

Rapid Method for Surface Residues of Organophosphorus Pesticides by Total Phosphorus

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A method is described for the rapid determination of surface residues of Diazinon, Guthion, and Imidan on whole fresh fruit. A simple wet ashing was sufficient to convert Diazinon and Guthion to the inorganic phosphate; however,

the addition of hydrobromic acid to the ashing step was necessary for Imidan. Correlation of results from the proposed method with those of other methods was acceptable.

The current use of broad-spectrum organophosphorus pesticides has led to problems of residue analysis. Many approaches to the problem have been reported, utilizing such chemical and physical methods as paper (Coffin and Savary, 1964) and thin-layer chromatography (Walker and Beroza, 1963), infrared spectrophotometry (Burchfield and Johnson, 1965), bioassay (Sferra *et al.*, 1962), enzyme analysis (Getz and Friedman, 1963), and gas chromatography. Most of these methods, however, have the distinct disadvantage of being either very time-consuming or requiring special instruments. The electron affinity gas chromatographic detector, which is very satisfactory for the chlorinated hydrocarbons, is insensitive to many of the organophosphorus compounds.

The microcoulometric detector, which has proved an efficient tool, is both expensive and requires the presence of a gas chromatograph. The new flame ionization detector also works well in the analysis of the organophosphorus pesticides but makes use of the gas chromatograph, which may not be available to the small research laboratory involved in spray application and formulation programs.

Many of these laboratories are not as concerned with legal tolerances as in the spray load applied for the control of insects. In this case a large number of samples from different spray programs must be analyzed immediately upon and at intervals after spraying. The rapid method is particularly well suited for this type of analysis; however, more sensitive methods must be resorted to if extremely low residues are encountered.

In the following procedure, surface residues of the pesticide are extracted from the crop and analyzed without cleanup. Since cleanup is avoided, a great deal of time is saved, allowing many samples to be completed within a short time. In addition, the method does not rely on the presence of specialized equipment.

Several procedures for the determination of organophosphorus pesticides by total phosphorus utilizing either a wet (Laws and Webley, 1961) or dry (Blinn, 1964) combustion have been proposed; however, these require a rather elaborate cleanup. In the following

procedure the pesticide is digested using a simple wet combustion and the phosphorus determined colorimetrically by the molybdenum blue complex method of Martin and Doty (1949).

Three of the insecticides with which this laboratory has been most concerned, *O,O*-diethyl *O*-(2-isopropyl-4-methyl-6-pyrimidinyl) phosphorothioate (Diazinon, Geigy Chemical Co.), *O,O*-dimethyl (*N*-phthalimidomethyl) phosphorodithioate (Imidan, Stauffer Chemical Co.), and *O,O*-dimethyl *S*-[4-oxo-1,2,3-benzotriazin-3(4*H*)-ylmethyl] phosphorodithioate (Guthion, Chemagro Corp.), have been determined satisfactorily. For Diazinon and Guthion, a simple wet-ashing process converted the compound to the inorganic phosphate. However, Imidan required a slight modification as described.

Methods and Materials

Extraction. A 500-gram sample of intact fruit was tumbled with redistilled petroleum ether (0.5 ml. per gram of sample) in a tightly sealed jar for 20 to 30 minutes. After tumbling, the solvent was decanted and filtered through a No. 12 Whatman filter paper cone containing about 50 grams of anhydrous sodium sulfate. The filtrate was collected and stored in a tightly sealed glass storage bottle.

Digestion and Color Development. A suitable aliquot of the extract was evaporated just to dryness in a stream of air. Five milliliters of concentrated nitric acid and 2 ml. of 1*N* sulfuric acid were added to the evaporated sample, and the solution was boiled until the volume had been reduced to about 2 ml. After the solution had cooled, 5 ml. of 1*N* perchloric acid was added and the solution reboiled on a hot plate. The solution was allowed to fume for about 1 minute, cooled, 2 ml. of distilled water were added, and the solution was reheated and fumed again for about 1 minute.

After the digested sample had cooled it was transferred to a 25-ml. glass-stoppered mixing cylinder using a total of about 10 ml. of rinse water. One milliliter of 8*N* sulfuric acid, 1 ml. of 15% (w./v.) ammonium molybdate solution, and 10 ml. of a 2-methyl-1-propanol-benzene (1 to 1, v./v.) mixture were added, in that order. After shaking the cylinder for 30 seconds, the layers were allowed to separate, and the lower aqueous layer was drained off with an aspirator. Sufficient ethanolic sulfuric acid (3.2% concentrated acid in absolute ethanol) was added to bring

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the sample to 12-ml. total volume, 0.3 ml. of fresh stannous chloride solution was added, and the solutions were thoroughly mixed. The absorbance was read immediately at 660 $m\mu$ on a Beckman Model B spectrophotometer and compared with the standard slope.

The stannous chloride solution should be made fresh from stock in the following manner. The stock solution is 10% (w./v.) stannous chloride in concentrated hydrochloric acid. This solution should be stored in a brown bottle and be remade fresh every 2 weeks. The dilute solution used in the analysis must be made fresh daily by diluting 1 ml. of concentrated stock to 5 ml. with 10*N* sulfuric acid.

