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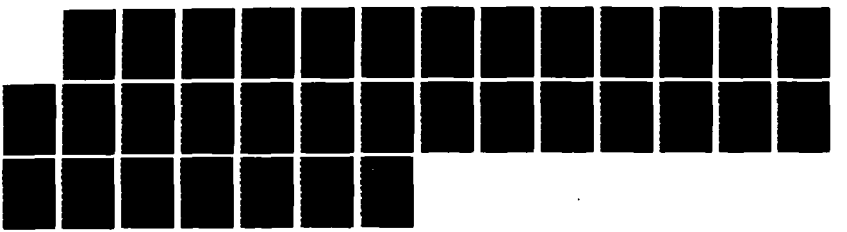

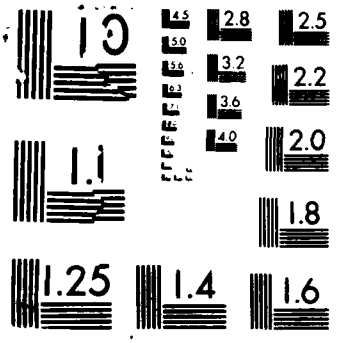
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Applied Research in Statistics - Mathematics - Operations Research

AN EVALUATION OF PROPOSED SAMPLING PROCEDURES FOR DETERMINING ORGANOTIN RELEASE RATES

by

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1. INTRODUCTION

Scientists at the David Taylor Naval Ship Research and Development Center (DTNSRDC) are currently developing and evaluating a new procedure for measuring the release rate of organotin from antifouling paint. As part of this procedure, a panel painted with organotin antifouling paint is placed in a test tank filled with water. The release rate of organotin is determined by measuring the increasing concentration in the water, and plotting it against time. The slope of this line as determined by linear regression provides an estimate of the organotin release rate.

When sampling of the test tank is completed, the painted panel is removed and kept in a separate holding tank for subsequent release-rate determinations. In this way, leaching rate can be accurately evaluated and studied over an extended period of time. When not in use, the test tank is cleaned and flushed in order to prepare it for subsequent usage.

Under the current sampling scheme, samples are extracted at six equally spaced points in time after placing the panel in the test tank. Three samples are taken at each sampling time, and five replicate measurements (i.e., subsamples) are made of each sample. However, because of saturation limitations, sampling must be completed before the tin concentration in the test tank reaches 50 ppb.

The objectives of this Desmatics technical report are to:

(1) develop a statistical model which describes the sampling procedure,

(2) present a method for estimating the release rate and obtaining corresponding confidence intervals,

(3) discuss the optimum number of subsamples which should be made and the optimum sampling times,

and (4) compare the current procedure against several different procedures which have been proposed.

Section 2 presents a proposed statistical model which describes the sampling process. Sections 3 and 4 present methods for estimating the release rate and constructing associated confidence intervals. Section 5 summarizes an analysis of some preliminary release-rate data. Section 6 discusses general sampling strategy, and Section 7 provides a discussion of two proposed ASTM sampling methods.

2. A STATISTICAL MODEL

It is postulated that the increase in tin concentration in the test tank over time can be adequately described by a linear response function with a subsampling component. Thus, the proposed model is as follows:

$$Y_{ijk} = \beta_0 + \beta_1 t_i + \varepsilon_{ij} + \delta_{ijk} \qquad \begin{matrix} i=1,2,\ldots,v \\ j=1,2,\ldots,m \\ k=1,2,\ldots,n \end{matrix} \qquad (2.1)$$

where

Y_{ijk} is the measured tin concentration of the kth subsample made from the jth sample taken at time t_i,

ε_{ij} is the error associated with the jth sample taken at time t_i,

and δ_{ijk} is the error associated with the kth subsample made from the jth sample taken at time t_i.

The intercept and slope of the regression line are represented by the parameters β_0 and β_1, respectively. The slope parameter β_1 represents the organotin release rate and indicates the change in the average tin concentration per unit increase in time. The parameter β_0 is the Y intercept of the regression line and indicates the value of the regression function at t=0. An intercept term is included in the model to account for possible trace quantities of tin which may not have been completely purged during cleaning and flushing of the test tank prior to testing.

