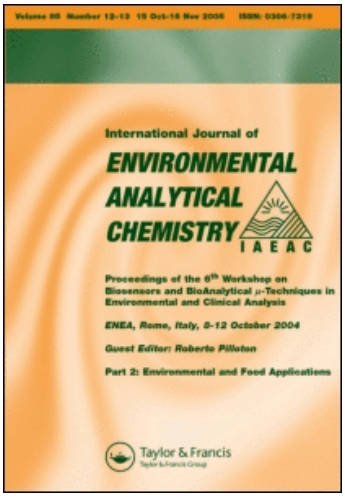

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Reliability of Spark Source Mass Spectrometry for Environmental Assessment†

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Spark source mass spectrometry (SSMS) is used for elemental analysis by the Process Measurements Branch of the United States Environmental Protection Agency's Industrial Environmental Research Laboratory as part of its phased approach to environmental source assessment. The source assessment is an evaluation of the physical, chemical, and biological characteristics of industrial process streams. The first phase, known as Level 1, is a screening phase which emphasizes completeness of detection of elements and classes of organic materials.

SSMS was chosen for Level 1 elemental analysis because it provides the most economical analysis for 73 elements within adequate limits of detection. Another important consideration is that SSMS doesn't require dissolution.

The trigger levels that indicate whether the next phase of source assessment is necessary are based on the requirement that the Level 1 data be precise within a factor of 3. Therefore, it is necessary that SSMS analysis provide elemental composition within the limits of 3 with a reasonable level of confidence. The results of a recent Level 1 analytical laboratory audit are examined to evaluate the reliability of SSMS in meeting the assessment goals.

These results indicate that SSMS generally fulfills the Level 1 requirements for reliability while at the same time meeting cost limitations. Elements which did not meet these requirements include beryllium, tellurium, cobalt, manganese, and scandium. Further studies have been initiated to improve analyses of these elements.

KEY WORDS: Reliability, spark source mass spectrometry, environmental assessment, fly ash.

INTRODUCTION

The Process Measurements Branch, Industrial Environmental Research Laboratory (IERL-RTP), United States Environmental Protection Agency,

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has developed a phased approach for assessment of environmental pollution from industrial/energy processes.[1] Experience in the field of source assessment indicated that although in the planning stage many source assessments based on measurement of specific pollutants may seem adequate in the final analysis, more data than had been collected may be required. Furthermore, after the assessments are complete, information is often desired on new pollutants. For these reasons, the complete environmental assessment (EA) has become the accepted policy for IERL-RTP.

In order to achieve a complete EA, it should be carried out with no *a priori* assumptions about the make-up of the streams. All process discharge streams (gas, liquid and solid) must be analyzed so that all possible hazards will be considered. Since the complete EA involves a considerable commitment of resources, it has been necessary to consider the most efficient approach to characterization of a source. The direct approach to EA entails the use of the highest level techniques such as gas chromatography, mass spectrometry, and high-performance liquid chromatography for organics; and atomic absorption spectrometry, wet-chemical methods, X-ray diffraction, and infrared spectrophotometry for inorganic analysis. An alternative is the phased approach in which each stream is first surveyed with a comprehensive, specifically defined procedure so that all components will be accounted for. Under the survey stage it is not necessary to require high precision and exact compound structure. This stage can then be followed by the use of specific techniques for more precise component definition. By using the two stages properly it will be possible to make the first stage general enough to account for a range of possible hazards and then allow the more concentrated use of sophisticated analytical tools to narrow in on the species which have been identified in the first stage. If information about temporal variations of hazardous components identified in the second stage is needed, then techniques more suited to long-term monitoring may be employed as the third phase of analysis.

