IH for the CSP 2: Standard Analytical Error Or Quadriture in Concentration Uncertainties

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Abstract

To interpret the results of air sampling, the industrial hygienist must take into account experimental uncertainty. Whenever a measurement is made, there is some uncertainty in the result. This is an undisputed fact of physics. When calculations are made based on those measurements, the uncertainties in the values going into the equations combine additively to give an uncertainty in the result. Uncertainties can be estimated analytically, that is by closely examining the entire measurement process, volumes, times, amounts of solutions used, calibration of instruments, statistical variance, etc., and using differential calculus to determine the final uncertainty in the calculation. This is a very time-consuming approach, however. Industrial hygienists estimate uncertainties in concentration measurements using the standard analytical error, or SAE. SAE's are tabulated for validated analytic methods, and represent the percent uncertainty in any one measurement.

Standard Analytic Error

If an industrial hygienist measures the concentration of one sample to be 20 ppm, and the SAE for that material is 0.20, the uncertainty in the concentration, ΔC, is,

$$\Delta C = (SAE)\, C = (0.20)\, 20 \text{ ppm} = 4 \text{ ppm} \quad . \qquad 2$$

We say that there is 95% confidence that the actual concentration was between 16 ppm and 24 ppm, or that there is 95% confidence that the actual concentration was 20 ppm + 4 ppm. Notice the concentration and the uncertainty have the same units. The upper confidence limit for the concentration, the value that the actual concentration is assumed to be below, is 24 ppm. The lower confidence limit for the concentration is 16 ppm. OSHA requires 95% confidence that an overexposure exists before a citation is issued, i.e., the lower confidence limit must be above the permissible exposure limit, PEL.

The SAE only applies to one concentration measurement. When concentration measurements are used in other calculations, such as time-weighted averages, the uncertainty in the result must be calculated.

Adding in Quadriture

Uncertainties may be added two ways, in quadriture or absolutely. When uncertainties add absolutely, the uncertainty of the sum is the sum of uncertainties. When uncertainties add in quadriture, the uncertainty is the square root of the sum of uncertainties squared. This is analogous to taking the hypotenuse of a right triangle as opposed to the sum of the other sides.

Suppose the uncertainty in the reading of a bathroom scale is 1%. If one bathroom scale is used to measure the weight of ten different people, we expect all the reported weights to be above the actual weight, or all to be below the actual weight. One scale would not be expected to weigh some people heavy and some light. The uncertainty in the sum of the weights of the ten people would be 1%. This is uncertainty that adds absolutely. If, however, ten different scales are used, we would expect some scales to report higher than the actual weight, and some to report lower. These errors would to some extent cancel each other out. The uncertainty in the combined weight of all ten people would be less using ten scales than if only one scale were used. Using one scale, uncertainties add absolutely. Using ten scales, uncertainties add in quadriture.

Uncertainties in contaminant concentrations are assumed to add in quadriture. In industrial hygiene, the goal of measurement is often to determine if employee exposure is above or below published limits, such as the OSHA Permissible Exposure Limits (PEL's), or the ACGIH Threshold Limit Values (TLV's). Because calculation of uncertainties in quadriture is somewhat tedious, the practice in industrial hygiene is to first determine uncertainties added absolutely, and if a conclusion can not be drawn, then calculate in quadriture. Uncertainties added in quadriture are always less than when added absolutely.

Time-Weighted Average

Usually, the analytical method does not allow a single sample to be drawn for the entire shift. When sampling for nuisance dust, for example, it is often necessary to draw a new sample every 15 minutes. The time-weighted average, TWA, air contaminant concentration is calculated to combine the results from many samples into one number representing the entire shift. "Time-weighted" means that if one sample ran twice as long as another, it will have twice the influence on the average. The TWA is given by,

$$TWA = \frac{C_1 t_1 + C_2 t_2 + C_3 t_3 + --- + C_n t_n}{t_1 + t_2 + t_3 + --- + t_n} ,$$

where C_i is the concentration, and t_i the duration of the i^{th} sample.

The uncertainty in the time-weighted average concentration is very easily calculated when uncertainties add absolutely. Neglecting the uncertainty in time, there is an equal percent uncertainty in every term in the numerator of the time-weighted average (equal to the SAE) so the percent uncertainty in the time-weighted average will be equal to the SAE for any individual measurement. The uncertainty in the time-weighted average, ΔTWA, when uncertainties are added absolutely is given by,

$$\Delta TWA = SAE \ (TWA) . \qquad 3$$

There are many mathematically equivalent ways of describing this uncertainty and determining if can be stated with confidence that an overexposure did or did not exist. Two are presented here. One is to determine the upper or lower confidence limit for the time-weighted average. If the upper confidence limit is below the PEL (or other limit), then it can be stated with 95% confidence that an overexposure was not observed. If the lower confidence limit is above the PEL, then it can be stated with 95% confidence that an overexposure was observed. Suppose the time-weighted average concentration was 29 ppm, the PEL was 25 ppm, and the SAE was 0.10. Obviously you will never be able to state with confidence that an overexposure was not observed when the TWA is greater than the PEL, so there is no need to calculate the upper confidence limit. There may, however, not be strong enough evidence to state with confidence that there was an overexposure. The lower confidence limit, LCL, for the TWA must be calculated,

$$\begin{aligned} LCL &= TWA - \Delta TWA \qquad (4) \\ &= TWA - SAE\ \ TWA \\ &= 29\text{ ppm} - 0.10\ (29\text{ ppm}) = 26.1\text{ ppm}\ . \end{aligned}$$

Since the lower confidence limit for the TWA is above the PEL, it can be stated with 95% confidence that an overexposure was observed.