It is important to note that the proposed model has two error components: ε_{ij} and δ_{ijk}. The error component ε_{ij} represents observed differences between samples (i.e., extracts) and is assumed to be normally distributed with mean zero and variance σ_1^2. The error component δ_{ijk} represents observed dif-

ferences between subsample determinations made on each sample and is assumed to be normally distributed with mean zero and variance σ_2^2. A final key assumption is that all error terms are assumed to be statistically independent of each other.

In the current DTNSRDC sampling procedure v=6, m=3, and n=5. The six sampling times have generally corresponded to either five to thirty minutes in five minute intervals or ten to sixty minutes in ten minute intervals. Other sampling intervals, however, cannot be ruled out as DTNSRDC continues with its experimentation.

3. ESTIMATION OF β_0 AND β_1

To make a valid statistical analysis of the proposed model, the mv sample averages (as determined by averaging the measured tin concentrations of the n subsamples made from each sample) are regressed against time. Define Z_{ij} as follows:

$$Z_{ij} = (Y_{ij1} + Y_{ij2} + \ldots + Y_{ijn})/n.$$

Thus,

$$\hat{\beta}_1 = \sum_{i=1}^{v} [(t_i-\bar{t}) \sum_{j=1}^{m} Z_{ij}]/m \sum_{i=1}^{v} (t_i-\bar{t})^2 \qquad (3.1)$$

and

$$\hat{\beta}_0 = (\sum_{i=1}^{v} \sum_{j=1}^{m} Z_{ij}/mv) - \hat{\beta}_1 \bar{t}, \qquad (3.2)$$

where $\bar{t} = (t_1+t_2+\ldots+t_v)/v$. It must be emphasized that equations (3.1) and (3.2) are appropriate only when the sampling is "balanced", that is, when m samples are taken at each of v sampling times, and n subsample determinations are made of each sample.

Let $\hat{Z}_{ij} = \hat{\beta}_0 + \hat{\beta}_1 t_i$, and define

$$s^2 = \sum_{i=1}^{v} \sum_{j=1}^{m} (Z_{ij}-\hat{Z}_{ij})^2/(mv-2). \qquad (3.3)$$

An estimate of the variance of $\hat{\beta}_1$ is given by

$$\hat{Var}(\hat{\beta}_1) = s^2/[m \sum_{i=1}^{v} (t_i-\bar{t})^2]. \qquad (3.4)$$

An estimate of the variance of $\hat{\beta}_0$ is given by

$$\hat{\text{Var}}(\hat{\beta}_0) = s^2 \left[\frac{1}{mv} + \frac{\bar{t}^2}{\sum_{i=1}^{v} (t_i - \bar{t})^2} \right] . \qquad (3.5)$$

4. CONFIDENCE INTERVALS FOR β_0 AND β_1

A $100(1-\alpha)\%$ confidence interval for β_1 is given by

$$\hat{\beta}_1 \pm k_\alpha \sqrt{\widehat{\mathrm{Var}}(\hat{\beta}_1)} \tag{4.1}$$

where k_α denotes the upper $100(1-\alpha/2)$ percentage point of Student's t distribution with $(mv-2)$ degrees of freedom. A $100(1-\alpha)\%$ confidence interval for β_0 is obtained in the same manner as that for β_1.

Note that when $m=3$ samples are extracted at each of $v=6$ sampling times, the factor k_α specified in (4.1) has $mv-2=16$ degrees of freedom associated with it.

5. ANALYSIS OF SOME PRELIMINARY DATA

DTNSRDC supplied Desmatics with some preliminary release-rate measurement data from a series of ten tests (i.e., measurement sessions) involving three different organotin antifouling paints. Desmatics was requested by DTNSRDC not to disclose the actual names of these paints. Accordingly, for the sake of discussion, these paints will be referred to as paints A, B, and C. Data from two tests was supplied for paint A and four each for paints B and C.