DESCRIPTION OF LEVEL 1

It can be seen that the survey phase (Level 1) is very important. It is depended on to call attention to any species present which could be hazardous to the environment. Under Level 1 specifically defined procedures accomplish the sampling and analysis in a thorough and efficient manner. These procedures have been designed as a result of considerable laboratory and field testing and must be followed meticulously to avoid pitfalls.[2] The analytical techniques which have been

selected for Level 1 are:

	Technique	*Quantity measured*
Physical	Cyclones	Particle size
	Optical microscopy	Morphology
Chemical	Spark source mass spectrometry	Elements
	Gas chromatography	Gases and vapors
	Liquid chromatography	Organic classes
	Infrared spectroscopy	Functional groups
	Low resolution mass spectrometry	Organic categories and compounds
Biological	Ames test	Mutagen determination
	Chinese hamster ovary test	*In vitro* toxicity
	Rabbit alveolar microphage test	*In vitro* toxicity
	Rodent acute toxicity test *in vivo* toxicity	*In vitro* toxicity
	Fish acute toxicity test *in vivo* toxicity	*In vitro* toxicity
	Algal bioassay	Growth response

These techniques have been chosen for their capacity to provide a complete, comprehensive set of information to determine the presence of any compound or family of compounds with a high degree of reliability. The Level 1 procedures combine them in a scheme which estimates the quantities present within a factor of 3. With the prescribed sample sizes, this precision is sufficient to trigger a response to go on to Level 2 analysis if any component is present at a level considered hazardous.

RATIONALE FOR SSMS ANALYSIS

According to the Level 1 philosophy, it is necessary to obtain an elemental analysis of the various samples. The types of samples encountered in Level 1 environmental assessments include inorganic solids, organic solids, aqueous solutions, organic solutions, samples sorbed on organic resins, and etc.

The main criterion considered in the choice of the elemental analysis technique was the ability to detect, in a 50-mg sample, all elements from beryllium to uranium, except gases and mercury, with a sensitivity consistent with proposed IERL-RTP multimedia environmental goals. Any technique chosen for Level 1 had to be capable of detecting this range of elements because Level 1 analyses must produce a complete characterization of a source without consideration of prior knowledge of

source species. This philosophy makes comparisons of all sources possible because of uniform sampling and analysis. Also, it precludes the possibility of missing species that might not be considered a threat now but may come under suspicion later. Other principal criteria were minimal sample preparation and minimal cost per element.

STATEMENT OF PROBLEM

Since SSMS is depended on to produce a large amount of data, it is important that its level of reliability be understood. The design point for Level 1 requires analyses within a factor of 3 of the true value with 95% confidence so that hazardous species may be detected at their hazard levels with the sample sizes designated for Level 1.

SSMS provides analytical data for 73 elements, which makes the evaluation of reliability a large undertaking. Also, the cost of a spark source run, while economical on a per-element basis, is high. Hence, multiple replicate runs from the same sample are limited. Adding to the difficulty is the absence of standard samples for environmental analysis, which are not recognizable.

The data for this study was generated from an audit carried out by IERL-RTP to check the performance of various laboratories involved in Level 1 assessments. The audit samples for the inorganic phase of Level 1 were prepared by an independent organization using the NBS 1633 fly ash as the basic component. The basic fly ash was diluted with silica and spiked with eight elements. The samples were then distributed to the six audited laboratories with instructions that they were to be processed in exactly the same manner as Level 1 field samples are processed. Since only one audited laboratory had SSMS capability, the others sent their samples out to two commercial laboratories. Beyond the Level 1 requirement, the laboratories were required to have each sample film read visually by the just disappearing line (JDL) technique and by recording densitometry (DEN). The analyses from this audit produced more SSMS data on a single sample than IERL-RTP had collected before. Even so, the total amount of data from this study is quite sparse. The sample analyzed by JDL yielded only 9 replicates while the sample analyzed by both JDL and DEN yielded 14 replicates. For the purposes of this study only those elements whose concentrations were between the minimum detection limits and 1% were chosen.

With the availability of these data a number of questions pertinent to Level 1 EA could be considered.

1) Is the accuracy of the analytical techniques "acceptable"? In

particular, are the two techniques comparable with regard to accuracy?

2) Is the elemental analysis by SSMS reliable with regard to precision? If so, what are the implications of the analytical error on the requirements for sampling error in order to achieve the reliability criteria of Level 1?

3) Which elements do not meet the Level 1 criteria for precision and require improvement in sample preparation or instrument operating techniques?

