Relationship between Correlations of Repeated Measurements and Correlations of Relative Standard Deviation Estimates of These Measurements; Application to Proficiency Analytical Testing Program Silica and Asbestos Data

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Abstract

Proficiency test programs require laboratories to periodically determine (at successive times or rounds) the amount of a particular compound in test samples. Often, determinations by the same lab are correlated. When trends in the coefficient of variation (CV_t for determinations at time t), also known as relative standard deviation, of analysis determinations are estimated, the correlation between estimated CV_ts should be estimated. Taylor series are used to derive an approximation for this correlation in terms of the correlation between individual lab determinations. The approximation suggests that the correlation between estimated CV_ts is smaller than that between lab determinations. To assess the approximation's accuracy, results of a simulation study are given.

Next a model is presented for correlations of lab determinations over multiple rounds of the Proficiency Analytical Testing Program(PAT). By using the Taylor series approximation with estimates of average correlations of PAT lab determinations, this model provides estimated average correlations of PAT CV_t estimates. The form of the correlation is also developed for predicted CV_ts modeled as functions of the mean. A decision can then be made whether to adjust for correlations in modeling PAT CV_t data.

The formulas for correlations are applied to PAT asbestos and silica data, previously analyzed elsewhere [1,2]. Conclusions from these papers still hold, in general, even after adjustment for correlation, though the confidence intervals for comparisons of interest are wider after adjustment for correlation.

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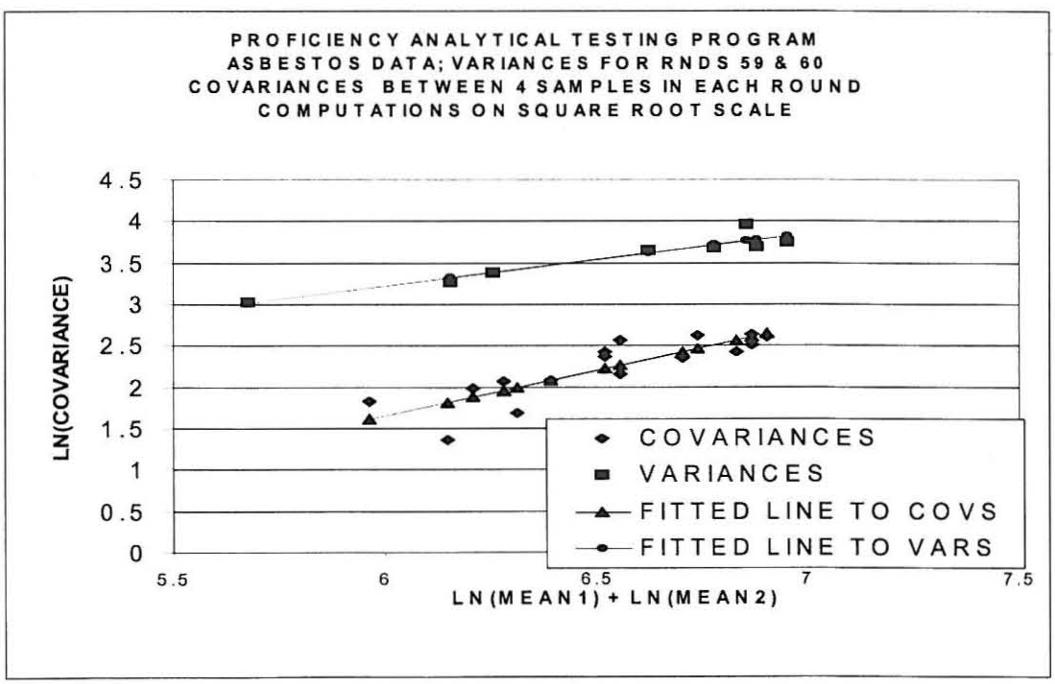
1) Introduction

In proficiency testing for analytical methods, participating laboratories at time t make determinations of the amount of analyte in test samples. At later times they are given different samples of the same analyte, and make new determinations. It is not uncommon that determinations by the same laboratory are correlated. If there is interest in studying the relative standard deviation (=CV=standard deviation/mean), also known as relative standard deviation, of the determinations over time, it is necessary to assess the correlation among the CVs. Although there may be substantial correlation between determinations by the same lab in different rounds, the correlation between the relative standard deviations of determinations in those two rounds is often much smaller.

The work presented here is organized as follows. In Section 2, a statistical model is presented for the form of the variances and covariances. Formulas for the correlation of the sample CV estimates from two different sample sets are given in Section 3. Simulation study results are provided in the next section. In Section 5 a model is suggested for the form of the covariances of determinations over a sequence of times. The consequences of this model for the width of confidence bands are shown, and illustrated with actual proficiency test data. The results given also provide corrections to CVs in a previous paper comparing bias and precision for analytical methods for analysis of silica. Section 6 uses results of Section 3 to obtain a formula for the correlation between CV estimates from different times when these estimates are smoothed values from each of these times. Additional corrections to the paper on silica[1] are provided for results concerning bias among silica methods. A summary of results is given in Section 7. This paper provides the needed corrections for the paper on PAT silica analyses, in three tables.

2) Statistical Model for Covariances and Variances

Figure 1



In 1972 researchers at the National Institute for Occupational Safety and Health (NIOSH) started the Proficiency Analytical Testing Program (PAT) to evaluate and improve the agreement of analyses obtained from several laboratories performing work for the Occupational Safety and Health Administration (OSHA). Today a much expanded program is administered by the American Industrial Hygiene Association (AIHA) to evaluate government and private laboratories conducting analysis of airborne substances in workplace air. Its purpose remains the evaluation of laboratory performance in the analysis of analytes such as asbestos, silica, metals, and organics. In this paper interest will be on using asbestos and silica data from PAT as examples.

In the Figure 1, a relationship can be observed between covariances and variances of test samples within the same round and the test sample means.

In the figure, ln(covariance) appears to be linearly related to [ln(mean1) + ln(mean2)] . Thus,

Covariance $\sim[(\text{mean1})(\text{mean2})]^a$ for some power a. (1)
Variance $\sim(\text{mean1})^a$

For lab i in sample s at time t,

$$y_{t,s,i}=\mu_{t,s} + e_{t,s,i} + w_{t,s,i} \,, \qquad (2)$$

where $w_{t,s,i}$ is independently distributed measurement error for lab i, $i=1,2,\ldots,n_t$, and $e_{t,s,i}$ is random error for differences among labs in sample s at time t, $s=1,\ldots,S$, and $\mu_{t,s}$ is the mean for sample s at time t. Normally distributed errors are assumed.

Assume, as in (1) above, that the variance and covariances are proportional to the means of the samples.

$$\begin{aligned} &\mathrm{Var}(y_{t,s,i})=[\, (r_t)^2 + (w_t)^2 \,]\, [\mu_{t,s}]^{2a(t)} \qquad (3) \\ &\mathrm{Cov}(y_{t,s,i}, y_{t,v,i}) = (r_t)^2[\mu_{t,s}]^{a(t)}\, [\mu_{t,v}]^{a(t)} \\ &\mathrm{Cov}(y_{t,s,i}, y_{t+1,r,i})=(b_{t,t+1})\, [\mu_{t,s}]^{a(t)}\, [\mu_{t+1,r}]^{a(t+1)}, \end{aligned}$$

where r_t^2, w_t^2 and $b_{t,t+1}$ are proportionality coefficients,and the subscript i indicates that covariances are for measurements by the same lab, and a(t) and a(t+1) are the appropriate powers at times t and t+1. The first covariance involves samples s and v in the same round; the second involves samples s and r from two consecutive rounds. Since the correlation is the ratio of the covariance between the two quantities of interest to the square root of the product of the two variances of these quantities, the corresponding correlations to the relations in (3) are:

$$Corr(y_{tsi}, y_{tvi}) = \frac{r_t^2}{r_t^2 + w_t^2} = \rho_t \qquad (4)$$

$$Corr(y_{tsi}, y_{t+1,ri}) = \frac{b_{t,t+1}}{[(r_t^2 + w_t^2)(r_{t+1}^2 + w_{t+1}^2)]^{0.5}} = \rho_{t,t+1}$$

3) Correlation between CV_ts in Different Rounds

For (u,v) normal [(3)], each with zero means,
$Cov[u^2,v^2]=2[Cov(u,v)]^2$, or $Corr[u^2,v^2]=[Corr(u,v)]^2$. (5)
An analogous result will now be obtained for
$Cov[(s_{t,s})^2,(s_{t+1,r})^2]$.