5.1 Constancy of Variance

Under the model described in Section 2, the estimator for β_1 defined in equation (3.1) is unbiased and has the smallest variance of any unbiased estimator. One of the features of that model is that the variance is constant across samples. If the variance is not constant, $\hat{\beta}_1$ is still unbiased but is no longer the minimum variance unbiased estimator.

It is not unusual when measuring concentrations to find that the variance of the observations is an increasing function of the true concentration. In such cases it is often possible to obtain a better estimate of the slope by first transforming (e.g., taking logarithms) the observations to stabilize the variance. In order to determine whether it would be appropriate to use a transformation for this data set, the mean and standard deviation of the five subsamples from each sample were calculated. (Note: The standard deviation is on the same scale as the mean and is generally more useful for this type of investigation.) Table 1 lists the correlations between these two statistics across samples for each of the ten tests. Also given are the corresponding

results obtained using the mean and standard deviation of the three sample averages at each time.

From Table 1, it is clear that there is no consistent relationship between the mean and standard deviation for either the subsamples or the sample averages; hence, there is no indication of a need to transform the variables in order to stabilize the variances.

5.2 Estimates of β_0 and β_1

Desmatics statistically analyzed the data to obtain estimates of β_0 and β_1 as well as estimates of their associated standard errors. The results are summarized in Table 2. Also included in this table are values of Δ_1, which is defined as

$$\Delta_1 = [k_{.9}\sqrt{\text{Var}(\hat{\beta}_1)}]/\hat{\beta}_1 \qquad (5.1)$$

where $k_{.9}=1.746$. The quantity Δ_1 represents the ratio of the half-width of a 90% confidence interval for β_1 to $\hat{\beta}_1$. A test is currently considered "successful" if the release-rate is predicted to within twenty percent at least ninety percent of the time. Thus, a successful test would be indicated if $\Delta_1 \leq 20\%$. As can be seen from an examination of Table 2, Δ_1 is less than or equal to 20% in only four of the ten tests.

Paint	Date of Test	Subsamples Number	Subsamples Correlation	Sample Averages Number	Sample Averages Correlation
A	4-4	18	-.186	6	.027
A	4-11	17	.168	6	.772
B	4-11	18	-.149	6	-.504
B	4-14	16	-.262	5	-.521
B	4-15	18	.653	6	.759
B	4-16	18	.543	6	-.303
C	4-10	18	.472	6	-.057
C	4-14	18	.050	6	.318
C	4-16	18	-.129	6	.045
C	4-24	17	.560	6	.740
Average		17.6	.172	5.9	.128

Table 1: Correlations between the mean and standard deviation of (1) the five subsamples from each sample and (2) the sample averages at each time.

Paint	Date of Test	$\hat{\beta}_0$	$\sqrt{\widehat{Var}(\hat{\beta}_0)}$	$\hat{\beta}_1$	$\sqrt{\widehat{Var}(\hat{\beta}_1)}$	Δ_1
A	4-4	24.3	3.15	.53	.081	26.7%
A	4-11	8.6	1.60	.51	.040	13.7%
B	4-11	8.3	1.39	1.01	.072	12.4%
B	4-14	7.4	1.47	.56	.072	22.4%
B	4-15	8.5	1.49	.66	.077	20.4%
B	4-16	3.3	1.59	.40	.082	35.8%
C	4-10	0	2.24	.63	.057	15.8%
C	4-14	2.7	1.82	.21	.047	39.1%
C	4-16	5.5	0.78	.19	.020	18.4%
C	4-24	.4	1.06	.18	.028	27.2%

Notes: (a) Units for β_0 and β_1 are ppb and ppb/min, respectively;

(b) $\Delta_1 = [k_{.9} \sqrt{\widehat{Var}(\hat{\beta}_1)}]/\hat{\beta}_1$;

(c) Paints A and C had the following sampling times: 10, 20, 30, 40, 50, and 60 minutes;

(d) Paint B had the following sample times: 5, 10, 15, 20, 25, and 30 minutes;

(e) All tests used m=3 samples and n=5 subsamples.