4) Since the limits of the distribution of SSMS data have been described empirically by multiplicative factors rather than additive factors, the data are assumed to follow (approximately) a log-normal distribution (rather than the normal distribution). Do the SSMS data validate this assumption?

STATISTICAL METHODS

Evaluation of the reliability of the SSMS data involves the application of various statistical methods. Statistical analyses were conducted for simple descriptive purposes (mean, standard deviation, percent standard deviation, etc.), to estimate and test the accuracy and precision of the analytical techniques (JDL and DEN), and to evaluate the distributional properties of the data.

The accuracy of the techniques is measured by the bias and % bias, where

$$\text{bias} = \text{observed mean} - \text{actual mean}$$
$$\%\ \text{bias} = 100 \times \text{bias/actual mean}.$$

In order to measure the precision, or measurement error, the percent (relative) standard deviation and the factor of precision were utilized. The percent standard deviation is the ratio of the observed standard deviation to the observed mean, while the factor of precision (FOP) is given by

$$FOP = \exp(s \cdot t),$$

where

t = appropriate percentile of the t-distribution

s = standard deviation of the logged data values.

The FOP corresponds to the ratio of the upper $100 \times (1-\alpha)\%$ confidence limit for a predicted observation to the estimate of the predicted observation (observed geometric mean). It expresses the confidence limits for the predicted observation as factors of its estimate.

Justification for this index involves the fact that the data are considered to follow the log-normal distribution; hence, the usual symmetric confidence interval about the mean is not valid. In the context of this study further support for this approach is based upon current empirical quantification of analytical results in terms of multiplicative factors instead of additive factors.

Tests of significance of the bias are based upon the assumption that the observed bias is approximately normally distributed with standard deviation equal to that of the observed mean. The test of significance of the difference in accuracies between JDL and DEN is based upon the same assumption regarding the observed means and is implemented by a two-sample test for equality of means, assuming equal variances.

No tests of significance for the precision were conducted; however, a measure of relative precision, the sensitivity ratio, is calculated for each element in the combined JDL/DEN data set. This ratio is defined as s_1/s_2, where s_1 and s_2 are the observed standard deviations for the two techniques. A reasonable range over which to expect this ratio to vary, assuming that the true precisions are the same, is 0.5 to 2.0.

Estimation of the analytical error from the data requires a clear definition of this error. We included all sources of variation associated with the same "measuring device". In particular, it was necessary to consider the variation due to the different audit laboratories. This source of variation was included in the analytical error for two reasons:

1) the audit laboratories sent *identical* samples to the same commercial laboratory for analysis. No systematic variation from sample to sample should therefore be expected; and
2) the within-sample variation was artificially low (near zero in a few cases) and probably underestimates the true analytical error.

The Kolmogorov statistic[3] was utilized to test and compare the goodness-of-fit of the normal and log-normal distributions. The test statistic is calculated by finding the maximum distance between the observed and hypothesized distribution functions for each set of data. The statistic is then compared to quantiles of the test statistic to determine statistical significance. Appendix 2 gives further details regarding this method.

A comparison of the two statistics derived from the normal and log-normal distributions can be used as a discriminator for choosing the "better-fitting" distribution. For those cases in which both hypothesized distributions are rejected by the test, no choice is made. Otherwise, the distribution whose test statistic is smaller is determined to be the distribution which better describes the data.

RESULTS

The results are presented in two sections, one for the JDL data and the other for the combined JDL and DEN data.

(a) JDL analysis

The results of the JDL analysis are summarized in Table I. Accuracy, as measured by the % bias, is given in the 5th column. Of the 24 elements analyzed, 13 were biased beyond 20% of the true concentrations. Ten of these biases were found to be statistically significant ($\alpha = 0.05$). Particularly inaccurate results were obtained for bromine and chlorine, both of which were grossly overestimated. Also poorly estimated were germanium, gallium, niobium, strontium, and samarium, all biased over 50%. Particularly accurate analyses were recorded for zinc, nickel, cobalt, vanadium, cerium, yttrium, and rubidium, all of which were less than 10% biased.

