

BSTT562 Project I

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1 Abstract

In this project, we want to reproduce the results presented in Table 3 Interlaboratory Data for Cadmium from Bhaumik and Gibbons [2005].

2 Introduction

A key characteristics of the data is its heteroscedasticity.

3 Data

This data is the experimental data for cadmium from an interlaboratory study conducted by Ford Motor Company (J. Phillips, personal communication). These data were generated as part of a blind interlaboratory study of laboratories that hold Michigan State Drinking Water Certifications for the parameters tested. Samples were prepared by an independent source, randomized, and submitted on a weekly basis over a 5-week period. Cadmium was analyzed by inductively coupled plasma atomic emissions spectroscopy using EPA method 200.7. The data set used for this example comprised five replicates at each of three concentrations (0, 20 and 100 $\mu g/L$) in each of the $q = 5$ laboratories. Using the first replicate from the first three laboratories as the new measurement (i.e., $q' = 3$), we would like to reproduce the results of point estimates, variances, confidence intervals and simulated confidence levels for the true concentrations in each of the three cases. The data is displayed as follows:

Table 1: Interlaboratory Data for Cadmium ($\mu g / L$)

| Lab | Replication | 0 | 20 | 100 |
|-----|-------------|--------|--------|---------|
| 1 | 1 | -3.000 | 10.000 | 92.000 |
| 1 | 2 | 4.000 | 20.000 | 100.000 |
| 1 | 3 | -4.000 | 17.200 | 97.800 |
| 1 | 4 | 3.000 | 24.000 | 100.000 |
| 1 | 5 | 3.100 | 19.100 | 109.000 |
| 2 | 1 | -0.060 | 17.815 | 90.455 |
| 2 | 2 | 0.010 | 17.305 | 87.610 |

| Lab | Replication | 0 | 20 | 100 |
|-----|-------------|---------|--------|---------|
| 2 | 3 | 0.115 | 16.570 | 85.550 |
| 2 | 4 | -0.055 | 17.360 | 89.925 |
| 2 | 5 | 0.340 | 18.120 | 90.070 |
| 3 | 1 | -7.400 | 27.100 | 107.400 |
| 3 | 2 | -2.100 | 19.400 | 108.100 |
| 3 | 3 | -11.400 | 9.000 | 83.800 |
| 3 | 4 | -11.100 | 10.500 | 81.900 |
| 3 | 5 | -1.400 | 19.300 | 94.200 |
| 4 | 1 | 1.000 | 21.000 | 96.000 |
| 4 | 2 | -2.126 | 16.049 | 90.650 |
| 4 | 3 | 0.523 | 16.082 | 89.388 |
| 4 | 4 | -2.000 | 17.000 | 91.000 |
| 4 | 5 | -0.551 | 15.489 | 85.867 |
| 5 | 1 | 0.000 | 18.000 | 91.000 |
| 5 | 2 | 0.000 | 19.000 | 101.000 |
| 5 | 3 | 0.000 | 19.000 | 102.000 |
| 5 | 4 | -1.000 | 18.700 | 92.700 |
| 5 | 5 | 0.038 | 19.790 | 99.884 |

4 The Model

To measure the true concentration of an analyte, x , a simple and straightforward method is to propose a linear calibration model as:

$$y = \alpha + \beta x + e \quad (1)$$

with normal assumption on errors. However because our data set has heteroscedastic variances, this simple linear models fails to explain the increasing measurement variation with increasing analyte concentration, which is also commonly observed in analytic data. On the other hand, a log-linear model, for example, $y = xe^\eta$, where η is a normal random variable with mean 0 and standard deviation σ_η also fails to explain the near-constant measurement variation of y for low true concentration level (x) Rocke and Lorenzato [1995]. To fix these two problems at the same time, Bhaumik and Gibbons [2005] proposed a log-normal model that combines both types of errors:

$$y_{ijk} = \alpha_i + \beta_i x_j e^{\eta_{ijk}} + e_{ijk}, \quad (2)$$

where y_{ijk} is the k th measurement at the j th concentration level in the i th laboratory, $i = 1, 2, \dots, q, j = 1, 2, \dots, r, k = 1, 2, \dots, N_{ij}$, x_j is the true concentration at the j th level, and α_i and β_i are the calibration parameters for the i th laboratory.

In this model the η_{ijk} 's represent proportional error at higher true concentrations, and we assume that the distributions of the proportional errors remain the same for all laboratories.

Note that for this particular model, when x is 0 or near 0, the model is reduced to:

$$\begin{aligned} y_{ijk} &= \alpha_i + \beta_j \times 0 \times e^{\eta_{ijk}} + e_{ijk} \\ y_{ijk} &= \alpha_i + e_{ijk} \end{aligned} \tag{3}$$

5 Analysis

We choose the Method of Moments to estimate the model parameters. The Method of Moments is straightforward and easy to implement when observations with lower concentrations are available, which happens to be the case with our Interlaboratory Data for Cadmium.

Why do we choose the Method of Moments: A good property of MOM: the estimates obtained by MOM are asymptotically efficient.

5.1 The Parameter Estimation Procedures (Using Data Separation Technique)

5.1.1 (Partial) Estimation Using Low-Concentration Observations

We estimate the variance σ_e^2 of the additive errors e_{ijk} 's (of the k th measurement at the j th concentration level in the i th laboratory, $i = 1, 2, \dots, q, j = 1, 2, \dots, r, k = 1, 2, \dots, N_{ij}$) that are present primarily at low-level concentrations and the calibration parameter α_i for the i th laboratory using low-concentration observations.