Let $n=n_t=n_{t+1}$ denote the number of labs participating at times t and t+1 , and suppose that the same labs are participating at each time. x_1 and x_2 are n-dimensional vectors of determinations, from the same n labs in consecutive rounds, t and t+1. Let **1** denote an n-dimensional column vector of 1s, and I_n the n-dimensional identity matrix. Let

$\mathbf{A}=\mathbf{I}_n - (1/n)\,\mathbf{1}\,\mathbf{1}'$,
$(s^2)_{ts}=[1/(n-1)]\,\mathbf{x}_1'\,\mathbf{A}\,\mathbf{x}_1$,
$(s^2)_{t+1,r}=[1/(n-1)]\,\mathbf{x}_2'\,\mathbf{A}\,\mathbf{x}_2$,
where $(s^2)_{ts}$ and $(s^2)_{t+1,r}$ are the sample variance estimates for their sample sets.
Let $\mathbf{x}'=[\ \mathbf{x}_1'\ \ \mathbf{x}_2'\ ]$, and

$$W=\begin{bmatrix} A & 0 \\ 0 & A \end{bmatrix}$$

$$2Cov(\mathbf{x}_1'\mathbf{A}\mathbf{x}_1,\ \mathbf{x}_2'\mathbf{A}\,\mathbf{x}_2)=Var(\mathbf{x}'\mathbf{W}\mathbf{x})-Var(\mathbf{x}_1'\mathbf{A}\mathbf{x}_1)-Var(\mathbf{x}_2'\mathbf{A}\,\mathbf{x}_2) \quad (6)$$

For x normally distributed with mean equal to mean (**x**) and variance-covariance matrix **C**[(3)] :

$$Var(\mathbf{x}'\mathbf{W}\mathbf{x})=2\{Trace[(\mathbf{WC})^2]\}+4[E(\mathbf{x}')]\mathbf{WCW}[\ E(\mathbf{x})], \quad (7)$$

where E(**x**) indicates the expected value of the variable **x**.

$$C=Var(x)=\begin{bmatrix} \mu_{t,s}^{2\alpha(t)}(r_t^2+w_t^2)I_n & \mu_{t,s}^{\alpha(t)}\mu_{t+1,r}^{\alpha(t+1)}b_{t,t+1}I_n \\ \mu_{t,s}^{\alpha(t)}\mu_{t+1,r}^{\alpha(t+1)}b_{t,t+1}I_n & \mu_{t+1,r}^{2\alpha(t)}(r_{t+1}^2+w_{t+1}^2)I_n \end{bmatrix}$$

$$WC = \begin{vmatrix} \mu_{t,s}^{2a(t)}(r_t^2 + w_t^2)A & \mu_{t,s}^{a(t)}\mu_{t+1,r}^{a(t+1)}b_{t,t+1}A \\ \mu_{t,s}^{a(t)}\mu_{t+1,r}^{a(t+1)}b_{t,t+1}A & \mu_{t+1,r}^{2a(t+1)}(r_{t+1}^2 + w_{t+1}^2)A \end{vmatrix}$$

$$(WC)^2 = \begin{vmatrix} Z1 & X \\ X & Z2 \end{vmatrix}$$

$$Z1 = [\mu_{ts}^{4a(t)}(r_t^2 + w_t^2)^2 + \mu_{ts}^{2a(t)}\mu_{t+1,r}^{2a(t+1)}b_{t,t+1}^2]A$$

$$Z2 = [\mu_{t+1,r}^{4a(t+1)}(r_{t+1}^2 + w_{t+1}^2)^2 + \mu_{t,s}^{2a(t)}\mu_{t+1,r}^{2a(t+1)}b_{t,t+1}^2]A$$

$$X = [\mu_{t,s}^{3a(t)}\mu_{t+1,r}^{a(t+1)}(r_t^2 + w_t^2) + \mu_{ts}^{a(t)}\mu_{t+1,r}^{3a(t+1)}(r_{t+1}^2 + w_{t+1}^2)]b_{t,t+1}A$$

Under the model given in equations (2) and (3), and since $E(\mathbf{x}_1'\mathbf{A})=0=E(\mathbf{x}_2'\mathbf{A})$,
$\mathrm{Var}(\mathbf{x}'\mathbf{W}\mathbf{x})=2\mathrm{Trace}[(\mathbf{WC})^2]$
$=2(n-1)\{[(r_t)^2+(w_t)^2]^2(\mu_{t,s})^{4a(t)} + [(r_{t+1})^2 + (w_{t+1})^2]^2(\mu_{t+1,r})^{4a(t+1)}\}$
$+ 4(n-1)[(\mu)_{t,s}]^{2a(t)}[\mu_{t+1,r}]^{2a(t+1)}(b_{t,t+1})^2$,

$\mathrm{Var}(\mathbf{x}_1'\mathbf{A}\mathbf{x}_1)=2(n-1)[\mu_{t,s}]^{4a(t)}[(r_t)^2+(w_t)^2]^2 =2(n-1)[\mathrm{Var}(y_{t,s,i})]^2$,
and analogously for $\mathrm{Var}(\mathbf{x}_2'\mathbf{A}\mathbf{x}_2)$. Thus, from (7),

$\mathrm{Cov}(\mathbf{x}_1'\mathbf{A}\mathbf{x}_1, \mathbf{x}_2'\mathbf{A}\mathbf{x}_2)=2(n-1)(b_{t,t+1})^2[(\mu_{t,s})^{2a(t)}][\mu_{t+1,r}]^{2a(t+1)}$.

$\mathrm{Cov}[(s_{t,s})^2,(s_{t+1,r})^2]=[2/(n-1)]\ \{(b_{t,t+1})^2[(\mu_{t,s})^{2a(t)}][(\mu)_{t+1,r}]^{2a(t+1)}\}$
$=[2/(n-1)]\ [\mathrm{Cov}(y_{t,s,i},y_{t+1,r,i})]^2$,

analogous to result (5).

From Taylor Series linearization, for a variable z_1,

$z_1^{0.5} \sim 0.5[E(z_1)]^{-0.5}[z_1-E(z_1)]$, and $\mathrm{Cov}(z_1^{.5},z_2^{.5}) \sim \{.25/[E(z_1)*E(z_2)]^{.5}\}\mathrm{Cov}(z_1,z_2)$.

Since $E[(s_{t,s})^2]=[[(r_t)^2+(w_t)^2](\mu_{t,s})^{2a(t)}$, we obtain

$$Cov(s_{t,s}, s_{t+1,r}) \sim \frac{b^2_{t,t+1}}{[(r_t^2 + w_t^2)(r_{t+1}^2 + w_{t+1}^2)]^{0.5}} \frac{[\mu_{t,s}^{a(t)}][\mu_{t+1,r}^{a(t+1)}]}{2(n-1)} = b_{t,t+1}\rho_{t,t+1} \frac{[\mu_{t,s}^{a(t)}][\mu_{t+1,r}^{a(t+1)}]}{2(n-1)} \tag{8}$$

Since $\mathrm{Var}(s_{t,s}) \sim \{.25/ E^2 [(s_{t,s})]\} \mathrm{Var} [(s_{t,s})^2]$
$\sim 0.25 \mathrm{Var} [(s_{t,s})^2] / E[(s_{t,s})^2] \sim 0.25 \mathrm{Var} [(s_{t,s})^2] / [\mathrm{Var}(y_{t,s,i})]$
$= 0.25(2)/(n-1) [\mathrm{Var}(y_{t,s,i})]$
$= \{1/[2(n-1)]\} [(r_t)^2 + (w_t)^2] [(\mu)_{t,s}]^{2a(t)}$,

$$\mathrm{Corr}(s_{t,s}, s_{t+1,r}) \sim [(b_{t,t+1})^2] / \{[(r_t)^2 + (w_t)^2][(r_{t+1})^2 + (w_{t+1})^2]\} = [\mathrm{Corr}(y_{t,s,i}, y_{t+1,r,i})]^2 \tag{9}$$

In many instances, analyses on the natural log scale will lead to approximately constant variance, in particular , if, on the original scale, a(t)=a(t+1)=1. In such instances, the standard deviation of the log-transformed data $\sim s_{t,s}$, and the above result applies to $\hat{cv}_{t,s} = s_{t,s}/\bar{y}_{t,s}$. If CVs are used directly, then we can obtain an analogous result as follows.

$\hat{cv}_{t,s} = s_{t,s}/\bar{y}_{t,s}$, and $\mathrm{Var}(\hat{cv}_{t,s}) \sim \{(CV_t)^2/[2(n-1)]\}\{1 + 2 (CV_t)^2\}$, from [4].