Relatively precise measurements were made on all of the elements with the notable exception of scandium, cobalt, and chlorine, whose errors approached 50% of the mean. When analyzed on the log-scale, cobalt and scandium had FOP's exceeding 3.0. Other elements which were quite imprecisely measured were bromine, gallium, manganese, tin and zirconium.

Statistical analysis of the distributional characteristics of the JDL data corroborated the assumption that the data follow an underlying log-normal distribution. For the 24 elements on which data were collected, 19 comparisons were made between the normal and log-normal goodness-of-fit statistics. Sixteen of these comparisons indicated a log-normal fit to the data. For four elements neither distribution was seen to yield a satisfactory fit to the data. While only nine data values were used in the fitting process, too few for a definitive decision regarding distributional form for a particular element, the totality of evidence from all 24 elements strongly supports the idea of an underlying log-normal distribution for these data. Table II summarizes these results.

The 7th column of Table I lists the sampling factor of precision (sFOP) which must be reached in order for the *total* factor of precision (accounting for both sampling and analytical error) to be less than 3.0 (see Appendix 1 for the derivation of sFOP). This index is a useful indicator of the sampling precision which would be required, assuming a particular analytical error, to reach the limits of variability imposed by Level 1 restrictions. For those elements whose analytical FOPs are already greater than 3.0, no estimate of the required sFOP can be calculated.

TABLE I

STATISTICAL SUMMARY: SSMS DATA ANALYZED BY THE JDL TECHNIQUE (N = 9)

ELEMENT	$\bar{X}$	S	% S	% BIAS	FACTOR OF PRECISION (FOP)[1]	SAMPLING FOP [2]
BR	41.89	12.74	0.30	610**	1.95	2.56
GE	5.67	1.41	0.25	−55**	1.81	2.65
GA	32.41	15.22	0.47	65*	3.05	–
ZN	108.3	28.80	0.26	6	1.87	2.61
CU	52.89	26.33	0.50	−16	2.43	2.22
CO	18.56	12.93	0.70	−0.2	3.71	–
MN	209.7	122.2	0.58	−13	3.27	–
CR	83.33	34.87	0.42	30	2.46	2.20
V	99.78	18.72	0.19	−4	1.51	2.83
SC	10.89	5.71	0.52	−16	3.39	–
CL	114.1	53.5	0.47	443**	2.63	2.07
NI	206.2	66.6	0.32	−0.4	1.88	2.61
PB	95.0	34.30	0.36	−37**	2.26	2.34
TL	1.44	0.53	0.37	−28*	2.32	2.30
SM	9.22	2.86	0.31	54**	1.84	2.63
CE	74.22	20.31	0.27	4	2.04	2.50

LA	56.0	23.82	0.43	40	2.92	1.85
SN	1.77	0.68	0.39	−36*	2.63	2.07
MO	7.78	1.99	0.26	−32**	1.95	2.56
NB	18.89	5.09	0.27	−53**	1.89	2.60
ZR	123.33	40.86	0.33	−16	2.06	2.49
Y	32.78	13.06	0.40	9	2.25	2.35
SR	603.3	184.0	0.30	−56**	2.22	2.37
RB	51.11	16.72	0.33	−9	2.07	2.48

1. $t = t_{\alpha}$; .975 = 2.306
2. Maximum such that total FOP ≤ 3.0

** Indicates statistical significance at α=0.01
* Indicates statistical significance at α= 0.05

Improvements in analytical techniques must be made in these cases before Level 1 requirements can be met. Since sFOP is calculated assuming a "large" number of observations would be used to measure sampling variability, then sFOP must be adjusted upward for sample sizes lower than 50 (Appendix 1).

(b) Combined JDL and DEN analysis

A particular goal of this investigation was to compare the two analytical techniques. Although only a limited amount of data was available for this purpose, comparisons were made on the basis of both precision and accuracy. The results of the two-sample *t*-tests indicate that there were no significant differences between the two techniques in terms of accuracy. In only one case was a difference judged "significant"; however, the absolute difference in biases was quite small. The 5th, 6th and 7th columns of Table III list the results of the comparisons. In terms of precision, the techniques do not differ in any fundamental way, as indicated by inspection of the sensitivity ratio (11th column, Table III). Because of these results, the data from the two techniques were lumped together for the remaining statistical analyses.

