Most environmental monitoring data are presented without regard to their accuracy. Rarely, if ever, are the data accompanied by quantitative measurements of the errors inherent in them. In spite of this, permits are being written with metals and cyanide at the detection level. This article, which is an expanded version of a paper presented by Tom Martin, CEF, at AESF SUR/FIN® ’93—Anaheim, describes several procedures to identify sources and quantify the magnitude of calibration errors. A study conducted by an independent laboratory indicates that some errors may be as high as ±100 percent of the mean concentration value.

Today, National Pollutant Discharge Elimination System Permits (NPDES) and sometimes even pretreatment permits are being written with metals and cyanide limits at ever-decreasing concentrations. This is being done without regard to the ability of current test methods to accurately quantify metal concentrations at these levels. In fact, an interlaboratory correlation study on the analytical variability in discharge monitoring analysis concluded that single data points should not be used for compliance determination. In addition, recent findings of the Battelle Corporation and others have cast a shadow of doubt on the accuracy of accumulated data on metal contamination measurements contained in the files of the U.S. Environmental Protection Agency (EPA). According to a recent report data collected from a U.S. Geological Survey monitoring program over a 30-40 year period, when analyzed by the EPA, showed even pristine waters were in violation of water quality standards for toxic metals.

These findings should bring into question the reliability of environmental monitoring data and the accuracy of the analytical procedures used to measure them. It is interesting, in view of these reports, that the accuracy of data obtained from environmental laboratories is rarely—if ever—questioned by the prosecutors of permit infractions.

Consider the Quandary Of an Indiana Jobshop
The following account actually happened to an electroplating shop in Indiana that discharges effluent directly into a small stream. A new NPDES permit was written that allowed a daily maximum of only 4.4 ppb of cadmium. This prompted the owners to completely remove all cadmium from the shop. One month, approximately one year after the removal of cadmium from the shop, an outside contract laboratory reported four values of cadmium at 4.5 ppb, which is a violation of 100 ppt over the permit limit. These results immediately raise questions of sample contamination in the collection or analysis procedure. But they also raise the question of the ability of the chemist or analytical procedure to distinguish between 4.5 and 4.4ppb. However, when evidence to support the indistinguishability between these numbers was presented to local water management personnel, it was soundly dismissed.

The key point of this article is that permit writers should consider accuracy problems with environmental monitoring data when writing permits. Indeed, all monitoring data should be accompanied by error calculations. World-renowned professor of analytical chemistry James N. Miller, Senior and Pro-Vice Chancellor of Loughborough University of Technology, Leicestershire, England, states that “No quantitative results are of any value unless they are accompanied by some estimate of the errors inherent in them.”

Trace metal concentration data obtained from spectroscopic measurements are subject to errors that affect the accuracy of the data. Fortunately, methods are available that provide solid estimates of these measurement errors and also allow for confidence intervals to be calculated. Procedures will now be described for calculating estimates of the error associated with concentration measurements obtained using calibration curves.

Calibration Curve Error
Random errors in the values for the slope and intercept of a calibration curve are of importance because of their effect on the accuracy of sample concentrations obtained from it. The uncertainty of sample concentrations obtained using the calibration curve may be estimated by a method to be described. Neither spike recoveries nor repeatability studies can measure these uncertainties because they neglect the error inherent in the calibration curve.

Calibration curves are constructed using a series of solutions having a “known” concentration of the element for which the concentration is to be determined in the samples. It is obvious that the accuracy of the standards used to prepare the calibration curve is of critical importance to the overall accuracy of the measurements. However, as a matter of convenience, the concentration of the calibration standards is assumed to be “exactly” as planned, thereby ignoring systematic and random errors, which are clearly present, that are a result of preparation. Many commercial environmental laboratories attempt to demonstrate the accuracy of their methodology using spike recoveries which, of course, ignore preparation errors and, in fact, complicate the matter. Stated plainly, calibration standards do not have “exact” concentrations. This will be demonstrated with propagation of error calculations.

Propagation of Error In Calibration Standard Preparation
Concentration data obtained using atomic absorption spectroscopy are arrived at using a procedure consisting of several steps involving volume, mass and instrumental measurements. Each is subject to an indeterminate uncertainty that contributes to the error of the final result. The propagation of error in the preparation of calibration standards will naturally have an effect on the accuracy of the standards and ultimately on the accuracy of the test samples.

