LIMIT OF DETECTION AND LIMIT OF IDENTIFICATION FOR STRAIGHT-LINE CALIBRATION CURVES

R. FERRUS(*), C. POLO(+), M. PEPIO(+) y F. TORRADES(*)

Universitat Politècnica de Catalunya

(*) Laboratori d'Anàlisi Química. ETSEIT.
c. Colom, 11. Terrassa
SPAIN
(+) Grup XVII: Estadística. ETSEIT.
c. Colom, 11. Terrassa
SPAIN

1. INTRODUCTION

Hubaux et al. (1970) (HV, hereafter) have used confidence-band statistics to determine the limit of detection, or minimum significative analytical signal, which may be assigned with a high probability to the presence of the analyte (substance to be found if present) in the submitted specimen, and the limit of identification, or minimum specimen analyte concentration, which, again with a high probability, will secure an analytical signal higher than the limit of detection. However, the HV approach implies that the variance of the error distribution of the analytical signals around their expectation should be a constant. This precluded the application of the HV approach to a set of calibration data obtained by Ferrús et al. (1985) (FT, hereafter), because the variance estimation from ten replications, at each of three analyte concentration levels in standard specimens, increased as the square of the mean analytical signal. In this paper we present a way of overcoming the difficulties due to heteroscedasticity in the FT data.

2. CONFIDENCE-BAND USING WEIGHTED LEAST SQUARES

The data from FT is in TABLE I. The exploratory analysis tell us that the variate Y is normally distributed, and the relationship between x and Y takes the form $\mathbf{Y} = \mathbf{X}\boldsymbol{\beta} + \varepsilon$, in matrix notation, where $E(\varepsilon)=0$ and $V(\varepsilon)=\mathrm{diag}(\sigma_1^2 \ldots \sigma_K^2) = \gamma V$. V being a diagonal matrix. Also, the data in TABLE I shows that the variance of Y is a function of x^2. Therefore, the model $\sigma^2 = \gamma x^{\varphi}$ was proposed, and

$$s^2 = \delta\sigma^2 = \delta\gamma x^{\varphi}$$

TABLE I. Calibration data for the barium sulphate gravimetry. **x**, mg sulphate ion added; **Y** mg barium sulphate found.

x	Y									
.996	.51	.53	.50	.56	.58	.56	.54	.49	.51	.53
2.989	1.51	1.46	1.43	1.68	1.55	1.60	1.61	1.54	1.42	1.61
4.981	2.52	2.21	2.38	2.58	2.49	2.56	2.54	2.32	2.27	2.60

Tort(1985) has pointed out the fast convergence to normality of the linear transformations of lgs. Accordingly, we change the model to

$$\lg s = ½\lg\gamma + ½\,\varphi\lg x + ½\lg\delta$$
$$= \alpha_0 + \alpha_1 \lg x + \eta$$

Once α_0 and α_1 are estimated by least squares, we can test the hypothesis $\varphi = 2$. In the present case, we obtain $\hat{\alpha}_0 = -3.526696$ and $\hat{\alpha}_1 = .9770021$, i.e., $\hat{\gamma} = 8.644717E-4$ and $\hat{\varphi} = 1.9540042$. With these results we cannot reject the hypothesis $\varphi = 2$, with 5% significance. Now, we apply the generalized least squares using $V = \mathrm{diag}(x_1^2 \ldots x_K^2)$. In order to test this model an estimatte of γ is required.

Taking as estimator that obtained from the function $s^2 = \delta \gamma x^2$, serious difficulties would arise regarding its probability distribution, thus it is better to estimate γ from the model $Y = X\beta + \varepsilon$. This estimator is independent of β^*, and its probability distribution is χ^2. From the data we obtain $\beta_0^* = .04377$, $\beta_1^* = .490858$, and $\gamma^* = 8.607E{-4}$. The close proximity to $\hat{\gamma} = 8.644717E{-4}$, resulting from the first approach, should be pointed out. We deal with genuine replications, so it is possible to test the straight line model with appropiate F-statistic. In the present case we may accept the model with 5% significance.

Finally, the probability boundaries for direct prediction of a further observation can be drawn, as it is known, from

$$Y_0 \in Y_0^* \pm t_{\alpha/2, \nu} \sqrt{(x_0^2 + v_0)}$$

By taking $\alpha = 5\%$ we obtain the confidence boundaries plotted in FIG. 1, where the effect of the variance increase with x is shown. FIG. 2 is a magnified detail of the region near the origin. The numerical values of the HV's parameters looked for are: limit of detection $Y_D = .1135$ mg $BaSO_4$ found, limit of identification $x_I = .2840$ mg SO_4^{2-} added. These results are to be compared with those reported by FT, .445 mg $BaSO_4$ found and 1.24 mg SO_4^{2-} added, respectively. As can be seen, the present approach gives limits which are about four times lower than those previously reported. A more detailed account of the statistical development outlined under heading 2. Confidence band using weighted least squares, can be found elsewhere (Polo y Pepió, 1986).

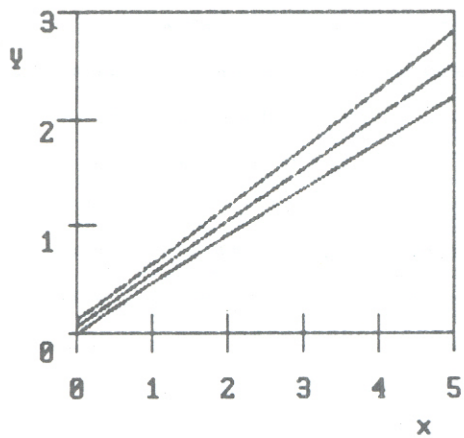

FIG.1. Regression of Y (mg $BaSO_4$ found) upon x (mg L^{-1} SO_4^{2-} added) with confidence boundaries due to heteroscedasticity.

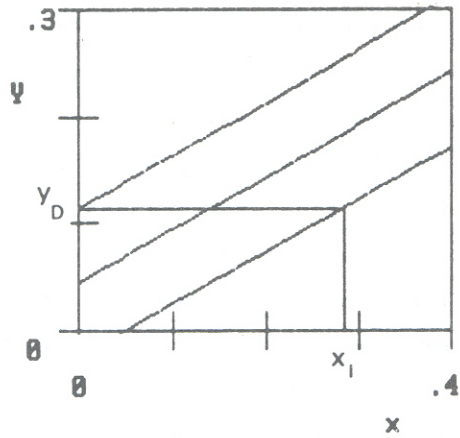

FIG.2. Magnified detail of FIG.1 showing the relationships among Limit of Detection, Y_D , Limit of Identification, x_I ,and confidence boundaries.

3. REFERENCES

Feigl, F., (1923). Tüpfel- und Farbreaktionen als mikrochemische Arbeitsmethoden. Mikrochemie, 1, 4-20.

Ferrús, R. and Torrades, F., (1985). Limit of Detection in Barium Sulphate Gravimetry for Water Analysis. Analyst, 110, 403-406.

Hubaux, A. and Vos, G., (1970). Decision and Detection Limits for Linear Calibration Curves. Anal. Chem., 42, 849-855.

Polo, C. and Pepió, M., (1986). Un Problema de Calibración con Heteroscedasticidad. I.I. 4/86. E.T.S.E.I.T.-U.P.C.

Tort-Martorell, X., (1985). Tesis Doctoral. E.T.S.E.I.B.-U.P.C.