A standard curve was prepared by adding 0, 20, 40, 60, 80, and 100 μ g. of pesticide to the digestion flask and proceeding as outlined above. The absorbance for 100 μ g. of pesticide was 0.432 for Imidan and Guthion and 0.414 for Diazinon. (Imidan and Guthion would be expected to have the same slopes, since they have the same molecular weight.)

The above procedure, although giving satisfactory results for Diazinon and Guthion, gave low results for Imidan owing to incomplete digestion. The digestion may be improved by first boiling the evaporated sample with 3 ml. of concentrated (48%) hydrobromic acid and 2 ml. of 1*N* sulfuric acid. After the volume has been reduced to about 2 ml, the solution is cooled, and 5 ml. of concentrated nitric acid are slowly added. This should be allowed to stand for 5 minutes; then the normal procedure beginning with the addition of the perchloric acid is followed.

Results and Discussion

This method has been successfully applied to the determination of Diazinon, Imidan, and Guthion on both apples and grapes. In most cases the value of the check sample (unsprayed fruit) was 0.03 ± 0.01 p.p.m. An occasional check, however, would give a blank of as high as 0.10 p.p.m. which could usually be traced to rupture of the fruit and the release of natural phosphates.

The accuracy of the method was tested by comparing the results obtained from this method with those obtained from other accepted methods. For example, Guthion on grapes was also determined by the method of Meagher *et al.* (1960), Diazinon by the method of Suter *et al.* (1955), and Imidan by a modification of the Stauffer method (Batchelder and Patchett, 1963).

A comparison was made of samples treated with Diazinon using the rapid method and that of Suter *et al.* (1955). The results given in Table I show a close correlation between the two methods, the average mean deviation being ± 0.2 p.p.m. over the entire range of sample concentrations. Recovery checks indicated a $95 \pm 7\%$ recovery of Diazinon added to check samples.

A similar determination was run on Guthion residues on grapes. The method of Meagher *et al.* (1960) gave results in good correlation with those of the rapid determination (Table II). Here the mean deviation between the two methods was ± 0.3 p.p.m.

Table I. Comparison of Methods for Determination of Diazinon Residues on Field Samples of Grapes

Sample No.	Rapid Method, P.P.M.	Suter ^a Method, P.P.M.
1	0 ^b	0 ^b
2	0.4	0.4
3	0.3	0.4
4	0.4	0.4
5	0.4	0.4
6	0.6	0.6
7	0.7	0.7
8	0.7	0.8
9	1.0	1.2
10	0.8	1.0
11	1.4	1.7
12	1.5	0.9
13	1.8	1.0
14	1.5	1.4
15	2.1	2.5
16	2.1	...

^a Suter *et al.*, 1955.

^b Average of duplicate samples.

Table II. Comparison of Methods for Determination of Guthion Residues on Field Samples of Grapes

Sample No.	Method of Meagher, ^a P.P.M.	Rapid Method, P.P.M.
1	0.4 ^b	0.5 ^b
2	0.8	0.7
3	0.9	0.3
4	0.9	0.5
5	1.3	0.8
6	1.6	1.4
7	2.0	1.9
8	2.2	2.1
9	2.3	2.5
10	3.0	3.3
11	3.1	3.4
12	4.6	4.3
13	6.6	5.2
14	7.1	6.1

^a Meagher *et al.*, 1960.

^b Average of duplicate samples.

over the range of concentrations used. A check of the recovery using spiked samples showed a $93 \pm 4\%$ recovery of added pesticide.

Application of the Stauffer method (Batchelder and Patchett, 1963) for the determination of Imidan in ripe grapes resulted in the formation of thick emulsions which were difficult to break. For this reason it has been customary in this laboratory to use the Goodwin *et al.* procedure (1961) for extraction even though its efficiency was less. Analysis was then completed by the standard Stauffer method. A comparison of this procedure with the rapid method is presented in Table III. The results obtained with the rapid method averaged about 0.2 p.p.m. below those obtained by the modified Stauffer method. How-

Table III. Comparison of Methods for Determination of Imidan Residues on Field Samples of Grapes

Sample No.	Rapid Method, P.P.M.	Stauffer Method, ^a Modified, P.P.M.
1	0.5 ^b	0.5 ^b
2	0.7	1.0
3	0.8	1.2
4	1.5	1.6
5	1.5	1.8
6	1.6	1.7
7	2.6	3.2
8	2.8	2.9
9	4.5	4.9
10	6.1	6.0

^a Batchelder and Patchett, 1963.

^b Average of duplicate samples.

ever, for the purpose of spray deposits the results are satisfactory.

An attempt to determine Zolone [(*O,O*-diethyl-dithiophosphorylmethyl)-3-chloro-6-benzoxalone, Chipman Chemical Co.] by the rapid method was unsatisfactory because of the poor solubility of this compound in the extraction system. Erratic results were obtained which tended to vary with each extraction.

The limitations of this method are obvious. The extraction procedure removes only surface residues which are soluble in the solvent employed. Fruit which has been damaged or cannot withstand the tumbling will give high results owing to the extraction of internal natural phosphates by the extraction solvent. Care must be taken, therefore, to run frequent checks on samples of unknown extraction characteristics.

The condition of only removing surface residues eliminates the application of this method to the determination of the systemic insecticides, since these compounds are absorbed into the tissue and not extracted by surface stripping. In general this method has been satisfactory for the rapid determination of Diazinon, Guthion, and Imidan on surfaces of apples and grapes.

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