$\mathrm{Cov}(\bar{y}_{t,s}, \bar{y}_{t+1,r}) = (1/n) (b_{t,t+1})[(\mu_{t,s})^{a(t)} (\mu_{t+1,r})^{a(t+1)}]$

$s_{t+1,r}$ is statistically independent of both $\bar{y}_{t,s}$ and $\bar{y}_{t+1,r}$, and an analogous result applies to $s_{t,s}$. This follows, since for a normally distributed vector x with Covariance matrix V, the quadratic form $x'W_2 x$ and vector Ex are statistically independent if $EV W_2=0$ [3].

$$W_2 = \begin{bmatrix} 0 & 0 \\ 0 & A \end{bmatrix} \quad E = \begin{bmatrix} 1' & 0' \\ 0' & 1' \end{bmatrix} \quad V = \begin{bmatrix} aI & bI \\ bI & cI \end{bmatrix} \quad EV = \begin{bmatrix} a1' & b1' \\ b1' & c1' \end{bmatrix} \quad EVW_2 = \begin{bmatrix} 0' & b1'A \\ 0' & c1'A \end{bmatrix}$$

$\mathbf{W_2}$ is a (2n)x(2n) matrix, each **0** in $\mathbf{W_2}$ is an (nxn) matrix of 0s, **E** is a 2x(2n) matrix, in which 1' denotes an n-dimensional row vector of 1s and **0'** an n-dimensional row vector of 0s. Thus, $\mathbf{x' W_2 x} = (n-1) (s_{t+1,r})^2$ and $E\mathbf{x} = (n\, \bar{\mathbf{y}}_{t}, n\, \bar{\mathbf{y}}_{t+1})'$. In the covariance matrix **V** each **I** is an n-dimensional identity matrix, $a=[(r_t)^2 + (w_t)^2] [(\mu)_{ts}]^{2a(t)}$, $c=[(r_{t+1})^2 + (w_{t+1})^2] [(\mu)_{t+1,r}]^{2a(t+1)}$, $b=(b_{t,t+1}) [(\mu)_{ts}]^{a(t)} [(\mu)_{t+1,r}]^{a(t+1)}$, as in eqn (3). Since we are only looking at one sample set within each round, the blocks of **V** are diagonal matrices. Since **1'A**=0, **EV** $\mathbf{W_2}$ =0, and the results follows.

From Taylor series approximation:
$\hat{cv}_{t,s} - E(\hat{cv}_{t,s}) \sim 1/E(\bar{y}_{t,s})[s_{t,s} - E(s_{t,s})] + [-E(s_{t,s})/E^2(\bar{y}_{t,s})][\bar{y}_{t,s} - E(\bar{y}_{t,s})] = a\, [s_{t,s} - E(s_{t,s})] + b\, [\bar{y}_{t,s} - E(\bar{y}_{t,s})]$,
Analogously, $\hat{cv}_{t+1,r} - E(\hat{cv}_{t+1,r}) \sim c\, [s_{t+1,r} - E(s_{t+1,r})] + d\, [\bar{y}_{t+1,r} - E(\bar{y}_{t+1,r})]$.

$\mathrm{Cov}(\hat{cv}_{t,s}, \hat{cv}_{t+1,r}) \sim ac\mathrm{Cov}(s_{t,s}, s_{t+1,r}) + bd\mathrm{Cov}(\bar{y}_{t,s}, \bar{y}_{t+1,r})$ (where the statistical independence between the standard deviation estimates and the means is applied)

$= 1/[E(\bar{y}_{t,s})E(\bar{y}_{t+1,r})]\mathrm{Cov}(s_{t,s} s_{t+1,r}) + [-E(s_{t,s})/E^2 (\bar{y}_{t,s})][-E(s_{t+1,r})/E^2 (\bar{y}_{t+1,r})]\mathrm{Cov}(\bar{y}_{t,s}, \bar{y}_{t+1,r})$, From equation (8) the first addend can be written as:

$b_{t,t+1}\{ \rho_{t,t+1} [(\mu_{t,s})^{a(t)-1} (\mu_{t+1,r})^{a(t+1)-1}]\}/[2(n-1)]$

$=\rho_{t,t+1} /[2(n-1)] \{b_{t,t+1} [(\mu_{t,s})^{a(t)-1} (\mu_{t+1,r})^{a(t+1)-1}]\}$

$=\rho_{t,t+1}/[2n-2]\{b_{t,t+1}/\{[(r_t)^2+(w_t)^2]^{.5}[(r_{t+1})^2+ (w_{t+1})^2]^{.5}\}[(r_t)^2+(w_t)^2]^{.5}[(r_{t+1})^2+ (w_{t+1})^2]^{.5} [(\mu_{t,s})^{a(t)-1} (\mu_{t+1,r})^{a(t+1)-1}]$

$=\rho_{t,t+1}/[2n-2]\{\rho_{t,t+1} CV_{t,s} CV_{t+1,r} \}$,

and the second addend can be written as:

$\{ [(r_t)^2+(w_t)^2]^{.5}(\mu_{t,s})^{a(t)} [(r_{t+1})^2 + (w_{t+1})^2]^{.5}(\mu_{t+1,r})^{a(t+1)}\}/ [(\mu_{t,s})^2(\mu_{t+1,r})^2]\} \{(1/n) (b_{t,t+1})[(\mu_{t,s})^{a(t)}(\mu_{t+1,r})^{a(t+1)}]\}$

$=[b_{t,t+1}/n]\{ [(r_t)^2+(w_t)^2]^{.5}/ (\mu_{t,s})^{2-2a(t)} \}\{ [(r_{t+1})^2 + (w_{t+1})^2]^{.5} /(\mu_{t+1,r})^{2-2a(t+1)}\}$

$=(1/n)b_{t,t+1}/\{ [(r_t)^2+(w_t)^2]^{.5} [(r_{t+1})^2 + (w_{t+1})^2]^{.5}\}\{ [(r_t)^2+(w_t)^2]/ (\mu_{t,s})^{2-2a(t)} \}\{ [(r_{t+1})^2 + (w_{t+1})^2] /(\mu_{t+1,r})^{2-2a(t+1)}\}$

$=(1/n)\rho_{t,t+1} (CV_{t,s})^2 (CV_{t+1,r})^2$,

where application is made of the following relation, based on equations (3):

$$CV^2_{t,s} = \{[(r_t)^2 + (w_t)^2] [\mu_{t,s}]^{2a(t)} / \mu_{t,s}{}^2\} = [(r_t)^2 + (w_t)^2] /[\mu_{t,s}]^{2-2a(t)}$$

Thus, $Cov(\hat{cv}_{t,s},\hat{cv}_{t+1,r}) \sim \rho_{t,t+1} /[2n-2]\{\rho_{t,t+1} CV_{t,s}CV_{t+1,r} + [2(n-1)/n](CV_{t,s})^2 (CV_{t+1,r})^2\}$

$\sim\rho_{t,t+1} /[2n-2]\{\rho_{t,t+1} CV_{t,s}CV_{t+1,r} + 2(CV_{t,s})^2 (CV_{t+1,r})^2\}$,

for large n. The natural logs of the sample CVs can also be used in subsequent analyses. Again by Taylor series linearization, it can be shown that since $\{\ln(\hat{cv}_t)-E \ln(\hat{cv}_t)]\} \sim [\hat{cv}_t- E(\hat{cv}_t)]/ E(\hat{cv}_t)$,

$Cov[\ln(\hat{cv}_{t,s}),\ln(\hat{cv}_{t+1,r})] \sim Cov(\hat{cv}_{t,s}, \hat{cv}_{t+1,r})/[E(\hat{cv}_{t,s})E(\hat{cv}_{t+1,r})]$

$\sim\rho_{t,t+1} /[2n-2]\{\rho_{t,t+1} + 2CV_{t,s} CV_{t+1,r}\}$

From Taylor series linearization, $Var[\ln(\hat{cv}_t)] \sim [1 + 2CV^2_t]/(2n-2)$.

Dividing the covariance expression by the square root of the product of the variances yields:

$Corr [\ln(\hat{cv}_{t,s}),\ln(\hat{cv}_{t+1,r})]\sim$

$$\rho_{t,t+1}\frac{[\rho_{t,t+1}+2CV_{t,s}CV_{t+1,r}]}{[(1+2CV^2_{t,s})(1+2CV^2_{t+1,r})]^{0.5}} \qquad (10)$$

$$<\rho_{t,t+1}$$

for $CV_{t,s}$ and $CV_{t+1,r}$ not too large,

Note that $\ln(\hat{cv}_{t,s})$ is of interest, since in the analysis of $\ln(\hat{cv}_{t,s})$, $var[\ln(\hat{cv}_{t,s})]\sim1/(2n-2)$, which can be used for weighting in least squares analysis.