Suppose the TWA had been 21 ppm. Since the TWA is below the PEL it obviously can not be stated with confidence that an overexposure was observed, but that does not necessarily mean it can be stated with confidence that an overexposure was not observed. The upper confidence limit for the time-weighted average must be calculated,

$$\begin{aligned} UCL &= TWA + \Delta TWA \qquad (5) \\ &= TWA + SAE\ \ TWA \\ &= 21\text{ ppm} + 0.10\ (21\text{ ppm}) = 23.1\text{ ppm}\ . \end{aligned}$$

In this example, since the upper confidence limit for the time-weighted average is below the PEL, it can be stated with 95% confidence that an overexposure was not observed.

Consider now a third example. Suppose the calculated TWA were 27 ppm. The lower confidence limit for the time-weighted average concentration is given by,

$$\begin{aligned} LCL &= TWA - \Delta TWA \\ &= TWA - SAE\ \ TWA \\ &= 27\text{ ppm} - 0.10\ (27\text{ ppm}) = 24.3\text{ ppm}\ . \end{aligned}$$

Since the lower confidence limit is below the PEL, but the measured value is above the

PEL, it can not be stated with 95% confidence whether or not an overexposure was observed. This result is in the gray area and uncertainties must be added in quadriture to reduce the uncertainty. To add uncertainty in quadriture, we must return to the equation used to calculate the TWA. To average three concentrations the equation is,

$$TWA = \frac{C_1 t_1 + C_2 t_2 + C_3 t_3}{t_1 + t_2 + t_3} \quad . \qquad 6$$

The uncertainty in this calculation, ΔTWA, ignoring uncertainty in time measurements and adding uncertainties in quadriture is,

$$\Delta TWA = \left[\frac{C_1^2 t_1^2 SAE^2 + C_2^2 t_2^2 SAE^2 + C_3^2 t_3^2 SAE^2}{C_1 t_1 + C_2 t_2 + C_3 t_3} \right]^{1/2} TWA$$

$$= \left[\frac{C_1^2 t_1^2 SAE^2 + C_2^2 t_2^2 SAE^2 + C_3^2 t_3^2 SAE^2}{t_1 + t_2 + t_3} \right]^{1/2}$$

$$= SAE \left[\frac{C_1^2 t_1^2 + C_2^2 t_2^2 + C_3^2 t_3^2}{t_1 + t_2 + t_3} \right]^{1/2} \quad . \qquad 7$$

Notice the numerator of the TWA cancels out the denominator of the preceding expression, leaving only the total time in the denominator of the result.

Let us assume that C_1 = 27 ppm, C_2 = 26 ppm, C_3 = 28 ppm, and t_1 = 180 min, t_2 = 150 min, t_3 = 150 min. The SAE is 0.10 or 10%. Substituting these values into equation 7 gives the uncertainty in the TWA,

$$\Delta TWA = 0.1 \left[\frac{(27\text{ ppm})^2 (180\text{ min})^2 + (26\text{ ppm})^2 (150\text{ min})^2 + (28\text{ ppm})^2 (150\text{ min})^2}{180\text{ min} + 150\text{ min} + 150\text{ min}} \right]^{1/2}$$

$$= 1.57\text{ ppm} \quad .$$

The lower confidence limit is always given by the value minus the uncertainty, or,

$$LCL = TWA - \Delta TWA = 27\text{ ppm} - 1.57\text{ ppm} = 25.43\text{ ppm} \quad .$$

With uncertainties slightly lowered by adding in quadriture, the lower confidence limit is now above the PEL and it can be stated with 95% confidence that an overexposure was observed.

The three examples given above are now described in a different manner. For each example we may ask, "What is the range of values in which there is 95% confidence that the true TWA lies?" For the first example we saw TWA = 29 ppm, and (adding uncertainties absolutely) ΔTWA = 2.9 ppm. The range of concentration in which there is confidence that the true TWA lies is 29 ppm + 2.9 ppm, or 31.9 ppm to 26.1 ppm, since this entire interval is above the PEL, it can be stated with 95% confidence that an over exposure was observed.

For the second example, TWA = 21 ppm and again adding uncertainties absolutely, ΔTWA = 2.1 ppm. The range of confidence is 21 ppm + 2.1 ppm, or 23.1 ppm to 18.9 ppm. Since this interval lies completely below the PEL, it can be stated with 95% confidence that an overexposure was not observed.

For the third example we saw TWA = 27 ppm, and adding uncertainties absolutely, ΔTWA = 2.7 ppm. The range of concentrations within which there was 95% confidence that the true TWA was found was 27 ppm + 2.7 ppm, or 29.7 ppm to 24.3 ppm. Since the PEL lies within this range, it can not be stated with confidence whether or not the employee was overexposed. We obtained a smaller estimate of uncertainty by adding in quadriture, ΔTWA = 1.57 ppm. With this smaller estimate of uncertainty, our confidence range is 27 ppm + 1.57 ppm, or 28.57 ppm to 25.43 ppm. The PEL is seen to fall below this entire range. Therefore, with uncertainty added in quadriture, it can be stated with 95% confidence that an overexposure was observed.

It should be noted that there are still other ways of describing these confidence tests. OSHA uses a method of estimating the uncertainty in the standardized concentration (the concentration divided by the PEL). No matter what method is used to describe the data, however, the conclusions regarding overexposures must be the same.