Professor Tyson emphasizes that spike recoveries do not measure accuracy, but rather measure precision. The spike recovery procedure assumes that there is no uncertainty in the sample, the spike or the recovery value. Accuracy is a measure of proximity to the true concentration. The true concentration is not known because of propagation of error through the spike recovery procedure.
The uncertainty of the standard concentration curve error is clearly a source of calibration curve error. For the purpose of demonstrating the effect of these uncertainties on the accuracy of the calibration standards, let us examine the procedure for the preparation of a 1.0 mg/L standard. The procedure typically involves the measurement of an aliquot of a commercially available 1000 mg/L standard and subsequent dilution to the appropriate volume. The calibration standard has an accuracy of ± 1 percent; the pipette, ± 0.7 percent; and the volumetric flask, ± 0.03 percent.

The propagation of error may be calculated as the maximum or minimum amount of uncertainty in the concentration of the calibration standard. However, it is usually calculated using equation (1), which provides a more probable measure of the uncertainty.

\[ \sigma_\text{c} = (\sigma_\text{S}/S)^2 + (\sigma_\text{P}/P)^2 + (\sigma_\text{V}/V)^2 \]

The standard deviation, \( \sigma_\text{c} \), of a 1.0 mg/L standard can be determined from the standard deviations of the standard, the pipette and volumetric flask as follows:

\[ (\sigma_\text{S}/S)^2 = (\pm 10/1000)^2 = 1 \times 10^{-4} \]
\[ (\sigma_\text{P}/P)^2 = (\pm 0.7/1000)^2 = 4.9 \times 10^{-5} \]
\[ (\sigma_\text{V}/V)^2 = (\pm 0.03/1000)^2 = 9.0 \times 10^{-6} \]

Using Equation 1, the standard deviation of the 1.0 mg/L is: \( \sigma_\text{c} = 0.0126 \) mg/L.

The concentration of the standard is then 1.0 mg/L ± 12.6 µg/L, and the coefficient of variation (CV) is 1.26 percent. If no errors cancel, however, the coefficient of variation can be as high as 1.7 percent, even if no systematic errors occur in preparation. This may seem insignificant, but uncertainty in the supposedly “exact” calibration standards contribute to errors in the calibration curve. These have a dramatic effect on the accuracy of sample concentrations obtained from the curve as demonstrated in a repeatability study performed at our request by an outside contract laboratory.

For the study, a chemist prepared standard solutions for the calibration curve from a commercially available 1000 ppm cadmium standard. Absorbance values were measured for the standards and a calibration curve constructed. The concentrations of the standards and their respective absorbance values are presented in Table 1, along with the regression function and correlation coefficient obtained from the best fit line. The calibration curve is shown in Fig. 1.

The measurement of the standard having a concentration of 0.01 ppm was repeated six times, along with another solution of “known” concentration that was not used in the calibration curve. The results are given in Table 2.

On the basis of the results, the chemist believed that the accuracy and the repeatability of the method were acceptable to a high degree of confidence.

### Table 1
Calibration Curve Data

<table>
<thead>
<tr>
<th>Std. Number</th>
<th>Std. Concentration</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>blank</td>
<td>0.000</td>
</tr>
<tr>
<td>2</td>
<td>0.010 ppm</td>
<td>0.004</td>
</tr>
<tr>
<td>3</td>
<td>0.100 ppm</td>
<td>0.041</td>
</tr>
<tr>
<td>4</td>
<td>0.200 ppm</td>
<td>0.082</td>
</tr>
<tr>
<td>5</td>
<td>0.500 ppm</td>
<td>0.196</td>
</tr>
</tbody>
</table>

Correlation coefficient \( r = 1.0 \)
Regression function \( y = 1.0835 \times 10^{-3} + 0.392x \)

