

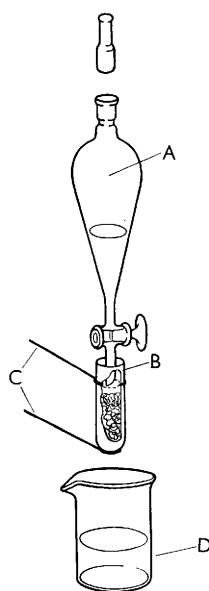
## Determination of Chlorinated Pesticides in Aqueous Emulsions

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A method is described for the determination of chlorinated pesticides that involves their adsorption on to granulated carbon, and their subsequent extraction and degradation by the Stepanow method. The inorganic chlorine is then determined potentiometrically.

A METHOD has been devised for the determination of chlorinated pesticides in aqueous suspension; it was intended in the first instance for use in the assessment of emulsion stability, but it could be applied to any insecticidal wash based on a halogenated active ingredient. Several methods currently in use to determine emulsion stability are based on visual observation of separated cream or oil after certain specified periods.<sup>1,2,3,4,5,6,7</sup> Such methods are in many instances satisfactory but there is an underlying assumption that the active principle separates wholly with the oil or cream. Clearly this need not always be so. The method devised is based on the determination of the pesticide in a portion of the aqueous phase at an appropriate time after mixing. Active material is absorbed from the aqueous phase on to granulated carbon contained in a Whatman extraction thimble supported on wire stirrups (Fig. 1). The carbon is dried and then placed in a suitable extraction apparatus. The



A = 125-ml Separating funnel

B = 22 x 80-mm Whatman extraction thimble

C = Wire supports for thimble

D = 250-ml Beaker

Fig. 1. Ground-glass jointed extraction assembly

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pesticide is removed from the carbon by continuous extraction with an isopropyl alcohol-benzene mixture containing metallic sodium. There is thus simultaneous extraction and reaction with sodium to produce inorganic chloride, which may be determined by any standard method. The method has been successfully applied to aqueous emulsions prepared from dieldrin, aldrin, endrin, DDT and lindane concentrates at about 0.2 per cent. level of active ingredient. Lower concentrations of active ingredient can be determined by increasing the volume of emulsion used (500 ml of emulsion containing 0.005 per cent. of active ingredient would provide sufficient chlorine, on the basis of a 60 per cent. content, to give a final titre of about 5 ml of 0.1 N silver nitrate solution). It may also be used for chlorinated phenoxy-acetic acids. The results in Table I show the recoveries that have been obtained.

TABLE I  
RECOVERY OF CHLORINATED PESTICIDES FROM AQUEOUS EMULSION

Sample	Operator 1		Operator 2		Operator 3	
	Added, g	Found, g	Added, g	Found, g	Added, g	Found, g
Dieldrin ..	0.196	0.190	0.191	0.191	0.0985	0.0980
Endrin ..	0.214	0.207	—	—	0.105	0.107
Aldrin ..	0.320	0.313	—	—	0.157	0.152
DDT ..	0.251	0.253	0.250	0.249	0.121	0.123
Lindane ..	0.197	0.197	0.195	0.192	0.0982	0.0994

#### METHOD

##### APPARATUS—

*Extraction assembly*—Ground-glass jointed, with 250-ml flask and straight tube extractor.

*Separating funnel*, 125-ml capacity.

*Beaker*, 250-ml capacity.

*Measuring cylinder*, 100 ml.

*Whatman extraction thimble*, 22 × 80 mm.

*Wire supports for thimble*.

*Vacuum desiccator*.

*Potentiometric titration apparatus with mercury(I) sulphate and silver electrodes*.

##### REAGENTS—

*Light petroleum*, boiling-range 40° to 60° C.

*Benzene*.

*Isopropyl alcohol*.

*Sodium sulphate*, anhydrous.

*Sodium metal*.

*Silver nitrate solution*, 0.1 N.

*Phosphorus pentoxide*.

*Nitric acid*, 50 per cent.

*Granulated carbon*—Nuchar C-190, fraction on 30 mesh. Obtainable from Kodak Limited, Kirkby, Liverpool.

##### PROCEDURE—

Fill a 22 × 80-mm extraction thimble to two-thirds of its volume with granulated carbon and fit the thimble in an upright position into the wire supports. Place a volume of emulsion, containing sufficient active material to give a final titre of between 5 and 50 ml of 0.1 N silver nitrate solution, into the 125-ml separating funnel and add to it anhydrous sodium sulphate at the rate of 1.5 g per 10 ml of emulsion. Shake the funnel vigorously to dissolve the sodium sulphate. Clamp the separating funnel above the thimble and run the emulsion through the carbon at a rate of about 5 ml per minute. Collect the eluate in a clean beaker. Use a small volume of eluate to wash out the separating funnel and elute the washings through the carbon. Transfer the combined eluates to the separating funnel, wash out the beaker with 25 ml of light petroleum and add this to the combined eluates. Shake the funnel and allow it to stand. Retain the light petroleum layer.

After the thimble has been thoroughly drained, place it on wads of filter-paper in a vacuum desiccator over phosphorus pentoxide. Evacuate the desiccator and leave the

thimble to dry for at least 3 hours. Transfer the thimble to the extraction tube, run 25 ml of isopropyl alcohol through the carbon, followed by the light petroleum from the separating funnel and 20 ml of benzene. Carefully add 3 g of sodium metal to the solvent mixture in the flask and reflux the mixture for  $2\frac{1}{2}$  hours. Cool the flask, add sufficient 50 per cent. isopropyl alcohol to dissolve unreacted sodium and then place the flask on a steam-bath to remove hydrocarbon solvent. Wash the mixture into a 250-ml beaker with 50 ml of water, neutralise with 50 per cent. nitric acid and add 10 ml in excess. Cool the solution and titrate it potentiometrically with 0.1 N silver nitrate solution by using mercury(I) sulphate and silver electrodes.

1 ml of 0.1 N silver nitrate solution  $\equiv$  0.003546 g of chlorine.

Determinations were made by operators 1 and 2 on 100 ml of emulsion prepared from 1 ml of concentrate and by operator 3 on 50 ml of emulsion containing 0.5 ml of concentrate. The measured volumes of concentrate were weighed to determine the actual weights of active ingredients added. The contents of active material in the original unemulsified concentrates were determined by the method described, omitting the carbon-adsorption stage.

The method has been accepted by the Ministry of Agriculture, Fisheries and Food for inclusion in the next issue of Technical Bulletin No. 1, Specifications and Methods of Analysis for Pesticides.

The authors thank the Government Chemist, Ministry of Technology, for permission to publish this paper.

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Received December 5th, 1966