

## Regression Techniques for Estimating Total DDT and TDE Residues in Tobacco

A procedure is described for estimating total residues of DDT and TDE in tobacco from the analysis of only a single component of each insecticide. Linear regression equations were derived from data from previous analyses. Standard errors of the predicted values and the coefficient of simple determination ( $r^2$ ) were calculated for each regression. Data from an independent source

were substituted into the equation, and the calculated values were in good agreement with the observed values. The regression equations should prove useful in quality control monitoring for these insecticides on tobacco and tobacco products and should shorten the time for analysis considerably.

Regulatory activities with respect to pesticide residues on tobacco and tobacco products have prompted refinements of analytical methods for these pesticide residues (Domanski *et al.*, 1972; Skrentny and Dorough, 1972). Refinements of separation methods often entail additional cleanup steps and, hence, increased analytical time. Cost and analytical time required by methods now available may prohibit many analyses presently desired for quality control. Thus, a critical need exists for rapid, less expensive analytical methods for pesticide residues on tobacco.

Frequently, the analysis of pesticide residues is complicated by the presence of several components in the original formulation, in addition to metabolites and degradation products of the parent pesticide. In the past, the presence of a number of components in different proportions usually required the analyst to make several dilutions and injections of each sample, thereby increasing the time for gas chromatographic analysis.

For some time we have realized that  $p,p'$ -DDT and  $p,p'$ -TDE in tobacco have a direct relationship to the total concentrations of these two pesticides. Total DDT is the sum of  $p,p'$ -DDT,  $o,p$ -DDT, and  $p,p'$ -DDE, and total TDE is the sum of  $p,p'$ -TDE,  $o,p$ -TDE, and  $p,p'$ -TDEE (deHCl- $p,p'$ -TDE). Although these relationships may seem obvious, it was necessary to establish that they remained constant over a period of time. Changes in the relative proportion of the components in the pesticide formulation and differences in metabolism and degradation rates due to climatic and curing conditions in different locations and years could lead to a poor correlation.

This paper describes a procedure for estimating total residues of DDT and TDE by the analysis of only a single component of each of these insecticides. Techniques for evaluating the precision of the estimates also are discussed.

**Source of Data.** The data used in the calculations of the regression (prediction) equations for DDT and TDE were obtained from 1968 and 1970 auction market surveys (Domanski and Sheets, 1973; Sheets and Jackson, 1970) and 1969 tobacco product surveys (Sheets and Jackson, 1970). Samples which contained residue values below the limit of detection were not included in the calculation of these regression equations.

**Statistical Computations.** Simple linear regressions were fitted according to standard techniques described in Snedecor and Cochran (1967). The prediction equations were used to predict total amounts of insecticide ( $\hat{Y}$ 's) from the major component (the original  $X$  readings used in deriving the regression equations).

In addition to estimation of the regression coefficients and standard errors of predicted values, the coefficient of simple determination  $r^2$  also was obtained for each regression.

Symbolically the regression equation has the form:

$$\hat{Y} = b_0 + b_1X$$

where  $\hat{Y}$  = the total amount of pesticide, *i.e.*, DDT or TDE (predicted value),  $b_0$  = intercept,  $b_1$  = slope, and  $X$  = amount of the major component ( $p,p'$ -DDT or  $p,p'$ -TDE).

The calculated regression equations for DDT and TDE are given in Table I. Other statistics necessary for the calculation of the standard error of a predicted value are also reported in the table.

The accuracy of the TDE and DDT equations for predicting total TDE and DDT levels for other data sets was evaluated using the data of Bugler and Naish (1970). These data were obtained from the American flue-cured tobacco crops in 1967, 1968, and 1970. These authors did not include  $p,p'$ -TDEE in the TDE analysis. Since the amount of  $p,p'$ -TDEE is usually small compared to the total TDE, it should not affect significantly the goodness of prediction of the total TDE from  $p,p'$ -TDE.

This study indicated that the equation produced a poor predicted value for the total insecticide residue when the value of the  $X$  component was less than the intercept ( $b_0$ ). These differences in the predicted and observed values could be due to exclusion of samples with residue values below the limit of detection. Since total concentration of DDT and TDE should be zero when their  $p,p'$  isomers are zero, the equations were fitted by forcing the line to pass through zero and setting a minimum value for  $X$  which could be substituted into the equation. These minimum values were the detection limits for the  $X$  components and were derived from the original data set from which the equations were calculated. These equations and minimum values for the  $X$  components are given in Table II.