4.) Simulation Studies to Check Formulas for Correlations

Since the derivation of equation (10) involves several approximations, via Taylor series linearization, we check the quality of the approximations by simulation studies. For two jointly normally distributed variables y_1 and y_2, with $\rho= Corr(y_1,y_2)$, we may write [4]:

$y_1=\mu_1 + \rho\ [Var(y_1)/Var(y_2)]^{.5}(y_2- \mu_2) + [(1- \rho^2)\ Var(y_1)]^{.5}\ \delta_1$,

for $\delta_1 \sim N(0, 1)$ and independent of y_2, $\mu_i=E(y_i)$, and $Var(y_i)$ denotes the variance of y_i, i=1 or 2.

Table I: Results of Simulation Study

A	B	C	D	E	F	G	H
CORR	CV_1 μ_1=30	CV_2 μ_2=20	EXP #	CORR SAMP MEANS	CORR LN(CV)	PRED CORR LN(CV)	|F-G|
0.20	0.20	0.20	1	0.202	0.0489	0.0519	0.003
			2	0.204	0.0594	0.0519	0.0075
0.40	0.40	0.40	1	0.406	0.218	0.218	0
			2	0.399	0.226	0.218	0.008
0.30	0.20	0.30	1	0.290	0.111	0.112	0.001
			2	0.305	0.107	0.112	0.005
0.30	0.267	0.40	1	0.312	0.127	0.125	0.002
			2	0.303	0.120	0.125	0.005

Let $CV_1=[Var(y_1)]^{.5}/\mu_1$, and similarly for CV_2, and $\delta_2 \sim N(0, 1)$, statistically independent of δ_1. Results in Table I are produced by the following simulated variables:

$$y_2 = \mu_2 + [\mu_2 CV_2]\delta_2 \qquad (11)$$
$$y_1 = \mu_1 + \rho[\mu_1 CV_1/\mu_2 CV_2](y_2 - \mu_2) + [1-\rho^2]^{0.5}\mu_1 CV_1 \delta_1$$

The statistically independent random variables (δ_1,δ_2) are generated via the "Call RANNOR" subroutine in SAS[5]. By specifying ρ, μ_1, μ_2, CV_1, and CV_2, we obtain the correlated pairs (y_1, y_2). For simulations, we chose μ_1=30 and μ_2=20, both in the range of the data studied. In each study 300 groups of 100 sets of 200 generated pairs were studied.

In the column G in the above table are the correlations based on equation (10), and in column F are the correlations of $\hat{cv}$ from the simulation based on equations (11). The results agree well. No absolute difference exceeds 0.008. (Column H)

5) Model for Effect of Correlation between Rounds

Assume constant correlation between times t,..,t+T-1, which constitute a period of interest. For lab i,

$Cov(y_{t,s,i},y_{t+k,r,i})=\rho[Var(y_{t,s,i})Var(y_{t+k,r,i})]^{.5}$, if no changes in lab
$= 0$, if change.

A change could denote, for instance, a change in equipment or personnel. If there is no change, the model specifies that the correlations between lab determinations are the same whether the rounds are consecutive or non-consecutive. Let f= probability of a change from one round to the next, and let $\bar{y}_{t,s}$ denote the average value of lab determinations on sample s at time t, and analogously for $\bar{y}_{t+1,r}$. It follows that:

$\text{Corr}(\bar{y}_{t,s},\bar{y}_{t+1,r}) \sim (1-f)\ \rho.$ (12)

$\text{Corr}(\bar{y}_{t,s},\bar{y}_{t+k,r}) \sim \rho(1-f)^k$, for rounds k time units apart, and

From (10), $\text{Corr}[\ln(\hat{cv}_{t,s}), \ln(\hat{cv}_{t+k,r})] \sim$

$$\frac{[(1-f)^k\rho][(1-f)^k\rho + 2CV_{t,s}CV_{t+k,r}]}{[(1+2CV_{t,s}^2)(1+2CV_{t+k,r}^2)]^{0.5}} \qquad (13)$$

Suppose that at times t and (t+1) there are $n_{t,t+1}$ labs participating in both rounds, and m_t additional labs at time t and m_{t+1} that participate at time (t+1). Thus,

$\text{Cov}(\bar{y}_{t,s}, \bar{y}_{t+1,r}) = 1/[(n_{t,t+1}+m_t)(n_{t,t+1}+m_{t+1})]\Sigma_{i=1,\ldots,n} \text{Cov}(y_{t,s,i}, y_{t+1,r,j})$,or

$$Cov(\overline{y_{t,s}},\overline{y_{t+1,r}}) = \frac{1}{[n_{t,t+1}+m_t][[n_{t,t+1}+m_{t+1}]} n_{t,t+1}[Corr(y_{t,s,i},y_{t+1,r,j})][Var(y_{t,s,i})Var(y_{t+1,r,j})]^{0.5}$$

For appropriately chosen β and g between 0 & 1,

$\text{Cov}(\bar{y}_{t,s},\bar{y}_{t+1,r}) \sim \beta g^{k-1}\ [\text{Corr}(y_{t,s,i},y_{t+1,r,i})][\text{Var}(y_{t,s,i})\text{Var}(y_{t+1,r,i})]^{.5}$.

Note that the product of β and [average value of $(n_{t+1}n_t)^{0.5}$] gives the approximate fraction of labs that participate on consecutive rounds. Denote this quantity by β′. Then,

$\text{Corr}(\bar{y}_{t,s},\bar{y}_{t+k,r}) \sim \rho(1-f)^k g^{k-1}\ \{\beta[\text{ average value of } (n_{t+1}n_t)^{0.5}]\} = \rho(1-f)^k g^{k-1}\beta' = \rho'_{t,t+k}$

We then use the above correlation between the means $\bar{y}_{t,s}$ and $\bar{y}_{t+k,r}$ as an estimate of the correlation between $y_{t,s,i}$ and $y_{t+k,r,i}$ to obtain, from (10):

$\text{Corr}[\ln(\hat{cv}_{t,s}), \ln(\hat{cv}_{t+k,r})] \sim$ (14)

$$\rho'_{t,t+k}\frac{[\rho'_{t,t+k} + 2CV_{t,s}CV_{t+k,r}]}{[(1+2CV_{t,s}^2)(1+2CV_{t+k,r}^2)]^{0.5}}$$

In using the above form for $\rho'_{t,t+k}$, we note that if the same labs participate in both rounds t and t+k, the formula is exact, since the correlation between the lab means at each time is the same as that between the individual labs.

From the above results, the variance of the mean value of $\bar{y}_{t,s}$ in the period of interest (time=t,...t+T-1) is:
Variance [mean($\bar{y}_{t,s}$, for all T times in the period)] $= \sigma^2/(nT) + [2/(T^2)]\Sigma_{i=1,...,T-1}(i)(\rho'_{t,t+T-i}/n)\sigma^2$.
Since the variance of the mean($\bar{y}_{t,s}$) under independence is $\sigma^2/(nT)$, the ratio of the two variances is

$$\sim\{1+[2/T]\Sigma_{i=1,...,T-1}(i)\,\rho'_{t,t+T-i}\}^{.5}. \quad (15)$$

For $\ln(\hat{cv}_{t,s})$, the corresponding ratio is:

$$\sim\{1+[2/T]\Sigma_{i=1,...,T-1}(i)[\rho'_{t,t+T-i}][\rho'_{t,t+T-i}+2\,CV_{t,s},CV_{t+T-i,r}]\}^{.5}. \quad (16)$$

We show below the multiplicative increase in the standard deviation of the average $\bar{y}$ or the average $\hat{cv}$ from 20 consecutive rounds, when the model allowing for correlation is compared to the independence model.