Table 2. Summary of Data Analysis.

5.3 Tests for Model Goodness of Fit

The model in Section 2 assumes a linear relationship between organotin concentration and time (that is, a constant release rate is assumed). Since multiple samples were taken at each time, it is possible to test whether this assumed model adequately describes the data. This is done by estimating the concentrations separately at each time, using the overall average of the sample averages. If the linear model is adequate, the differences between the individual sample averages and the regression line should not be significantly larger than the differences between those values and the overall averages at each time.

The error sum of squares for the regression model may be split into two components: pure error and lack of fit. If the lack of fit component is large relative to the pure error component, model inadequacy would be indicated. Table 3 gives the values of the goodness of fit test statistics for each of the ten test runs. Values close to one indicate a good fit while values much larger than one indicate the need for a different model.

The p-values in the table are the smallest significance levels at which the hypothesis of no lack of fit would be rejected. A p-value less than .05 is usually considered sufficient evidence to reject a null hypothesis.

Half of the test runs show significant lack of fit of the linear model (at the .05 significance level). Desmatics therefore examined the data plots for each of these runs. No clear evidence of a curvilinear relationship was visible. Therefore, it appears that the linear trend model is adequate

Paint	Date of Test	Test Statistic	p-value
A	4-4	2.02	.156
A	4-11	2.86	.075
B	4-11	3.98	.028
B	4-14	0.46	.764
B	4-15	3.44	.043
B	4-16	1.88	.178
C	4-10	4.65	.017
C	4-14	2.87	.070
C	4-16	3.42	.044
C	4-24	8.47	.002

Table 3. Goodness of Fit Tests for the Ten Test Runs.

but that the error structure is not. In fact, the sample averages at any given time tend to be closer together than they would be if they were independently distributed about the regression line. This suggests the need for an additional error term in the model which affects all samples at a given time in the same way. In other words, there is most likely some degree of correlation between samples taken at the same time, perhaps because of gradient effects at the location in the test tank where samples are extracted. If so, this correlation should probably be taken into account. Desmatics recommends that additional data be analyzed in order to more fully evaluate the situation. If, however, it is determined that an additional error term should be incorporated into model (2.1), some important consequences would be as follows:

(1) The estimator $\hat{\beta}_1$ defined in (3.1) would still be valid but the degrees of freedom associated with its confidence interval, see (4.1), would decrease from (mv-2) to (v-2);

(2) The estimate of the variance of $\hat{\beta}_1$ given in (3.4) would no longer apply. Preliminary indications are that the revised estimate would increase the standard error of $\hat{\beta}_1$ by nearly 30% over those values given in Table 2;

(3) The combination of fewer degrees of freedom and larger standard error would increase Δ_1 by about 60% over those values given in Table 2.

This is an important issue which Desmatics plans to discuss with DTNSRDC scientists and study more closely once more data becomes available. Some alternatives DTNSRDC may wish to consider are:

(1) avoid taking consecutive samples so close together,

(2) collect samples at a different location in the test tank,

or (3) sample several locations in the test tank and then combine the samples into a single composite sample.

5.4 Regression Through the Origin

If there are no trace quantities of tin in the test tank at the beginning of a run, then the regression line should go through the origin. If, on the other hand, such traces do exist, forcing the line through the origin will result in a biased estimate of the slope.

In order to determine the effects on the estimated slope of forcing the regression line to go through the origin, Desmatics performed these regressions and compared the results to those obtained from the full model. The estimated slopes for the two models are given in Table 4 along with the percent increase which results from removing the intercept from the model. Obviously, the change in the estimated slope can be drastic.

