and SCHECHTER, M.S. J. Agr. Food Chem. 6, 845 (1958).