Table II: Increases in Standard Deviation due to Correlation

	Average Value ($\bar{y}_{t,s}$)		(β'=g=0.95) Equation (15)	Average ln(CV) (using CV=0.25) (β'=g=0.95) Equation. (16)		
ρ	(1-f)					
	0.5	0.7	0.9	0.5	0.7	0.9
0.05	1.04	1.08	1.18	1.01	1.01	1.03
0.15	1.12	1.23	1.48	1.02	1.05	1.12
0.25	1.19	1.36	1.73	1.04	1.09	1.23
0.35	1.25	1.48	1.94	1.07	1.15	1.37
	Average Value ($\bar{y}_{t,s}$)		(β'=0.83;g=0.97) Equation (15)	Average ln(CV) (using CV=0.38) (β'=0.83; g=0.97) Equation. (16)		
ρ	(1-f)					
	0.7	0.8	0.9	0.7	0.8	0.9
0.05	1.07	1.11	1.17	1.02	1.04	1.06
0.10	1.14	1.21	1.32	1.05	1.07	1.12
0.15	1.21	1.30	1.45	1.08	1.12	1.19
0.20	1.27	1.39	1.58	1.11	1.16	1.26
0.25	1.33	1.47	1.69	1.14	1.21	1.33
0.30	1.38	1.54	1.80	1.17	1.25	1.41
0.35	1.45	1.64	1.93	1.20	1.31	1.50
0.40	1.50	1.71	2.03	1.24	1.36	1.58

If σ^2 were known, and if the factor in the above table is 1.25, say, then the upper and lower confidence limits for the mean value are each 25% further from the sample mean than when there is no correlation. Multipliers are much smaller for $\ln(\hat{cv}_t)$ than for ($\bar{y}_t$). Ignoring correlation can lead to underestimation of the variance of the mean, whether of average $\bar{y}$ or average $\hat{cv}$. With real data σ^2 is not known, but is estimated from the data, and the estimated value is used in calculating confidence limits. This estimate is made via weighted least squares, and the ratios in table II do not indicate the ratios of confidence interval width because the ratio of the standard deviation from unweighted least squares compared to that from weighted least squares will not, in general, be 1.

In one kind of proficiency test study (say, study type A) the aim might be to obtain an estimate of the mean for a period. The PAT asbestos data provide an example of study type A. Results for a subset of the rounds are presented here. The rounds were divided into three groups of 10: 33-42, 56-65, and 76-85. For each of these groups the table below presents the average correlation between rounds as a function of the difference k between their round numbers and the average within round correlation for determinations by the same round. All results are based on data transformed to the square root scale to better attain normality.

Table III: **Example Data: PAT Asbestos Data**

Results on Square Root Scale:

Time Period (Rounds)	Est. Avg. Within Corr	Est. Corr. Between Rnds (t,t+k)				Pooled $\hat{cv}$	Avg. # Labs	1-f	β'^	g
		K=1	2	3	4					
33-42	0.72	0.43	0.35	0.35	0.29	0.35	85	0.91	0.88	0.96
56-65	0.65	0.29	0.21	0.17	0.15	0.22	181	0.78	0.96	0.98
76-85	0.61	0.24	0.20	0.14	0.11	0.22	393	0.82	0.92	0.96
AVERAGE: **0.66**		**0.32**	**0.25**	**0.22**	**0.18**	**0.26**	**220**	**0.84**	**0.92**	**0.97**

^ $\beta'=\beta$(average value of the square root of $n_t n_{t+1}$). See text preceding eq(14).

The average correlation within rounds~0.66. The average ratio Corr(k+1)/Corr(k) is 0.84~(1-f). Since (1-f) ρ=[average correlation for k=1]= 0.32, and (1-f)~0.84 , therefore, ρ~0.32/0.84=0.38. The average $\hat{cv}$~ 0.26. From the data, β'~0.92 and g~0.97. Since β and g are greater than .8 and .9, respectively, we think (14) gives an acceptable approximation for the correlations. From equation (14), the correlation of $[\ln(\hat{cv}_t),\ln(\hat{cv}_{t+1})]$~0.11, a considerable reduction from 0.3. Correlations for $[\ln(\hat{cv}_t),\ln(\hat{cv}_{t+k})]$ for various k values are:

Table IV: Correlations for $[\ln(\hat{cv}_t),\ln(\hat{cv}_{t+k})]$

k=1	k=2	k=3	k=4	k=5	k=6	k=7	k=8
0.111	0.079	0.057	0.041	0.030	0.022	0.017	0.013

An alternative kind of proficiency study (say, study type B) might compare several analytical methods, each participating lab choosing one method from among these methods. Although labs using different methods in the same round are not correlated, those using the same method from round to round could produce correlated results. If the CVs of the methods were to be compared for some period of time, the same problem that was discussed above would arise. The response function might be $v_t = \ln(CV_1) - \ln(CV_2)$ for each round of interest. The results would be similar to those for Study A, except that all variances are multiplied by 2, since v_t is a difference of two statistically independent variables. Since most labs did not change methods from one round to the next, covariances between rounds were also the sum of the individual between round method covariances. An example of Study B is the PAT silica proficiency test data[6]. For silica there are three major analytical methods, each used on each round of the program. Statistical analyses of either differences between the CVs of these methods or of the mean determinations by these methods are of interest, as well as how these differences have changed over time. All determinations were treated as approximately normally distributed on the original scale.

Table V:Results for the Silica Analytical Methods

Time Period (Rounds)	Method	Est. Corr. Within Round	Estimated Correlation between Rounds				Pooled $\hat{cv}$	Avg. # Labs	1-f	β'^	g
			k=1	k=2	k=3	k=4					
31-40*	CO	0.47	0.24	0.13	0.11	0.14	0.61	31	0.66	0.77	0.96
31-40	XRD	0.51	0.13	0.26	0.23	0.17	0.39	16	0.63	0.74	0.95
51-60	CO	0.55	0.25	0.28	0.22	0.20	0.42	35	0.80	0.88	0.97
51-60	IR	0.66	0.36	0.33	0.25	0.31	0.36	17	0.86	0.87	0.98
51-60	XRD	0.59	0.32	0.27	0.27	0.30	0.34	41	0.94	0.88	0.98
81-90	CO	0.47	0.20	0.24	0.21	0.21	0.32	30	0.86	0.79	0.98
81-90	IR	0.52	0.18	0.21	0.17	0.21	0.26	28	0.96	0.89	0.99
81-90	XRD	0.69	0.181	0.151	0.23	0.089	0.25	59	0.69	0.89	0.99
AVGS		0.56	0.23	0.23	0.21	0.20	0.37	32	0.80	0.84	0.98

*Too few infrared labs in rounds 31-40 to do computations.

^ $\beta' = \beta$(average value of the square root of $n_t n_{t+1}$). See text preceding eq(14).

The factor (1-f)~0.80 is the average value over methods within time period and over all three time periods. Estimates were based on averages of ratios of correlations from successive rounds. For these data the interest was in comparing both CVs and means of the three methods. For the CVs, a minimum and maximum loading were chosen from each round at which the CV was used for comparing the corresponding CVs of the three methods. The average correlation $\rho(1-f)$ (average for k=1) is 0.23, which results in an estimate of ρ as 0.29. Since the average CV was 0.37 the estimated correlation for the CVs on successive rounds was about 0.071. Since β' and g were greater than .8 and .9, respectively, we think (14) gave an acceptable approximation for the correlations. Only for the infrared method in rounds 31-40 was there a problem, since the number of labs participating increased from 2 to over 15 during that time. We will ignore this problem here. Correlations for various values of k are given in the table below:

Table VI: Correlations for $[\ln(\hat{cv}_t),\ln(\hat{cv}_{t+k})]$

k=1	k=2	k=3	k=4	k=5	k=6	k=7	k=8
0.071	**0.051**	**0.037**	**0.027**	**0.020**	**0.015**	**0.011**	**0.009**

For periods of length 20 rounds, for $\rho \sim 0.3$ and $(1-f)\sim0.8$, the standard deviation of the estimated average value of the CV increased by about 1.25, according to the Table II above. The original results, as given in Table III of reference (6), have been corrected to take the correlation of determinations into account. The corrected results are shown in the appendix, as Table A1. Although the increase in variance due to correlation makes many of the lower confidence limits closer to 1, the main conclusion remains the same– that the colorometric method, for periods 5,7, and 8, had greater variability than the two other methods.

The comparison of means required statistical adjustment of the data, and the consequences of correlation for these analyses are discussed in the next section.

These results are intended to give some idea of the consequences of correlations in lab determinations between rounds. If smoothing is done within each time period, the results may differ, and a weighted analysis may also produce deviations from the results shown here. Weighted least squares is the best approach in working with such data.

6.) Using Adjusted Values when Loadings Change between Rounds

Suppose that ln(sample $\hat{cv}$) in round t is a linear or quadratic function of the mean $\bar{y}$. What is the correlation of predicted values from successive rounds?