Paint	Date	$\hat{\beta}_1$	$\hat{\beta}_1^*$	Increase
A	4-4	.53	1.09	106%
A	4-11	.51	.70	37%
B	4-11	1.01	1.39	38%
B	4-14	.56	.88	57%
B	4-15	.66	1.05	59%
B	4-16	.40	.56	40%
C	4-10	.63	.64	2%
C	4-14	.21	.28	33%
C	4-16	.19	.32	68%
C	4-24	.18	.19	6%

Table 4: Comparison of Estimated Slopes From Regressions With and Without the Intercept Terms. $\hat{\beta}_1$ is the Estimate From the Model With an Intercept While $\hat{\beta}_1^*$ is the Corresponding Estimate With No Intercept Fitted.

6. SAMPLING STRATEGY

It can be shown that the variance of the slope estimate is given by

$$\text{Var}(\hat{\beta}_1) = (n\sigma_1^2+\sigma_2^2)/nm \sum_{i=1}^{v} (t_i-\bar{t})^2, \qquad (6.1)$$

where σ_1^2 and σ_2^2 are the two variance components introduced in Section 2. An estimate for $\text{Var}(\hat{\beta}_1)$ was, of course, given earlier in equation (3.4).

Examination of equation (6.1) leads to the following conclusions:

(a) An increase in n or m (or both) will reduce the variance of the slope estimate $\hat{\beta}_1$;

(b) An increase in m (the number of samples at each sampling time) will have more of an effect than an increase in n (the number of subsamples made for each sample) in reducing $\text{Var}(\hat{\beta}_1)$;

(c) If either σ_1^2 or σ_2^2 (or both) can be made smaller, $\text{Var}(\hat{\beta}_1)$ can be made smaller. This could be accomplished by extracting more homogeneous samples or by improving the measurement technique;

(d) An increase in $\sum_{i=1}^{v} (t_i-\bar{t})^2$ will reduce $\text{Var}(\hat{\beta}_1)$. This could be accomplished by judicious selection of the sampling times.

6.1 Estimates of the Variance Components σ_1^2 and σ_2^2

In order to compare alternative sampling strategies, estimates of the variance components σ_1^2 and σ_2^2 are needed. Desmatics obtained estimates of these components of variance from an analysis of the preliminary data provided by DTNSRDC. These estimates are summarized in Table 5. The pooled estimates of σ_1^2 and σ_2^2 are $4.44(\text{ppb})^2$ and $4.20(\text{ppb})^2$, respectively. Thus, the variation among subsamples is roughly equivalent to the variation among samples taken at

Paint	Date of Test	σ_1^2	σ_2^2
A	4-4	25.49*	9.94*
A	4-11	3.29	6.39
B	4-11	3.10	3.81
B	4-14	6.49	4.37
B	4-15	4.16	3.14
B	4-16	6.57	3.20
C	4-10	7.94	5.70
C	4-14	7.23	2.82
C	4-16	0.46	4.33
C	4-24	0.69	4.03
	POOLED AVERAGE	4.44	4.20

*Not Included in Calculation of Pooled Average

$\hat{\sigma}_1 = \sqrt{4.44} = 2.11$ppb

$\hat{\sigma}_2 = \sqrt{4.20} = 2.05$ppb

Table 5. Estimates of the Variance Components σ_1^2 and σ_2^2.

the same times.

6.2 Five Versus Three Subsamples

It has been proposed that the DTNSRDC sampling procedure be changed so that only three subsample determinations be made from each sample instead of five. It is clear that the use of three subsamples will result in a loss of precision. The problem, then, is to estimate the precision of the proposed strategy involving n=3 subsamples to the current strategy involving n=5 subsamples.

In general, if the precision of a "new" sampling strategy relative to an "old" sampling strategy is desired, one calculates (in percent) the relative precision (RP) of new to old as

$$(100\%)[\hat{V}_N(\hat{\beta}_1)/\hat{V}_O(\hat{\beta}_1)]^{1/2}, \tag{6.2}$$

where $\hat{V}_N$ and $\hat{V}_O$ are variance estimates corresponding to the new and old strategies, respectively.

An RP (of new to old) of 100% indicates that the two sampling schemes are equally precise in estimating β_1. An RP less (greater) than 100% indicates that the new scheme is more (less) precise in estimating β_1 than the old scheme is.

