C53 Is Your Analytical Result Accurate?

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The goal of this presentation is to demonstrate how the method of standard additions (MSA) is an excellent test to determine the accuracy of an analytical result.

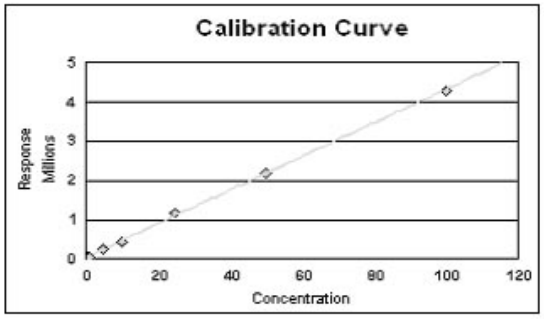
This presentation will impact the forensic community and/or humanity by acting as a reminder that there is a method to check the accuracy of analytical results.

New analytical instruments and more sophisticated analytical methods have lead the data user to rely unconditionally on the accuracy of the environmental measurement. Yet, this measurement is of lower concentrations of a pollutant than ever measured in the past. Environmental chemists, engineers, companies, and regulators are presently concerned with low parts per trillion concentrations. For example, a company has a permitted concentration of mercury of 150 parts per trillion in their plant's effluent to the local sewer authority. Elemental mercury at the parts per trillion levels can be measured by USEPA method 1631 Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry.

The Method: Method 1631E is for the determination of mercury in the concentration range of 0.5 to 100 ng/L (parts per trillion). The sample must be obtained using USEPA method 1669: Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels. In an ultra clean laboratory, the sample is oxidized producing mercury plus two (Hg^{++}). After the oxidation process the mercury ions are reduced to elemental mercury and removed from solution by purging with an inert gas. The elemental mercury is trapped and hopefully many interferences are not trapped and thus, removed from the analysis. The trap is heated releasing the elemental mercury, which is moved to a second trap with the inert gas, and again hopefully removing interferences. The second trap is heated and the elemental mercury is moved to a cell to be measured by atomic fluorescence spectrometry.

The Calibration: The calibration curve from 0.5 to 100 ng/L is given in Figure 1. The correlation coefficient for this calibration curve is 0.999. The instrument responses to low concentrations of mercury in pure water indicate that the method and the laboratory are doing very well.

Figure 1



The Analysis: The effluent sample is analyzed after it has been diluted by a factor of 10. The sample that enters the instrument contains what is then measured at 21 ng/L. After a multiplication by the dilution factor of 10, the reported concentration is 210 ng/L. This is a permit violation. The laboratory is certified for this method by the state and has performed the analysis according to the method. The sample was diluted, thus reducing the possibilities of interferences causing false positives. Is the reported result accurate?

The Method of Standard Additions (MSA): In USEPA SW-846 method 7000A, the method of standard additions is described. This technique is best seen in Figure 2. When the MSA was applied to the diluted sample, the results strongly indicated that the reported value was wrong. The MSA experiments are given in Table 1. The MSA plot is given in Figure 3. With a R^2 of 0.809, the MSA shows there is so much positive interference in the method for this sample that the real mercury concentration may be "ND" (non-detected).

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Figure 2

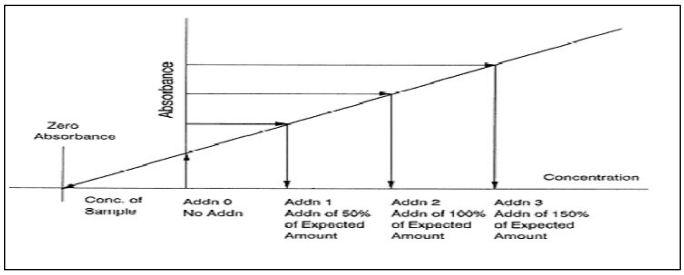
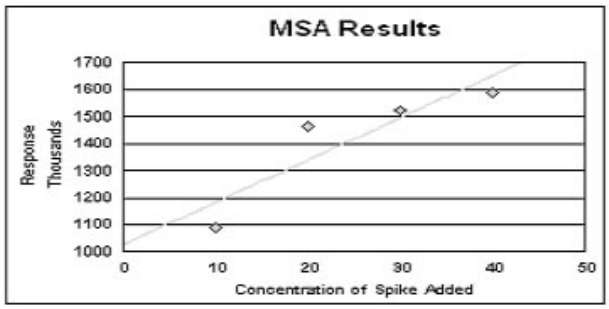


Table 1
Mercury Analysis by Method 1631E

Spike Concentration	Original Concentration	Expected Concentration	Measured Concentratio
10 ng/L	21 ng/L	31 ng/L	23 ng/L
20 ng/L	21 ng/L	41 ng/L	31 ng/L
30 ng/L	21 ng/L	51 ng/L	33 ng/L
40 ng/L	21 ng/L	61 ng/L	34 ng/L

Figure 3



Conclusion: All results from any analytical method can be checked for accuracy using the method of standard additions. The MSA is applicable to organic analyses as well as inorganic analyses by any quantitative method.

Method of Standard Additions, Calibration, Mercury

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