From the s determinations at each time t form an S-dimensional vector $\mathbf{v}_t$ of $\ln(\hat{cv})$s. The predicted CV at loading z is $\mathbf{x}'(\mathbf{X}_t'\mathbf{X}_t)^{-1}\mathbf{X}_t'\,\mathbf{v}_t$, for $\mathbf{x}'=(1\ z)$, say, where $\mathbf{X}_t$ is the design matrix for fitting the linear function of average measurement $\bar{\mathbf{y}}$.

First, we need $\mathrm{Cov}[\,\mathbf{x}'(\mathbf{X}_t'\mathbf{X}_t)^{-1}\mathbf{X}_t'\,\mathbf{v}_t\,,\mathbf{x}'(\mathbf{X}_{t+1}'\mathbf{X}_{t+1})^{-1}\mathbf{X}_{t+1}'\,\mathbf{v}_{t+1}]$
Let $c=\mathrm{Cov}[\,\ln(\hat{cv}_{t,s}),\ln(\hat{cv}_{t+1,r})]$. Since, by Taylor series,
$\mathrm{Var}[\,\ln(\hat{cv}_{t,s})]\sim 1/(2n-2)[1+2(CV_{t,s})^2\,]$, equation (14) yields

$$c\sim\frac{1}{2\sqrt{(n_t-1)(n_{t+k}-1)}}\rho'_{t,t+1}[\rho'_{t,t+1}+2CV_{t,s}CV_{t+1,r}],$$

If the CV values are small relative to between-round correlation of individual lab determinations, then c is approximately constant and $\mathrm{Cov}(\mathbf{v}_t, \mathbf{v}_{t+1}) = c\mathbf{1}\mathbf{1}'$, $\mathbf{1}$ an S-dimensional vector of 1s. Because the first column of $\mathbf{X}_t$ is the vector $\mathbf{1}$ and

$$(\mathbf{X}_t'\mathbf{X}_t)^{-1}\mathbf{X}_t'\mathbf{1} = (1\ 0)', \text{ therefore, } \mathrm{Cov}\,[\mathbf{x}'(\mathbf{X}_t'\mathbf{X}_t)^{-1}\mathbf{X}_t'\,\mathbf{v}_t\,,\ \mathbf{x}'(\mathbf{X}_{t+1}'\mathbf{X}_{t+1})^{-1}\mathbf{X}_{t+1}'\,\mathbf{v}_{t+1}] \sim c. \tag{17}$$

Even if $\mathbf{X}_t$ and $\mathbf{X}_{t+1}$ are formed from different average measurements, the form of the covariance is unchanged.

Second we need $\mathrm{Var}\,[\mathbf{x}'(\mathbf{X}_t'\mathbf{X}_t)^{-1}\mathbf{X}_t'\mathbf{v}_t]$, for which we need a result analogous to equation (10) for $d = \mathrm{Cov}[\ln(\hat{cv}_{t,s}), \ln(\hat{cv}_{t,v})] \sim$

$$\frac{1}{2n-2}\rho_t[\rho_t + 2CV_{t,s}CV_{t,v}],$$

where ρ_t has been defined in equation (4). d is approximately constant if $2CV_{t,s}CV_{t,v}$ is small relative to the within round correlation ρ_t.

$\mathrm{Var}\,[\mathbf{x}'(\mathbf{X}_t'\mathbf{X}_t)^{-1}\mathbf{X}_t'\mathbf{v}_t] = [\mathbf{x}'(\mathbf{X}_t'\mathbf{X}_t)^{-1}\mathbf{X}_t']\,\mathrm{Var}(\mathbf{v}_t)\,[\mathbf{x}'(\mathbf{X}_t'\mathbf{X}_t)^{-1}\mathbf{X}_t']' \sim [\mathbf{x}'(\mathbf{X}_t'\mathbf{X}_t)^{-1}\mathbf{X}_t']\,((d\mathbf{1}\mathbf{1}' + \{\mathrm{Var}[\ln(\hat{cv}_{t,s})] - d\}I_S))[\mathbf{x}'(\mathbf{X}_t'\mathbf{X}_t)^{-1}\mathbf{X}_t']'$,

$= [\mathbf{x}'(\mathbf{X}_t'\mathbf{X}_t)^{-1}\mathbf{X}_t']\,(d\mathbf{1}\mathbf{1}')[\mathbf{x}'(\mathbf{X}_t'\mathbf{X}_t)^{-1}\mathbf{X}_t']' + [\mathbf{x}'(\mathbf{X}_t'\mathbf{X}_t)^{-1}\mathbf{X}_t']\{\mathrm{Var}[\ln(\hat{cv}_{t,s})] - d\}I_S\}[\mathbf{x}'(\mathbf{X}_t'\mathbf{X}_t)^{-1}\mathbf{X}_t']'$

$= d$ [derived as in eqn (17) above]
$+[\mathbf{x}'(\mathbf{X}_t'\mathbf{X}_t)^{-1}\mathbf{X}_t']\,[(1 + 2\,CV_{t,s}^{\ 2})/(2n-2) - d]I_S\,[\mathbf{x}'(\mathbf{X}_t'\mathbf{X}_t)^{-1}\mathbf{X}_t']'$

$= d + [1/(2n-2)]\{1 + 2\{CV_{t,s}^{\ 2}\} - \rho_t[\rho_t + 2\,CV_{t,s}CV_{t,v}]\,]\mathbf{x}'(\mathbf{X}_t'\mathbf{X}_t)^{-1}\mathbf{x}.$
$= d + [1/(2n-2)]\{(1 - \rho_t^{\ 2}) + 2CV_{t,s}[\,CV_{t,s} - \rho_t CV_{t,v}]\,\}\mathbf{x}'(\mathbf{X}_t'\mathbf{X}_t)^{-1}\mathbf{x}.$

An analogous result can be derived for $\mathrm{Var}\,[\mathbf{x}'(\mathbf{X}_{t+1}'\mathbf{X}_{t+1})^{-1}\mathbf{X}_{t+1}'\,\mathbf{v}_{t+1}]$. In evaluating the above relations the average values of $\hat{cv}_{t,s}$ and $\hat{cv}_{t+1,r}$ in the time period may be used in place of $CV_{t,s}$ and $CV_{t+1,r}$. The values c and d will then be constant during the time period.

The correlation between predictions on successive rounds may be approximated by the ratio:

$$\frac{\rho'_{t,t+1}[\rho'_{t,t+1} + 2CV_{t,s}CV_{t+1,r}]}{[\rho_t][\rho_t + 2CV_{t,s}^2] + [(1-\rho_t^2) + 2CV_{t,s}(CV_{t,s} - \rho_t CV_{t,v})]x'(X_t'X_t)^{-1}x} \tag{18}$$

For non-successive rounds, the numerator is changed to:

$$\rho'_{t,t+k}\,[\,\rho'_{t,t+k} + 2CV_{t,s}\,CV_{t+k,r}] \tag{19}$$

The term $\mathbf{x}'(\mathbf{X}_t'\mathbf{X}_t)^{-1}\mathbf{x}$ will vary with the z at which the fitted values are determined.

In the above derivation, the components of the **X** matrix were treated as fixed quantities. In applications, however, the CV [or ln(CV)] may be modeled as a function of the sample means in each round. For large sample sizes, the results above should be approximately true, since sample means are consistent for the true means. For PAT asbestos data, a model was constructed[1] to study the change in CV over rounds at the 300 fibers/mm^2 concentration. Data were assumed approximately normally distributed on the square root scale. At this fiber concentration, $z=(300)^{.5}=17.3$. Within round, predicted values for CVs at z=17.3 were determined via a model quadratic in the average amount measured. The median value of $x'(X_t'X_t)^{-1}x$ was computed for each round to be ~ 0.56. The other values required in equations (18) and (19) were those obtained earlier for these data: the average correlation between determinations by a lab in a round was ~ 0.66; the average $\hat{cv}$ over all rounds was ~ 0.26; the average correlation between labs in successive rounds was 0.32. The covariances of $\hat{cv}$s between rounds t and (t+k) are given below, based on equations (18) and (19):

Table VII: Correlations for Adjusted Value in Analysis of Asbestos CV Data

k=1	k=2	k=3	k=4	k=5	k=6	k=7	k=8
0.15	0.10	0.075	0.054	0.040	0.029	0.022	0.017

These correlations are, on average, about 0.012 greater than those obtained when unadjusted $\hat{cv}$ values were used. The correlation structure specified by equations (18) and (19) was used in a weighted least square analysis of the asbestos CV data and there was no change in differences identified as statistically significant in reference [1], though confidence bands are wider when the correlation was allowed for.