### Table 2
Repeatability Study Using Cd Standard Solutions

<table>
<thead>
<tr>
<th>Trial</th>
<th>Absorbance</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.004</td>
<td>0.008</td>
</tr>
<tr>
<td>2</td>
<td>0.004</td>
<td>0.008</td>
</tr>
<tr>
<td>3</td>
<td>0.004</td>
<td>0.009</td>
</tr>
<tr>
<td>4</td>
<td>0.005</td>
<td>0.009</td>
</tr>
<tr>
<td>5</td>
<td>0.004</td>
<td>0.008</td>
</tr>
<tr>
<td>6</td>
<td>0.005</td>
<td>0.008</td>
</tr>
<tr>
<td>7</td>
<td>0.004</td>
<td>0.008</td>
</tr>
</tbody>
</table>

Avg. = 0.0043
Avg. = 0.0083

### How to Estimate Sample Concentration Error

The standard procedure to calculate the error of a concentration value obtained from a given absorbance value has been elaborated in analytical chemistry books.

![Fig. 1—AAS calibration curve used in repeatability study.](image1)

![Fig. 2—Calibration curve; 95-percent confidence interval.](image2)
Equation (2) is the general form used to estimate the standard deviation of a concentration calculated from a calibration curve. Details on the use of this equation may be found in references 3 and 6.

\[
(2) \quad S_{xo} = \frac{1}{b} \left( \frac{1}{m} + \frac{1}{n} + \frac{(y_0 - \bar{y})^2}{b^2 \sum (x_i - \bar{x})^2} \right)^{1/2}
\]

Table 3 contains the standard deviation calculated using equation (2), and the 95-percent confidence interval (t = 2.57) for each calibration standard concentration. The standard deviation and the 95-percent confidence interval were calculated for the \(X_o\) values obtained by substituting the absorbance values of the calibration standards into the regression function. Figure 2 graphically shows the 95-percent confidence interval for the calibration curve. The calibration curve may fall anywhere in the interval, as a result of errors in the slope and \(y\)-intercept.

Sample concentrations calculated using this calibration curve obviously have an uncertainty because of the uncertainty in the calibration curve. The sample concentration uncertainty may also be calculated using Equation 2. Once the standard deviation, \(S_{xo}\), is estimated, it may then be used to calculate confidence intervals for the concentration value, using the student t-test.

This method for error calculation was applied to a datum provided in the repeatability study described earlier. The same calculation was repeated for the 0.02 solution that was not used in the calibration curve. The results were:

<table>
<thead>
<tr>
<th>Absorbance</th>
<th>(X_o)</th>
<th>(S_{xo})</th>
<th>95% Confidence Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.004</td>
<td>7.44 x 10^3</td>
<td>3.60 x 10^3</td>
<td>0.007 ± 0.009 ppm</td>
</tr>
<tr>
<td>0.041</td>
<td>0.1018</td>
<td>3.05 x 10^3</td>
<td>0.102 ± 0.008 ppm</td>
</tr>
<tr>
<td>0.082</td>
<td>0.2064</td>
<td>3.00 x 10^3</td>
<td>0.206 ± 0.008 ppm</td>
</tr>
<tr>
<td>0.196</td>
<td>0.4971</td>
<td>5.38 x 10^3</td>
<td>0.497 ± 0.014 ppm</td>
</tr>
</tbody>
</table>

from the data above, the 95-percent confidence interval that was calculated for the 0.02 ppm standard is 0.018 ± 0.015 ppm. This is ±83 percent of the mean value. Based on this result and good scientific practice, we feel comfortable in questioning the accuracy of any set of atomic absorption measurements that are not accompanied by error calculations. The concentration intervals of the calibration standards were, in some cases, more than 200 percent of the mean concentration value.

“**Our purpose has not been to criticize, but to encourage laboratories to include estimates of error with their results.”**

Software is Available

Our purpose has not been to criticize laboratory personnel for poor analytical technique, but rather to encourage laboratories to include estimates of error with their results. Software is currently available to assist in performing these calculations. There is a need for good scientific practices to be applied to environmental monitoring procedures. In fact, there must be a method established to test the accuracy of data generated that considers all sources of error before permit writers or infraction prosecutors—proceed.

**References**

1. C. Wilber and M.T. Kennedy, Eliminate NPDES Permit Violations with Analytical Variability Adjustments, or why single point data cannot be used to determine compliance, Water Environment Federation, Alexandria, VA (1993).


5. Product Bulletins from Hach Scientific, Loveland, CO; Wheaton, Millville, NJ; and Fisher Scientific.


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