The regression equations fitted through the origin were applied to the data of Bugler and Naish. The results are given in Table III. When the value for  $X$  was below the minimum detectable concentrations, total residues were assigned the less than value (for total DDT, <0.06 ppm; for total TDE, <0.10 ppm).

The calculated values for total DDT and TDE were in good agreement with the observed values (Table III), even though Bugler and Naish (1970) used a different analytical procedure than was used for obtaining the data from which the regression equations were calculated. We applied the equation to the TDE data reported by Skrentny and Dorough (1972), who compared eleven different methods of extraction. In all cases the equation, when fitted through the origin, gave good estimates of the observed total TDE. The differences between the observed and calculated values are within the precision of the analytical techniques used to determine the concentration of these insecticides in tobacco (Domanski *et al.*, 1972).

In a previous study (Domanski and Sheets, 1973) we reported that a tedious separation procedure using column chromatography on Florisil was needed to separate endosulfan I from  $p,p'$ -DDE, endrin from  $o,p$ -DDT, and diel-

**Table I. Regression Equations and Related Statistics for Predicting Total Insecticide from Major Components**

| Pesticide | Regression equation        | r <sup>2</sup> | n   | $\bar{X}$ | $\Sigma x^2$ | $s_{y,x}$ |
|-----------|----------------------------|----------------|-----|-----------|--------------|-----------|
| DDT       | $\hat{Y} = 0.201 + 1.185X$ | 0.976          | 292 | 7.58      | 34,834.17    | 2.037     |
| TDE       | $\hat{Y} = 0.325 + 1.194X$ | 0.987          | 292 | 15.80     | 138,306.64   | 3.158     |

**Table II. Regression Equations Fitted through the Origin**

| Pesticide | Regression equation | Minimum value for X, ppm |
|-----------|---------------------|--------------------------|
| DDT       | $\hat{Y} = 1.185X$  | 0.05                     |
| TDE       | $\hat{Y} = 1.194X$  | 0.08                     |

**Table III. Observed and Predicted Values Calculated from the Regression Equations Fitted Through the Origin for Total DDT and TDE from the Data of Bugler and Naish (1970)**

| X, p,p'-DDT, ppm | Y, total DDT observed, ppm | $\hat{Y}$ , total DDT calculated, ppm | X, p,p'-TDE, ppm | Y, total TDE observed, ppm | $\hat{Y}$ , total TDE calculated, ppm |
|------------------|----------------------------|---------------------------------------|------------------|----------------------------|---------------------------------------|
| 11.2             | 14.4                       | 13.3                                  | 63.0             | 80.2                       | 75.2                                  |
| 8.9              | 10.8                       | 10.6                                  | 47.0             | 63.3                       | 56.1                                  |
| 16.8             | 19.9                       | 19.9                                  | 53.5             | 69.1                       | 63.9                                  |
| 24.0             | 30.1                       | 28.4                                  | 49.0             | 61.0                       | 58.5                                  |
| 17.6             | 20.5                       | 20.9                                  | 44.4             | 57.2                       | 53.0                                  |
| 26.3             | 29.6                       | 31.2                                  | 43.8             | 54.6                       | 52.3                                  |
| 15.6             | 18.8                       | 18.5                                  | 38.4             | 48.0                       | 45.9                                  |
| 18.6             | 21.2                       | 22.0                                  | 33.0             | 40.8                       | 39.4                                  |
| 13.0             | 14.6                       | 15.4                                  | 29.6             | 35.4                       | 35.3                                  |
| 20.0             | 24.3                       | 23.7                                  | 36.0             | 45.6                       | 43.0                                  |
| 17.6             | 21.1                       | 20.9                                  | 35.0             | 43.4                       | 41.8                                  |
| 9.1              | 10.9                       | 10.8                                  | 27.5             | 35.5                       | 32.8                                  |
| 11.0             | 13.6                       | 13.0                                  | 29.6             | 35.6                       | 35.3                                  |
| 16.8             | 20.9                       | 19.9                                  | 30.2             | 37.5                       | 36.1                                  |
| 7.7              | 9.1                        | 9.1                                   | 28.5             | 33.6                       | 34.0                                  |
| 8.5              | 10.4                       | 10.1                                  | 21.2             | 26.0                       | 25.3                                  |
| 13.0             | 15.3                       | 15.4                                  | 23.0             | 27.8                       | 27.5                                  |
| 9.0              | 10.5                       | 10.7                                  | 14.3             | 18.3                       | 17.1                                  |
| 7.5              | 9.4                        | 8.9                                   | 13.1             | 16.3                       | 15.6                                  |
| 11.0             | 12.8                       | 13.0                                  | 13.2             | 16.5                       | 15.8                                  |
| 6.2              | 7.1                        | 7.3                                   | 11.4             | 14.0                       | 13.6                                  |
| 8.6              | 9.7                        | 10.2                                  | 0.1              | 0.1                        | 0.1                                   |
| 3.4              | 4.0                        | 4.0                                   | 0.3              | 0.4                        | 0.4                                   |
| 4.0              | 4.4                        | 4.7                                   | 0.05             | 0.1                        | <0.1                                  |
| 8.4              | 9.7                        | 10.0                                  | 0.3              | 0.4                        | 0.4                                   |
| 1.8              | 2.1                        | 2.1                                   | 0.2              | 0.2                        | 0.2                                   |
| 1.3              | 1.6                        | 1.5                                   | 0.01             | 0.02                       | <0.1                                  |
| 1.3              | 1.6                        | 1.5                                   | 1.9              | 2.1                        | 2.3                                   |
| 0.4              | 0.5                        | 0.5                                   | 0.4              | 0.5                        | 0.5                                   |
| 2.0              | 2.3                        | 2.4                                   | 3.7              | 4.5                        | 4.4                                   |
| 1.0              | 1.3                        | 1.2                                   | 1.6              | 1.8                        | 1.9                                   |