Assuming that (1) the new design would involve n=3 subsamples per sample and m=3 samples per sampling time, (2) the old design would involve n=5 subsamples per sample and m=3 samples per sampling time, and (3) the estimates of σ_1^2 and σ_2^2 (as given in Table 5) would remain unchanged, the RP of new to old would be approximately 105%. Thus, the sampling procedure involving three

subsamples is only 5% less precise than the procedure involving five subsamples. This loss of precision is offset, of course, by a reduction in sampling costs.

A practical interpretation of the RP (of new to old) where the total number of samples (i.e., mv) is equal is that it expresses the width of a confidence interval for β_1 based on the new sampling procedure relative to the corresponding interval width based on the old sampling procedure. Consequently, if the old procedure yields, for example, a confidence interval with width equal to W, then one can expect that the new procedure would yield an interval (of similar confidence) of widtn (RP)W. It should be noted tnat if the total number of samples (mv) is not equal in the two schemes, the statistical factor k_α, see (4.1), used in confidence interval construction would not be the same in the two schemes; therefore this factor would be an additional consideration in comparing confidence interval widths. It is clear, however, that reducing the number of subsamples from n=5 to n=3 should have a relatively minor effect on the precision of $\hat{\beta}_1$.

6.3 Optimum Number of Subsamples

Let C_1 denote the cost of taking a sample (i.e., extract) and C_2 denote the cost of making a subsample determination. Then the total cost of sampling for a balanced strategy is $v(mC_1+mnC_2)$. Ideally, the optimum number of subsamples would be that value of n which minimizes the variance of $\hat{\beta}_1$ subject to a fixed cost. Accordingly, it is easy to show that the optimum value of n is given by

$$\hat{n}(\text{optimal}) \approx \sqrt{\frac{\hat{\sigma}_2^2 C_1}{\hat{\sigma}_1^2 C_2}} \quad . \tag{6.3}$$

From Table 5, $\hat{\sigma}_1^2=4.44$ and $\hat{\sigma}_2^2=4.20$, so that

$$\hat{n}(\text{optimal}) \approx (.97)\sqrt{C_1/C_2} \quad . \tag{6.4}$$

As an illustration of this result, suppose it costs four times as much to prepare a sample than it does to make a single subsample determination (i.e., $C_1=4C_2$), then

$$\hat{n}(\text{optimal}) \approx .97(2) = 1.94$$

or n=2 if rounded.

6.4 Optimum Sampling Times

Examination of equation (6.1) indicates that the optimum sampling times $t_1, t_2, \ldots, t_v$ are those times which would maximize $\sum_{i=1}^{v} (t_i-\bar{t})^2$. This suggests that only two sampling times be used (i.e., v=2), and that these times be separated as much as possible. For example, the initial sampling time (t_1) might correspond to the time elapsed to reach a measurable tin concentration in the test tank; the final time (t_2) would be the time elapsed for the tin concentration to reach 50 ppb. If a total of eighteen samples are to be extracted, this implies that nine samples would be taken at each of the two sampling times (i.e., v=2 and m=9). Although such a sampling scheme provides the smallest variance for the slope $\hat{\beta}_1$ among all schemes involving eighteen samples (i.e., mv=18), it should be emphasized that this scheme is of no use at all if one desires to be able to check possible lack of fit of the

regression line.

In the preliminary data analyzed by Desmatics, sampling was done according to either the scheme {m=3, n=5, and t=5,30(5)} or {m=3, n=5, and t=10,60(10)}. Consider, then, the four alternative schemes presented in Table 6. In this table, estimates of the variance of $\bar{x}_1$ for each scheme were obtained via equation (6.1) and using the estimates of σ_1^2 and σ_2^2 provided in Table 5. Accordingly, the RP scheme A' to A (or of scheme B' to B) is 68%. Schemes A' and B' therefore offer a 32% gain in precision when compared to their counterparts A and B. Each of the four schemes requires eighteen samples and five subsamples per sample.