The weights to be used for each round's data depended not just on the correlation structures developed above, but also on changes in variance of the estimated Cvs. Different forms were tried for these variances – no changes in variance, variance proportional to degrees of freedom of the CV estimate, variance proportional to the estimated residual variance of the model used to obtain the CV estimate. Although different weightings produced considerable difference in confidence interval width, the same conclusions applied as were indicated in [2]: more recent rounds had lower CVs than the earlier rounds.

For the PAT silica data discussed in the previous section there was interest in comparing the means of the three methods in each round during each period. Medians for each method on each sample were used. Because the aim was to make comparisons over time, predicted values were made at four fixed concentrations of silica. To do this a linear regression model was fitted relating the median method determination to an estimate of the actual loading. This estimate was treated as a given rather than as a random quantity. Results analogous to equations (18) and (19) can be obtained here, too. The differences are as follows:

The expression for the value of c given above equation (17) is not valid when the components of the vector v are means or medians (which we treat the same), and have variances and covariances proportional to a power of the associated true means or medians, as given by equation (3):

$Var(y_{t,s,i}) = [\ (r_t)^2 + (w_t)^2\ ]\ [\mu_{t,s}]^{2a(t)}$
$Cov(y_{t,s,i}, y_{t,v,i,}) = (r_t)^2 [\mu_{t,s}]^{a(t)}\ [\mu_{t,v}]^{a(t)}$
$Cov(y_{t,s,i}, y_{t+1,r,i}) = (b_{t,t+1})\ [\mu_{t,s}]^{a(t)}\ [\mu_{t+1,r}]^{a(t+1)}$,
The Taylor series first order approximation for $[\mu_{t,v}]^{a(t)}$ (= w + j $\mu_{t,v}$) seems to be good in the relatively narrow range of concentration values used with silica. Using this approximation, we obtain that under the above covariance structure, the corresponding value of c is $[1/n](b_{t,t+1})\ z^{2\alpha}$, for $n = n_t = n_{t+1}$. (In making the above approximation, we use the approximation that $X_t'X_t)^{-1}X_t'\mu = (\ 0\ \ 1\ )'$, where μ is the vector of means for each of the samples. Clearly this result is only an approximation, since in the matrix X_t, the means are approximated by the sample medians.) After division by $\{[(r_t)^2+(w_t)^2][(r_{t+1})^2+(w_{t+1})^2]\}^{0.5}$ this becomes, for arbitrary k, $(1/n\ )\rho_{t,t+k}\ z^{2\alpha}$, or $(1/n_{t,t+k}\ )\rho'_{\ t,t+k}\ z^{2\alpha}$, when the changes in lab participation are taken into account.

Also, as above, we treat $Var[\mathbf{x}'(X_t'X_t)^{-1}X_t'\mathbf{v}_t] \sim Var[\mathbf{x}'(X_{t+1}'\ \mathbf{X}_{\ t+1})^{-1}\mathbf{X}_{t+1}'\ \mathbf{v}_t]$. Write
$Var[\mathbf{x}'(X_t'X_t)^{-1}X_t'\mathbf{v}_t] = [\mathbf{x}'(X_t'X_t)^{-1}X_t']\ Var(\mathbf{v}_t)\ \ [\mathbf{x}'(X_t'X_t)^{-1}X_t']'$
$\sim [1/n]\{[\mathbf{x}'(X_t'X_t)^{-1}X_t']\ [(\mathbf{r}_t)^2\ \mathbf{v}_t^{\alpha}\ \ \mathbf{v}_t^{\alpha}\ '\ ][\mathbf{x}'(X_t'X_t)^{-1}X_t']' +$
$(1/n)\ [\mathbf{x}'(X_t'X_t)^{-1}X_t']\ (\mathbf{Diagonal}\{[(\mathbf{r}_t)^2 + (\mathbf{w}_t)^2\ ]\ [\mu_{t,s}]^{2a(t)})\}$ - $Diagonal\{\ (\mathbf{r}_t)^2\ \mathbf{v}_t^{\alpha}\ \ \mathbf{v}_t^{\alpha}\ '\}\ ][\mathbf{x}'(X_t'X_t)^{-1}X_t']'\}$.

The first addend above has the same form as that used in calculating the value of the numerator, except that here it is within round correlation. Thus, the first addend can be shown to be approximately equal to $(1/n)\ \ (r_t)^2\ z^{2\alpha}$. For the second addend bounds can be obtained.
$(1/n)\ [\mathbf{x}'(X_t'X_t)^{-1}X_t']\ (\mathbf{Diagonal}\{[(\mathbf{r}_t)^2 + (\mathbf{w}_t)^2\ ]\ [\mu_{t,s}]^{2a(t)})\}$ - $\mathbf{Diagonal}\{\ (\mathbf{r}_t)^2\ \mathbf{v}_t^{\alpha}\ \ \mathbf{v}_t^{\alpha}\ '\}\ ][\mathbf{x}'(X_t'X_t)^{-1}X_t']'$.
$=(1/n)[\mathbf{x}'(X_t'X_t)^{-1}X_t']\ (Diagonal[\ (w_t)^2\ \ ]\ [\mu_{t,s}]^{2a(t)})[\mathbf{x}'(X_t'X_t)^{-1}X_t']'$. The expression is bounded by $(1/n)(w_t)^2\ \min[\mu_{t,s}]^{2a(t)}\ \ [\mathbf{x}'(X_t'X_t)^{-1}\mathbf{x}]$ and $(1/n)(w_t)^2\ \max[\mu_{t,s}]^{2a(t)}\ \ [\mathbf{x}'(X_t'X_t)^{-1}\mathbf{x}]$, but the estimated median value of $[\mu_{t,s}]^{2a(t)}$ was used in the approximation given below. This approximate expression for the value of the correlation between successive times for means or medians is:

$$\frac{b_{t,t+1}z^{2\alpha}}{r_t^2 z^{2\alpha} + w_t^2 med(\mu_{t,s})^{2\alpha} x'(X'_t X_t)^{-1}x} \approx \frac{\rho'_{t,t+1}z^{2\alpha}}{\rho_t z^{2\alpha} + w_t^2 med(\mu_{t,s})^{2\alpha} x'(X'_t X_t)^{-1}x} \approx \frac{\rho'_{t,t+1}}{\rho_t + [w_t^2/(r_t^2+w_t^2)](med(\mu_{t,s})^{2\alpha}/z^{2\alpha})x'(X'_t X_t)^{-1}x} \qquad (20)$$

For non-successive rounds, the numerator in (20) must be replaced by $\rho'_{\ t,t+k,}$ for a form of correlation as is given in equation (14).

The above results can be applied to the PAT silica data. The minimum and maximum media are 0.031 and 0.194, respectively. The median value of $\mu_{t,s}$ was approximately 0.1. In the calculations below we took α=1. The median values for $[\ \mathbf{x}'(X_t'X_t)^{-1}\mathbf{x}]$ were calculated at each of the four loadings over all rounds studied. Since $\rho_t = r_t^2 / (\ r_t^2 + \ w_t^2\ ) \sim 0.56$, then $w_t^2 / (\ r_t^2 + \ w_t^2\ )\ \sim 0.44$. The correlation was 0.23 between successive rounds, and the pooled CV was 0.37. Notice that the second addend in the denominator of (20) was very small compared to the first addend, and, thus, the value of $\rho'_{\ t,t+k,}$ determined the value of the expression. We obtained, for instance , for z=0.12:

Table VIII : Correlation for Adjusted Silica Means

k=1	k=2	k=3	k=4	k=5	k=6	k=7	k=8
0.277	0.217	0.171	0.134	0.105	0.082	0.064	0.051

Weighted least squares was used to obtain the correct confidence limits for the comparisons of the three methods. The confidence bands corresponding to statistically significant differences are given in Table A2, and these correct those given in Table II of reference [6]. Fewer differences were statistically significant at the overall 5% level. In general, the colorometric method still tended to give lower values than the two other methods, but the statistically significant differences were at the higher loadings– 120 and 150 µg. Many of the method differences that were called statistically significant in [1] at the lower concentration levels were not significant after correction for correlation. This applied in particular to the matrices like coal or calcite, for which there were fewer rounds of data. Since method biases may have been smaller at lower loadings, widening the confidence limits made many of these no longer statistically significant.