TABLE II **KOLMOGOROV GOODNESS-OF-FIT STATISTICS**

JDL ONLY DATA (N=9)								JDL AND DENSITOMETER COMBINED DATA (N=14)			
ELEMENT	NORMAL	LOG-NORMAL	"BETTER" FITTING DISTRIBUTION	ELEMENT	NORMAL	LOG-NORMAL	"BETTER" FITTING DISTRIBUTION	ELEMENT	NORMAL	LOG-NORMAL	"BETTER" FITTING DISTRIBUTION
BR	0.212	0.172	LOG-NORMAL	PB	0.257	0.225	LOG-NORMAL	NI	0.209	0.150	LOG-NORMAL
GE	0.237	0.208	LOG-NORMAL	TL	0.356**	0.356**	–	AS	0.275**	0.222	LOG-NORMAL
GA	0.242	0.199	LOG-NORMAL	SM	0.332**	0.324**	–	CD	0.246*	0.156	LOG-NORMAL
ZN	0.149	0.128	LOG-NORMAL	CE	0.196	0.196	–	BE	0.283**	0.192	LOG-NORMAL
CU	0.417**	0.346**	–	LA	0.171	0.152	LOG-NORMAL	U	0.137	0.156	NORMAL
CO	0.319**	0.257	LOG-NORMAL	SN	0.300*	0.348**	–	PT	0.357**	0.313**	–
MN	0.304**	0.251	LOG-NORMAL	MO	0.211	0.252	NORMAL	GD	0.290**	0.308**	–
CR	0.342**	0.255	LOG-NORMAL	NB	0.175	0.223	NORMAL	ND	0.145	0.145	–
V	0.236	0.163	LOG-NORMAL	ZR	0.310	0.255	LOG-NORMAL	I	0.180	0.155	LOG-NORMAL
SC	0.183	0.153	LOG-NORMAL	Y	0.271	0.203	LOG-NORMAL	TE	0.187	0.218	NORMAL
CL	0.159	0.083	LOG-NORMAL	SR	0.191	0.216	NORMAL	SB	0.241*	0.181	LOG-NORMAL
NI	0.234	0.163	LOG-NORMAL	RB	0.220	0.186	LOG-NORMAL	SE	0.180	0.158	LOG-NORMAL

* – Statistical significance at $\alpha = 0.05$

** – Statistical significance at $\alpha = 0.01$

TABLE III

STATISTICAL SUMMARY: SSMS DATA ANALYZED BY JDL AND DENSITOMETER TECHNIQUES (N = 14)

ELEMENT	$\bar{X}$	S	% S	% BIAS OVERALL	% BIAS JDL	% BIAS DEN	TEST OF JDL vs. DEN	FACTOR OF PRECISION [1]	SAMPLING F.O.P.	SENSITIVITY RATIO
NI	197.9	62.7	0.32	−4	1	−10	NS	1.87	2.56	1.49
AS	34.71	10.21	0.29	2	7	−4	NS	1.73	2.66	1.47
CD	5.71	2.89	0.51	−79	−75	−83	NS	2.56	2.00	3.84
BE	5.13	6.54	1.27	−15	−37	8	NS	14.91	–	0.60
U	11.93	4.57	0.38	99	107	91	NS	2.37	2.16	0.59
PT	16.0	3.9	0.24	−83	−83	−82	NS	1.66	2.71	1.10
GD	3.07	1.33	0.43	−17	−34	3	NS	2.38	2.15	0.53
ND	18.07	6.28	0.35	1.5	3	0.2	$p < 0.10$	2.05	2.42	1.84
I	0.521	0.238	0.45	−63	−60	−65	NS	2.87	1.72	1.04
TE	0.414	0.235	0.57	−83	−86	−80	NS	3.24	–	0.66
SB	3.57	1.45	0.41	5	18	−8	NS	2.27	2.24	2.03
SE	18.43	2.14	0.12	19	18	20	NS	1.27	2.94	1.14

1. $t = t_{.975} = 2.16$

In general, the overall accuracy of the SSMS data from the combined set was poor. Of the 12 elements, five were biased beyond 50% of their true value. The biases of six elements were judged statistically significant ($\alpha = 0.05$); these included cadmium, uranium, platinum, iodine and tellurium. Elements whose overall biases were quite small (<10%) included nickel, arsenic, antimony, and neodymium.