If the four schemes in Table 6 are modified so that only n=3 subsample determinations are made per sample instead of n=5, the RP of scheme A' to A (or scheme B' to B) still works out to about 68%.

Another situation of interest arises when sampling is done over a thirty minute period (e.g., scheme A), but sampling actually could have been extended over a sixty minute period (e.g., scheme B). In such a situation, the RP of the latter scheme to the former is 50%. Thus, scheme B offers a 50% gain in precision when compared to scheme A. This latter statement holds whether n=5 or n=3 subsamples per sample are used in each scheme. Thus, it is very advantageous to sample the test tank for as long as possible (i.e., up until the tin concentration in the test tank reaches 50 ppb).

Scheme	v	m	n	Sampling Times (min)	$\sum_{i=1}^{v} (t_i-\bar{t})^2$	$\hat{Var}(\hat{\beta}_1)$
A	6	3	5	5,10,15,20,25,30	437.5	4.023×10^{-3}
B	6	3	5	10,20,30,40,50,60	1750	1.006×10^{-3}
A'	2	9	5	5,30	312.5	1.877×10^{-3}
B'	2	9	5	10,60	1250.0	0.469×10^{-3}

Table 6. Four Alternative Sampling Schemes: Each Scheme Requires Eighteen Samples and Five Subsamples Per Sample.

7. PROPOSED ASTM METHOD

The American Society for Testing and Materials (ASTM) is currently considering two alternative sampling schemes for release-rate determination. In the first (ASTM Method #1), only one sample with three subsample determinations is used to determine the release rate. In the second method (ASTM Method #2), two samples, each with three subsample determinations, are used. Neither of these methods provide an empirical estimate of the precision of $\hat{\beta}_1$; thus, confidence intervals cannot be obtained under these schemes.

7.1 ASTM Method #1

The ASTM method based on only one sample has several disadvantages. First, and most seriously, this method implicitly assumes that the regression line extends through the origin. The data analyses presented in Section 5, however, strongly indicated the need for a nonzero intercept. As noted previously, the primary consequence of neglecting the initial organotin concentration is that the slope estimate will be biased. (A more complete discussion of this method is provided below.) Second, an empirical estimate of the precision of the slope estimate $\hat{\beta}_1$ cannot be obtained with this method.

In order to examine some statistical properties of this method, let Z_1, Z_2, and Z_3 denote the measured tin concentration of the three subsample determinations made from a single sample taken at time t. Define $\bar{Z}=(Z_1+Z_2+Z_3)/3$, and thus

$$\hat{\beta}_1 = \bar{Z}/t . \qquad (7.1)$$

It is not difficult to show that the expected value of $\hat{\beta}_1$ is $\beta_1+\beta_0/t$. Thus the estimate $\hat{\beta}_1$ defined in (7.1) is biased by an amount β_0/t. Further, the relative bias is given by $\beta_0/(t\beta_1)$, which can be rather substantial. Examine, for example, the data presented in Tables 2 and 4.

The mean square error of $\hat{\beta}_1$ can be shown to be

$$\text{Var}(\hat{\beta}_1) + (\text{bias})^2 = [\sigma_1^2+\sigma_2^2/3+\beta_0^2]/t^2. \tag{7.2}$$

However, since the bias term cannot effectively be ignored, the mean square error is of no real intrinsic interest. In conclusion, it is Desmatics' opinion that ASTM Method #1 is not a viable sampling procedure to follow.