drin from *o,p*-TDE. This separation is not critical when the total DDT is estimated from the primary component using the equations presented in this paper. Analysts can now elute the DDT's and TDE's rapidly from the Florisil column with 6% diethyl ether in petroleum ether, analyze the *p,p'* isomers on a gas chromatograph, and estimate the totals from the regression equations.

Tobacco is normally stored for 4 years or more before being manufactured into products, and data from tobacco product studies (Domanski *et al.*, 1973; Sheets and Jackson, 1970) indicate that there are no changes in the relative proportions of the compounds that make up the total residues of DDT and TDE during storage and manufacture. Since DDT and TDE are no longer registered for use on tobacco, changes in the commercial product which might affect the ability of the regression equations to estimate accurately the total residues of these insecticides

will not occur. Due to the large amounts of tobacco from previous crops being stored, these regression equations will be useful in screening procedures for DDT and TDE. We emphasize that these equations are only intended as an estimate of the total residue, and if accurate residue values are required, the analyst must determine the quantity of each component making up the total residue.

These regression techniques may be applicable to other pesticide analyses involving two or more compounds which make up a total residue, but this technique cannot be used indiscriminantly. In deriving an equation for a particular pesticide, the analyst must account for all major metabolites and degradation products and verify that they are not subject to change. The data used to derive the equation must represent the different conditions to which the pesticide would be subjected and should also be collected over a period of time so that possible variations in the commercial product would also be taken into account. A low *r*<sup>2</sup> value would indicate that some other factors affect the final residue and the simple regression technique would not be applicable. The derived equation should also be tested preferably on data from an independent source.

We have derived a regression equation for total endosulfan which is the sum of endosulfan I, endosulfan II, and endosulfan sulfate. The total endosulfan residue is estimated from the endosulfan sulfate concentration. The present endosulfan equation was derived from the 1970 auction market data (Domanski and Sheets, 1973). As previously stated, changes in relative proportions of the components making up the total residue may be dependent upon a number of factors. Data from a survey of 1972 auction market tobacco will be used to verify the accuracy of this regression equation in estimating the total endosulfan residue from the concentration of endosulfan sulfate.

#### ACKNOWLEDGMENT

We appreciate the financial support of this research provided by The American Tobacco Co., Brown and Williamson Tobacco Corp., Liggett and Myers, Inc., P. Lorillard, Philip Morris, Inc., R. J. Reynolds Tobacco Co., and Tobacco Advisory Committee (United Kingdom).

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Received for review April 2, 1973. Accepted September 13, 1972. Contribution from the North Carolina State University Agricultural Experiment Station. Published with the approval of the Director of Research as paper no. 3967 of the Journal Series. Pesticide Residue Research Laboratory and the Department of Statistics, North Carolina State University, Raleigh, N. C. 27607.