Assuming that observations corresponding to zero or near-zero are available. Let y_{i0k} be the k th measured concentration corresponding to the true low-level concentration from laboratory i and n_{i0} is the number of samples with true low-level concentrations submitted to laboratory i :

- (1) Estimate σ_e^2 by the variance of the observations with zero or near-zero concentrations (y_{i0k}) by

$$\hat{\sigma}_e^2 = \frac{1}{q} \sum_{i=1}^q \left(\frac{\sum_{k=1}^{n_{i0}} (y_{i0k} - \bar{y}_{i0})^2}{n_{i0} - 1} \right) \tag{4}$$

- (2) Estimate α_i from the observations with zero or near-zero concentrations (y_{i0k}) by

$$\hat{\alpha}_i = \frac{\sum_{k=1}^{n_{i0}} y_{i0k}}{n_{i0}} \tag{5}$$

5.1.2 (Partial) Estimation Using Higher-Concentration Observations

(1) Let $z_{ijk} = \frac{(y_{ijk} - \alpha_i)}{x_j}$ and $u_{ijk} = \frac{e_{ijk}}{x_j}$.

Using the estimate $\hat{\alpha}_i$ of α_i we compute the z_{ijk} 's by

$$\begin{aligned} y_{ijk} &= \alpha_i + \beta_i x_j e^{\eta_{ijk}} + e_{ijk} \\ y_{ijk} - \alpha_i &= \beta_i x_j e^{\eta_{ijk}} + e_{ijk} \\ \frac{y_{ijk} - \alpha_i}{x_j} &= \beta_i e^{\eta_{ijk}} + \frac{e_{ijk}}{x_j} \text{ (given } x'_j \text{ s have higher concentrations)} \\ z_{ijk} &= \beta_i e^{\eta_{ijk}} + \mu_{ijk} \\ \frac{z_{ijk}}{\beta_i} &= e^{\eta_{ijk}} + \frac{\mu_{ijk}}{\beta_i} \text{ (given } \beta_i \neq 0). \end{aligned} \tag{6}$$

(2) Let

$$\gamma = E(e^\eta) = e^{\sigma_\eta^2/2}, \quad \mu_{zi} = E(z_{ijk}), \quad \sigma_{zi}^2 = \frac{\sum_{j=1}^r \text{var}(z_{ijk})}{r}, \quad \sigma_\mu^2 = \frac{\sigma_e^2 \sum_{j=1}^r 1/x_j^2}{r} \tag{7}$$

Using equation (6) we can calculate

$$\frac{\mu_{zi}}{\beta_i} = \gamma \text{ and } \frac{\sigma_{zi}^2}{\beta_i^2} = (\gamma^4 - \gamma^2) + \frac{\sigma_\mu^2}{\beta_i^2}. \tag{8}$$

(3) Replacing γ by $\frac{\mu_{zi}}{\beta_i}$ in the second part of equation (8) we obtain the following equation:

$$\beta_i = \sqrt{\frac{\mu_{zi}^4}{\sigma_{zi}^2 - \sigma_\mu^2 + \mu_{zi}^2}} \text{ and } \sigma_\eta^2 = \frac{2 \sum_{i=1}^q \ln(\mu_{zi}/\beta_i)}{q}. \tag{9}$$

To estimate β_i and σ_η from equation (9), we need estimates of μ_{zi} , σ_{zi}^2 , and σ_μ^2 (the error variance of the model (6)).

(4) Let n_{ij} be the number of observations with higher concentrations collected from the i th laboratory for concentration level j and $n_i = \sum_{j=1}^r n_{ij}$, then

$$\begin{aligned} \hat{\mu}_{z_{ij}} &= \frac{\sum_{k=1}^{n_{ij}} z_{ijk}}{n_{ij}}, \quad \hat{\mu}_{z_i} = \frac{\sum_{j=1}^r \hat{\mu}_{z_{ij}}}{r}, \\ \hat{\sigma}_{z_i}^2 &= \frac{\sum_{j=1}^r \sum_{k=1}^{n_{ij}} (z_{ijk} - \hat{\mu}_{z_{ij}})^2 / (n_{ij} - 1)}{r}, \quad \hat{\sigma}_\mu^2 = \frac{\sum_{j=1}^r \hat{\sigma}_e^2 / x_j^2}{r} \end{aligned} \tag{10}$$

(5) Therefore We can calculate the estimates of the variance of the proportional error at higher true concentrations σ_η^2 and the calibration parameter β_i for the i th laboratory as

$$\hat{\beta}_i = \sqrt{\frac{\hat{\mu}_{z_i}^4}{\hat{\sigma}_{z_i}^2 - \hat{\sigma}_{\mu}^2 + \hat{\mu}_{z_i}^2}} \text{ and } \hat{\sigma}_{\eta}^2 = \frac{2 \sum_{i=1}^q \ln(\hat{\mu}_{z_i}/\hat{\beta}_i)}{q} \quad (11)$$

5.2 Point Estimation of X

Suppose that the same analyte with an unknown true concentration X is tested in q' independent laboratories, and that $Y_1, Y_2, \dots, Y_{q'}$ are the corresponding new observations. We want to compute a point estimate of X using the available information from each of the q' laboratories and then combine them.

6 Table/Discussion

References

- Dulal K Bhaumik and Robert D Gibbons. Confidence regions for random-effects calibration curves with heteroscedastic errors. *Technometrics*, 47(2):223–231, may 2005.
- David M. Rocke and Stefan Lorenzato. A two-component model for measurement error in analytical chemistry. *Technometrics*, 37(2):176–184, may 1995.