7.2 ASTM Method #2

The ASTM method based on two samples has the advantage of providing an unbiased estimate of β_1, but still has the disadvantage of not providing an empirical estimate of the precision of $\hat{\beta}_1$. Nevertheless, the performance of this method can still be evaluated using equation (6.1). In this method, v=2, m=1, and n=3. Note that for v=2, $\sum_{i=1}^{v} (t_i-\bar{t})^2=(t_2-t_1)^2/2$. Thus

$$\text{Var}(\hat{\beta}_1) = 2(\sigma_1^2+\sigma_2^2/3)/(t_2-t_1)^2. \tag{7.3}$$

Substituting the estimates $\hat{\sigma}_1^2=4.44$ and $\hat{\sigma}_2^2=4.20$ into (7.3) yields

$$\text{Var}(\hat{\beta}_1) = 11.68/(t_2-t_1)^2. \tag{7.4}$$

For t_1=5 minutes and t_2=30 minutes, this gives $\text{Var}(\hat{\beta}_1)$ = .0187; for t_1=10 minutes and t_2=60 minutes, this gives $\text{Var}(\hat{\beta}_1)$ = .0047.

Table 7 summarizes all the sampling strategies involving n=3 subsamples considered heretofore. Schemes C and C' correspond to the ASTM method #2 over 60 and 30 minutes sampling periods, respectively. Scheme A corresponds to the DTNSRDC sampling scheme in which m=3 samples are taken at each of six sampling times given by t=10,60(10) minutes. Scheme A' is the 30 minute counterpart of Scheme A. The RP of scheme C to scheme A (or scheme C' to scheme A') is 205%. Thus, the standard error of $\hat{\beta}_1$ under scheme C(C') would be approximately twice as large as that which would be obtained under scheme A(A'). It was mentioned previously, of course, that scheme C or C' provides insufficient data to obtain confidence intervals.

In scheme B, m=9 samples are taken at each of the two sampling times 10 and 60 minutes. In scheme B', m=9 samples are taken at each of the two times 5 and 30 minutes. A quick calculation will show that the RP of scheme C to scheme B (or scheme C' to B') is 300%. Thus, in this case, the standard error of $\hat{\beta}_1$ under scheme C(C') would be approximately three times larger than that which would be obtained under scheme B(B').

7.3 Modified ASTM Method #2

Suppose that ASTM Method #2 is modified so that additional samples are collected at the two sampling times. It has already been indicated (section 6.4) that taking m=9 samples at each of two times is about 32% more precise than the DTNSRDC scheme of taking m=3 samples at each of six equally spaced times (i.e., schemes A or A' in Table 7). The breakpoint for 100% relative precision of a scheme involving two sampling times (t=10 and t=60 minutes) to

Scheme	v	m	n	Sampling Times (min)	$\hat{Var}(\hat{\beta}_1)$
A	6	3	3	10,20,30,40,50,60	1.112×10^{-3}
B	2	9	3	10,60	0.519×10^{-3}
C	2	1	3	10,60	4.672×10^{-3}
A'	6	3	3	5,10,15,20,25,30	4.450×10^{-3}
B'	2	9	3	5,30	2.076×10^{-3}
C'	2	1	3	5,30	18.688×10^{-3}

Table 7. Six Alternative Sampling Schemes. Each Requires n=3 Subsamples Per Sample.

scheme A is m=4.2 samples. That is, collecting four samples at each of two (endpoint) times should yield approximately the same standard error for $\hat{\beta}_1$ as would collecting three samples at each of six equally spaced times, where in both schemes n=3 subsamples are made from each sample. However, to obtain 90% confidence intervals for β_1 of approximately equal width, then m=5 samples should be collected at the two sampling times. This latter scheme requires ten samples compared to the eighteen samples which scheme A requires.

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Scientists at the David Taylor Naval Ship Research and Development Center are currently developing and evaluating a new procedure for measuring the release rate of orgnaotin from antifouling paint. As part of this procedure, a panel painted with organotin antifouling paint is placed in a test tank filled with water. The release rate of organotin is determined by measuring the increasing concentration in the water, and plotting it against time. The slope of this line as determined by linear regression provides an estimate of the organotin release rate.

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(20. continued)
The objectives of this technical report are to:

(1) develop a statistical model which describes the sampling procedure,

(2) present a method for estimating the release rate and obtaining corresponding confidence intervals,

(3) discuss the optimum number of subsamples which should be made and the optimum sampling times,

(4) compare the current procedure against several different procedures which have been proposed.

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