Based upon the magnitude of the FOP, beryllium and tellurium are problem elements with regard to precision. Each of these elements had FOPs larger than 3.0. The analytical precision associated with cadmium and iodine could be improved as well. Sampling error for these four elements would have to be quite small for Level 1 requirements to be met.

Evaluation of the distributional form of the combined data yielded similar results to the JDL data. Of the 12 elements analyzed, 9 were seen to be described satisfactorily by the log-normal distribution. Where discrimination between the normal and log-normal distributions was possible, seven out of nine elements were better fitted by the log-normal distribution (Table II). This evidence gives added support to the notation that SSMS data are log-normally distributed.

TROUBLESOME ELEMENTS

The results of the statistical analyses of the SSMS identified some "troublesome" elements for which analytical measurement is not satisfactory. These elements were inaccurate beyond a factor of 50%, or too imprecise to be measured within a factor of 3 with 95% confidence, or both.

Those elements measured by JDL only which did not meet at least one of the criteria are bromine, chlorine, cobalt, gallium, germanium, manganese, niobium, samarium and strontium. Of these elements gallium met neither criteria.

The elements measured by both JDL and DEN and which did not meet at least one of the two criteria are beryllium, cadmium, iodine, platinum, tellurium and uranium. Tellurium was the only element meeting neither criteria.

CONCLUSIONS

In spite of the relatively small amount of data to work with, some general conclusions are warranted from this study. First, SSMS provides elemental analyses which meet Level 1 requirements satisfactorily while remaining cost effective. Secondly, SSMS does not provide a completely satisfactory analysis for each element. Indeed, this is quite impossible since various conditions favoring the analysis of certain elements inhibit the analysis of other elements.

With regard to the particular questions posed at the beginning of the study, the following conclusions can be made:

1) Visual reading of SSMS films yields results which are comparable to densitometry; however, both techniques fail to give satisfactory accuracy on a few elements.

2) Most of the elements were analyzed within the limits of precision required by Level 1. If the sampling error for these elements is no larger than that of the analytical error, then for a majority of elements the overall requirements of Level 1 for variability will be met.

3) Certain "troublesome" elements have been identified and studies have been initiated to improve the analytical results from these elements.

4) SSMS data appears to follow the log-normal distribution, justifying the concept of multiplicative limits in distribution, which has been used to characterize the variability of the data in this report.

Of the mentioned troublesome elements, iodine and tellurium were present in low enough concentrations so that their response would be in the flat or "toe" region of the calibration curve where poor precision could be expected.

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Appendix 1

KOLMOGOROV GOODNESS-OF-FIT TEST

The Kolmogorov goodness-of-fit statistic is one of several statistics that can be used to test the goodness-of-fit of a parametric distribution to data. A particular variation of this statistic can be used to test whether a group of data arises from an underlying normal distribution (or a log-normal distribution, if applied to logged data). The test statistic is defined to be the maximum vertical difference between the hypothesized and observed distribution functions. Hence,

$$D = \sup_x |F(x) - S(x)|$$

where

$F(x)$ = "hypothesized" distribution function

$S(x)$ = "observed" distribution function.

Figure 1 gives a pictorial representation of D.

The hypothesis that the data follow a normal (or log-normal) distribution is rejected at the 0.05 level of significance if D exceeds the 0.95 quantile (Ref. 3, Table 15, p. 398).

