

Propagation of Error:

We suppose that X and Y are asymptotically normally distributed with means μ_X and μ_Y and variances σ_X^2 and σ_Y^2 covariance σ_{XY} respectively

Suppose that $f(x,y)$ is at least twice differentiable function from the plane to the line.

Let $\hat{\theta} = f(X,Y)$.

Then the approximate (asymptotic) probability distribution of $\hat{\theta}$ is normal with mean $f(\mu_X, \mu_Y)$ and variance

$$\frac{\partial f}{\partial X}(\mu_X, \mu_Y)^2 \sigma_X^2 + \frac{\partial f}{\partial Y}(\mu_X, \mu_Y)^2 \sigma_Y^2 + 2 \frac{\partial f}{\partial X}(\mu_X, \mu_Y) \frac{\partial f}{\partial Y}(\mu_X, \mu_Y) \sigma_{XY}.$$

Maximum Likelihood:

Let the data say which is the most likely value of variance.

Normal likelihood:

$$f(\mu, \sigma^2 | x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{1}{2} \frac{(x-\mu)^2}{\sigma^2}\right).$$

For multiple observations X_1, \dots, X_n we write the likelihood:

$$L(\mu, \sigma^2) = \prod_i f(\mu, \sigma^2 | x_i) .$$

Variance = $E(\text{score function})^2$.

Interpretation:

Cross Validation:

We suppose that we have n observations (possibly multivariate) Y_1, \dots, Y_n .

Let $\hat{Y} = g(Y_1, \dots, Y_n)$. We assume that g is a smooth function of the data (functional of the empirical distribution function.)

Let $\hat{Y}_{-i} = g(Y_1, \dots, Y_{i-1}, Y_{i+1}, Y_n)$.

Then the cross validated estimate of Mean Squared Prediction Error is:

$$\sum_i (Y_i - \hat{Y}_{-i})^2 / n.$$

The chemical counterpart is interlaboratory comparisons.....

Jackknife:

Let \bar{g} above be the sample average. Then

$$\hat{\theta}_i^* = ng(Y_1, \dots, Y_n) - (n-1)g(Y_1, \dots, Y_{i-1}, Y_{i+1}, Y_n).$$

Then for an arbitrary g let

$$\hat{\theta} = g(Y_1, \dots, Y_n)$$

$$\hat{\theta}_i^* = ng(Y_1, \dots, Y_n) - (n-1)g(Y_1, \dots, Y_{i-1}, Y_{i+1}, Y_n).$$

Then the Jackknife estimate of variance is $1/n$ times the sample variance of $\hat{\theta}_i^*$, $i=1, \dots, n$.

Modification: Use different number of deleted and use regression to get the rate.

The chemical counterpart is the blank correction

Monte Carlo Experiments:

Generate random data sets according to a reasonable model and use the sample mean square estimator to assess the errors.

The chemical counterpart is the use of standards to evaluate a chemical measurement method.

Bootstrap:

We suppose that we have n observations (possibly multivariate) Y_1, \dots, Y_n .

Write:

$$(Y_1, \dots, Y_n) = (\text{model}(1), \dots, \text{model}(n)) + (\varepsilon_1, \dots, \varepsilon_n).$$

Then for any estimator $\hat{\theta}$ do a Monte-Carlo experiment drawing errors from the calculated $(\varepsilon_1, \dots, \varepsilon_n)$. This is usually done with replacement

The chemical counterpart is the use a recycling recombination. We'll call it the chemical bootstrap. We will modify this by adding many different models.

Sampling Cases.

Bias Evaluation By Standard Addition.

We suppose that we have n observations (possibly multivariate) Y_1, \dots, Y_n .

Write:

$$(Y_1, \dots, Y_n) = (\text{model}(1), \dots, \text{model}(n)) + (\varepsilon_1, \dots, \varepsilon_n).$$

Then form estimates of $(\text{model}(1), \dots, \text{model}(n))$. Let's call them $\hat{\theta}(Y_1, \dots, Y_n)$ and form:

$$(Y_1^*, \dots, Y_n^*) = (Y_1, \dots, Y_n) + \hat{\theta}(Y_1, \dots, Y_n).$$

We then repeat the estimation process and see if

$$\hat{\theta}(Y_1^*, \dots, Y_n^*) - \hat{\theta}(Y_1, \dots, Y_n) = \hat{\theta}(Y_1, \dots, Y_n).$$

A Generalization of the jackknife:

We suppose that we have n observations (possibly multivariate) Y_1, \dots, Y_n .

Let $\hat{Y} = g(Y_1, \dots, Y_n)$. We assume that g is a smooth function of the data (functional of the empirical distribution function.)

Let $\hat{Y}_{-\{i,j,\dots\}} = g(Y_1, \dots, Y_{i-1}, Y_{i+1}, \dots, Y_{j-1}, Y_{j+1}, \dots, Y_n)$.

Suppose that n is large (say 100).

Then we compute the sample variance using all the

$\hat{Y}_{-\{i,j,\dots\}}$ that are missing 10 (an arbitrary number k) Y 's. We repeat the process using all the $\hat{Y}_{-\{i,j,\dots\}}$ that are missing 20, 30, 50 etc. (an arbitrary number k) Y 's. If the computing gets difficult then subsamples should be used.

Note that this can be used with the bootstrap also

Then we use regression to predict the variance for sample size n . For many estimates its variance

uses the formula c/n . We simply need to estimate c by regression. If we use m/n of our sample in the estimates $\hat{Y}_{-i,j,\dots}$ then the sample variance of the estimate is approximately $(1-m/n)$ times the variance of an estimate of a single $\hat{Y}_{-i,j,\dots}$.

We try finding the variance of the sample median using subsamples of size 300, 500, 700

ROW	C2	C3
1	0.536606	0.0033333
2	0.269747	0.0020000
3	0.140774	0.0014286

We get the formula $1.47\sigma^2/n$. The correct asymptotic answer is $(\pi/2)\sigma^2/n = 1.57\sigma^2/n$.

This trick can also be used to get a jackknife estimate of bias.

Principals for uncertainty evaluation:

1. Some of the information must come from outside of the experimental data: model, sampling scheme, sources of error list,...
2. If an estimator is a smooth function of the data (a smooth functional of the distribution function) then simulations can be helpful. This is the form of sensitivity analysis to the data.
3. The evaluation should be consistent (at least superficially.) This means that the evaluation should be done for more than one set of parameters. The results should make sense among parameter values. Parameters should include sample size and model parameters.

▣ ▶ For Statisticians to Evaluate Estimation Method

<input type="checkbox"/>	• Maximum Likelihood	Statistician	Statistics	No
<input type="checkbox"/>	• Propagation of error	Both	General Science	No
<input type="checkbox"/>	• Cross Validation	Both	Statistics	Int Co
<input type="checkbox"/>	• Jackknife (Use only subsamples)	Statistician	Statistics	
<input type="checkbox"/>	• Monte Carlo Experiments	Both	General Science	
<input type="checkbox"/>	• Bootstrap	Statistician	Statistics	Re ch bo
<input type="checkbox"/>	• Bias Evaluation by Standard Addition	Statistician	Chemistry	St Ac

▣ ▶ For Chemists to Evaluate Analytical Technique

<input type="checkbox"/>	• Standards	Scientist	General Science	
<input type="checkbox"/>	• Standard Addition	Scientist	Chemistry	Di