Table II provides an idea of the increase in standard deviation when the correlation is taken into account. This is only approximate, since, in addition to accouting for correlation, the analyses also used weights to account for the different degrees of freedom associated with the different variance estimates. Because of the application of weights, it was not appropriate to simply multiply the original confidence interval upper and lower bounds by a correction factor. Weighted least squares had to be used. Also, in the reanalysis the analyses presented for the silica medians in Table II were done by taking the differences between pairs of methods and analyzing these. For instance, for comparisons of colorometric and xray-diffraction in period 5 at 0.09 mg, for each round the colorometric median at 0.09 was subtracted from the corresponding xray-diffraction median, and the analyses were performed for those fifteen differences.

As was mentioned above with regard to the asbestos analyses, the forms of weights used in the weighted least squares analyses depended not just on the correlation structure, but also on the different variance forms for the predicted median values for each of the three silica methods. These forms included constant variance, variance proportional to the degrees of freedom of the predicted median, or variance proportional to the degrees of freedom, but also taking into account the correlation between predicted medians whose predictions came from the same least squares regression . Although different weightings produced some differences in confidence interval width (especially in group 5 analyses, where there were fewer labs for infra-red and x-ray diffraction), the main conclusions were similar. The results shown in Table A2 assumed variances proportional to the degrees of freedom of each median value.

The within-laboratory RSDs given in Table IV of the original silica paper [1] were also revised, and appear in Table A3 of the appendix. The correlations of the within -laboratory estimates will be similar to that of the total RSDs. Thus, similar corrections were used for the RSDs of Table A3.

7) Summary

Theoretical results and simulations carried out here confirmed that the correlations associated with the CVs are considerably smaller than that associated with the individual measurements. This is useful in subsequent statistical analyses of the CVs, since the formulas for the correlations can be used to identify the form of the variance covariance matrix needed to do weighted least squares. These results, in addition to providing estimates of correlations from past studies, led to corrections for confidence bands shown in reference [(1)]. Although confidence bands are wider, the conclusions of the original studies still apply. For the asbestos CV study [(2)], there was reduction in CV for more recent periods, compared with earlier periods. For the silica data [(1)], the colorometric method, for periods 5,7, and 8, had greater relative variability than the two other methods. For biases between silica methods, the colorometric method tended to give lower values than the two other methods, though the differences that were statistically significant were at the higher loadings– 120 and 150 μg. In the original paper, more differences at the lower loadings were called statistically significant, especially at lower masses and for matrices for which there were fewer rounds of data. Much of the theoretical material presented here also appeared in reference [(7)].

8) References

1.) Shulman, S.A., J.H. Groff, and M.T. Abell. Performance of Laboratories Measuring Silica in the Proficiency Analytical Testing Program. American Industrial Hygiene Assocation Journal. 53:49-56(1992).

2.) Schlecht, P.C. and S.A. Shulman: Phase Contrast Microscopy Asbestos Fiber Counting Performance in the Proficiency Analytical Testing Program. American Industrial Hygiene Association Journal. 56:480-489(1995).

3.) Searle, S.R. Linear Models. John Wiley & Sons, N.Y., 435, 64-66, 57, 59(1971).

4.)Hald, A. Statistical Theory with Engineering Applications, John Wiley & Sons, N.Y., p.301(1952).

5.) Hoel, Paul G. Introduction to Mathematical Statistics, Fourth Ed. John Wiley & Sons, N.Y. P. 154(1971).

6.) SAS User's Guide: Basics, Version 5 Edition. SAS Institute, Cary, NC, p.267.

7.)Shulman, S. "Relating Correlation between Lab Proficiency Test Measurements at Different Times to that between Estimated Coefficients of Variation." 2000 Proceedings of the Section on Physical and Engineering Sciences of the American Statistical Association, pp. 102-6..

Table A1: Table III, reference (6) -Revised: Total CVs of Silica Methods in Different Periods

Period(Rounds)	Loading (μg)	Overall $s_{r,t}$*	Method	Method $s_{r,t}$	$s_{r,t}$ (True) comparison	95% Confidence Limits on Ratio for each (Period, Loading) Combination
1(1-9)	min	0.693	COL	0.693		
	max	0.547	COL	0.547		
2(10-15)	min	0.430	COL	0.430		
	max	0.355	COL	0.355		
3(16-18)	min	0.677	COL	0.677		
	max	0.525	COL	0.525		
4(19-29)	min	0.698	COL	0.698		
	max	0.529	COL	0.529		
5(30-45)	Min	0.679	COL IR XRD	0.869 0.650 0.454	COL>IR COL>XRD	COL/IR=(1.08, 2.23) COL/XRD=(1.48,2.31)
	Max	0.441	COL IR XRD	0.562 0.379 0.353	COL>IR COL>XRD	COL/IR=(1.17, 2.11) COL/XRD=(1.36, 1.96)
6(46)	Min	0.666	COL IR XRD	0.576 0.791 0.611		
	Max	0.599	COL IR XRD	0.412 0.734 0.605		
7(47-62)	Min	0.389	COL IR XRD	0.447 0.347 0.365	COL>IR COL>XRD	COL/IR=(1.04,1.62) COL/XRD=(1.06, 1.50)
	Max	0.349	COL IR XRD	0.384 0.350 0.310		
8 (63-101) all matrices	Min	0.378	COL IR XRD	0.433 0.345 0.348	COL>IR COL>XRD	COL/IR=(1.02,1.38) COL/XRD=(1.07,1.38)
	Max	0.293	COL IR XRD	0.339 0.241 0.290	COL>IR COL>XRD	COL/IR=(1.01,1.36) COLL/XRD=(1.08,1.39)

*** Overall** $s_{r,tw} = (s^2_{r,\,t,\,col} + s^2_{r,t,\,ir} + s^2_{r,\,t,\,xrd})^{0.5}$

Table A2: Table II of reference (6) - Revised: Bias of Silica Medians by Method, within Periods, at Several Loadings

Period(Rounds)	Loading (μg)	Methods differing at 2.5% Level for Each (Period, Loading) Combination	Confidence Intervals for Biases((μg)
5(30-45)	60	NONE	
	90	NONE	
	120	NONE	COL-XRD=(-27.0, -0.223)
	150	COL<XRD	COL-XRD=(-35.8 , -5.31)
7(47-62)	60	NONE	
	90	COL<XRD	COL-XRD=(-17.9,-2.16)
	120	COL<XRD IR<XRD	COL-XRD=(-27.7, -9.27) IR-XRD=(-34.4,-3.05)
	150	COL<XRD IR<XRD	COL-XRD=(-39.2, -14.6) IR-XRD=(-47.9,-1.1)
8 Talc (rns 63-76, 78-80, 82,83, 87,90,91,94,98)	60	COL>XRD	COL-XRD=(1.89, 8.70)
	90		
	120	COL<IR COL<XRD	COL-IR=(-22.4, -5.66) COL-XRD=(-16.5,-3.42)
	150	COL<IR IR<XRD	COL-IR=(-34.0, -10.9) COL-XRD=(-26.6, -8.49)
8 Calcite (86,89,93,97,101)	60	NONE	
	90	NONE	
	120	NONE	
	150	COL<IR	COL-IR=(-50.1, -2.40)
8 Talc and Coal (81,85,95,99)	60	NONE	
	90	NONE	
	120	NONE	
	150	NONE	
8 Coal (77,84,88,92,96,100))	60	NONE	
	90	NONE	
	120	COL<IR	COL-IR=(-26.1, -4.04) COL-XRD=(-26.3,-0.868)
	150	COL<IR	COL-IR=(-38.3, -7.81) COL-XRD=(-42.6,-1.35)

Table A-3, Original Table IV - Wthin Laboratory CVs of Silica

Period(Rounds)	Ovarall*	Metho d	Loading (µg) RSD	Methods compariuson	90% Conf. Intervals
5(30-45)	0.317	COL	0.423	COL > IR	COL/IR=(1.15, 2.90)
		IR	0.240	COL>XRD	COL/XRD=(1.24, 2.31)
		XRD	0.240		
7(47-62)	0.236	COL	0.292	COL > IR	COL/IR=(1.25, 2.09)
		IR	0.181	COL>XRD	COL/XRD=(1.08, 1.61)
		XRD	0.226		
8 (63- 101)	0.194	COL	0.218	COL > IR	COL/IR=(1.04, 1.42)
		IR	0.181	COL>XRD	COL/XRD=(1.05, 1.37)
		XRD	0.179		

* Overall $s_{r,w} = (s^2_{r,w,col} + s^2_{r,w,ir} + s^2_{r,w,xrd})^{0.5}$