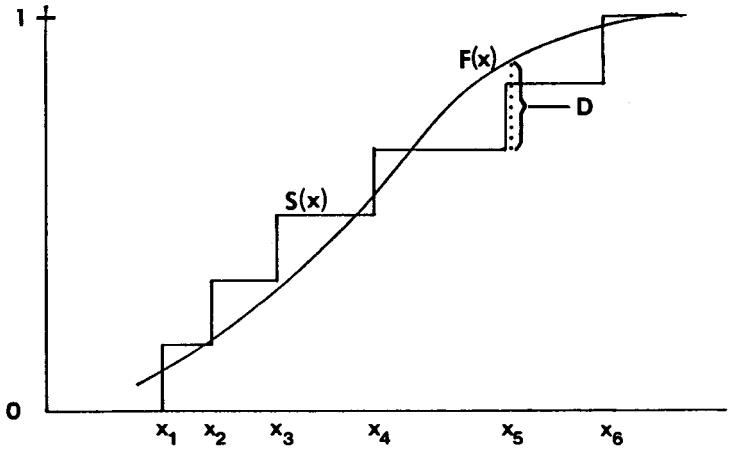

FIGURE 1

Appendix 2

FACTOR OF PRECISION

The factor of precision (FOP) is defined as the ratio of the upper limit of a two-sided $100 \times (1-\alpha)\%$ confidence interval for a predicted observation or measurement to the estimate of the predicted observation of the variable being measured. It is interpreted as an index which expresses the confidence limits for an observation as a multiplicative factor of the predicted value estimated from the data.

A necessary assumption which accompanies this approach to constructing confidence intervals is that the data from which the FOP is estimated follow an underlying log-normal distribution.

The derivation of the FOP can be described in a series of steps:

1) Obtain the sample data, denoted by $(x_1, x_2, \ldots, x_{n_1})$.

2) Let $x' = \log(x)$.

3) Calculate $\bar{x}'$ and s', the sample mean and sample standard deviation of the values of $\log(x)$.

4) Construct the $100\times(1-\alpha)\%$ confidence interval for the predicted value of x', which is

$$(\bar{X}'\pm t_1\cdot s'),$$

where

$t_1=(1-\alpha/2)-$percentile of the t distribution with n_1-1 degrees of freedom.

5) $\text{FOP}=\dfrac{\exp(\bar{X}'\pm t_1 s')}{\exp(\bar{X}')}=\exp(t_1\cdot s').$

The allowable factor of precision for sampling error (sFOP) is calculated such that the total FOP, involving both sampling and analysis in the error, will not exceed 3. The derivation of sFOP proceeds as follows:

1) Let

$$s^2=s_1^2+s_2^2,$$

where

$s_1^2=$analytical error (measured on the log-scale)

$s_2^2=$sampling error (measured on the log-scale).

2) Require that $\exp(s\cdot z)=3.0$, where $z=(1-\alpha/2)-$percentile of the standard normal distribution

3) $s=\dfrac{\ln 3}{z}$

4) Since $\text{FOP}=\exp(s_1-t_1)$, $s_1=\dfrac{\ln \text{FOP}}{t_1}$

5) $s_2^2=s^2-s_1^2=\left(\dfrac{\ln 3}{z}\right)^2-\left(\dfrac{\ln \text{FOP}}{t_1}\right)^2$

6) $\text{sFOP}=\exp(z\cdot s_2)=\exp\left(z\left[\left(\dfrac{\ln 3}{z}\right)^2-\left(\dfrac{\ln \text{FOP}}{t_1}\right)^2\right]^{0.5}\right).$

Since sFOP is calculated assuming an unknown (but large) number of observations would be used to measure sampling variability, then the calculation must be adjusted if the sample size is known. Let n_2 represent the number of observations used to measure sampling error (n_1 is the number of observations used to measure analytical error). The calculations are adjusted by:

1) Step 3: $s=\dfrac{\ln 3}{t_3}$, where $t_3=(1-\alpha/2)$ percentile of the t-distribution with n_1+n_2-2 degrees of freedom

2) Step 5: $s_2^2 = \left(\frac{\ln 3}{t_3}\right)^2 - \left(\frac{\ln \text{FOP}}{t_1}\right)^2$

3) Step 6: $\text{sFOP} = \exp(s_2 . t_2) = \exp\left(t_2 \left[\left(\frac{\ln 3}{t_3}\right)^2 - \left(\frac{\ln \text{FOP}}{t_1}\right)^2\right]^{0.5}\right)$

where $t_2 = (1 - \alpha/2)$ percentile of the t-distribution with $n_2 - 1$ degrees of freedom.