0154.000 ADDRESSING SPIKE AND SURROGATE RECOVERY AS THEY RELATE TO MATRIX EFFECTS IN WATER, AIR, SLUDGE AND SOIL MATRICES POLICY

Level One **Arizona Department of Environmental Quality**

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Issue Date: October 23, 1998

PURPOSE

The Arizona Department of Health Services (ADHS) has not established a comprehensive policy on the issue of matrix spike or surrogate recoveries because they do not have the authority to establish criteria by which ADEQ will either accept or reject data.

This policy will assure that all data submitted to ADEQ meets regulatory requirements and are legally defensible by establishing alternative criteria for when the established method recovery acceptance criteria for matrix spikes and/or surrogates are exceeded.

ADEQ is concerned with the assumption that if spike and/or surrogate recoveries exceed method acceptance criteria and that if those results can be duplicated without re-extracting the sample, the failure of that quality control criteria is a result of matrix effects. Duplication of out-of-range results can be the result of influences other than matrix effects and could be indicative of the method or instrument being out-of-control.

The ADEQ QA/QC Unit believes a more accurate and reliable assessment of possible matrix effects can be established using either a (1) dilution technique, (2) the method of standard additions, or (3) analyzing a laboratory fortified blank (LFB) or a laboratory control sample (LCS). Because ADEQ is a regulatory agency, compliance results must be able to meet all legal constraints and uphold all analytical method requirements.

AUTHORITY

A.A.C. R18-4-106 and R9-14-608.

DEFINITIONS

Data: For the purposes of this policy, data is defined as 'raw data' (examples include but are not limited to calibration curves, chromatograms, spectras, sample preparation and injection logs etc.) and does not include laboratory reports. (Contact the QA unit for further information.)

Laboratory Fortified Blank (LFB): (aka blank spike) An aliquot of organic free reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology (analytical process) is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

Laboratory Fortified Blank Duplicate (LFBD): (aka blank spike duplicate) A duplicate sample of the aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFBD is analyzed exactly like a sample, and its purpose is to determine whether the methodology (analytical process) is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

Laboratory Control Sample (LCS): A sample of clean dirt or sand to which known quantities of the method analytes are added in the laboratory. The LCS is extracted and analyzed exactly like a sample, and its purpose is to determine whether the methodology (sample preparation and analytical process) is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

Laboratory Control Sample Duplicate (LCSD): A duplicate sample of clean dirt or sand to which known quantities of the method analytes are added in the laboratory. The LCSD is extracted and analyzed exactly like a sample, and its purpose is to determine whether the methodology (sample preparation and analytical process) is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method

detection limit.

Laboratory Fortified SampleMatrix (LFM): (aka matrix spike) An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results and therefore determines to what degree the method is successful in analyzing the target analytes. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

Laboratory Fortified Sample Matrix Duplicate (LFMD): (aka matrix spike duplicate) A duplicate sample of the aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFMD is analyzed exactly like a sample, andits purpose is to determine whether the sample matrix contributes bias to the analytical results and therefore determinesto what degree the method is successful in analyzing the target analytes. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFMD corrected for background concentrations.

Matrix: The predominant material, component or substrate which contains the analyte of interest. Matrix is not necessarily synonymous with phase (liquid or solid).

Matrix Interference: Also referred to as matrix effects. Matrix spike interference are those chemical and/or physical interferences that impede the analytical instrumentation in detecting the true value concentration of a target analyte within a sample. One possible source of matrix interferences may be caused by contaminantsthat are co-extracted from the sample and result in a positiveor negative bias. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the sample matrix.

Method of Standard Additions: A technique used most commonly in metals analysis by atomic absorption; however, it can be applied in many areas of the laboratory. It serves to correct for matrix effects in the sample. Aliquots of a sample are spiked with at least three different concentrations of a standard.

Surrogate: A pure analyte, which is extremely unlikely to be

found in any sample, and which is added to a sample aliquot in known amounts before extraction and is measured with the same procedures used to measure other sample components. A surrogate behaves similarly to the target analyte and its use is most often used with organic analytical procedures. The purpose of a surrogate analyte is to monitor method performance with each sample.

POLICY

ADEQ will not accept test results for regulatory purposes when the LFM and/or surrogate recovery exceed the acceptance criteria unless the laboratory has demonstrated that the sample itself is responsible for the QC results exceeding the methods acceptance criteria.

RESPONSIBILITY

The ***ADEQ Program staff*** will be responsible for reviewing the final report or the quality control summary sheets which accompany the final results of the laboratory analysis to verify that matrix spikes and/or surrogate recoveries were within the acceptance criteria. If the program staff are uncertain as to how to evaluate the final report, or if required information is missing, it shall be the responsibility of the program staff to forward the information to the ADEQ QA/QC Unit for review and recommendations.

The ***ADEQ QA/QC Unit*** will review data referred by program staff to ensure that the procedures outlined in Attachment A of this policy were followed by the laboratory and to report their findings to the appropriate ADEQ program staff.

APPLICABILITY

This policy is applicable to all types of water, air, sludge, and soil matrices regardless of the method of analysis.

PROCEDURES

The ***ADEQ program staff*** shall review the final report or the quality control (QC) summary sheet which accompanies the final

report. ADEQ program staff shall assess the results of the LFM and LFMB on the QC Summary sheet to determine if the recoveries are within the acceptance range. If the LFM or LFMB results exceed the established recovery criteria, ADEQ program staff will assess the recovery criteria for those out of range analytes in either the LFB/LFBD or LCS/LCSD. If the required information is not included with the final report or program staff are uncertain as how to evaluate the final report, they shall notify the QA/QC Unit so the QA/QC staff can perform a more thorough evaluation of the results.

The ***ADEQ QA/QC staff***, if necessary, shall request a laboratory data package to review the raw data, determine the validity of the results and compliance with the ADEQ data reporting policy. The QA/QC Unit shall also submit in writing, to the program staff, the data validation findings and the ADEQ QA/QC Unit's recommendations.

ATTACHMENT A

LABORATORY PROCEDURES

The ADEQ policy for addressing spike and surrogate recovery as they relate to matrix effects in water, air, sludge and soil matrices suggests three different techniques (analysis of an LFB/LFBD or LCS/LCSD pair, dilution procedure, or the standard additions technique) which may adequately explain the out-of-range QC results of samples. These three techniques do not represent an all inclusive list for demonstrating matrix effects within a sample and laboratories may have alternate and valid techniques to demonstratematrix interference. These alternate techniques should be discussed with and approved by the ADEQ QA Unit prior to analysis to avoid the rejection of data.

ADEQ also requires the analyses of either an LFB/LFBD, LCS/LCSD or LFM/LFMD pair to satisfy the precision requirements for drinking water methods. More useful information can be obtained regarding precision when comparing samples containing target analytes. Very little usefulprecision information is obtained when comparing the instrument precision using two samples that are non detect. Whenever included in the analytical batch, the laboratory must report the results of the LFB/LFBD or LCS/LCSD in addition to the LFM/LFMD to ADEQ and shall include the numerical values established by the laboratory for the QC acceptance criteria whenever the method has not provided any.

While the method would require a re-extraction of that sample, to confirm matrix interference, if the LFM and/or the LFMB fall outside the method's acceptance criteria, ADEQ will accept the results of the LFB/LFBD or LCS/LCSD which demonstrate that the analytical process is in control. The LFB/LFBD and LCS/LCSD provide an interference free matrix such that if the surrogates and/or matrix spike analytes are within the method's acceptance criteria, then there is compelling data that an instrument is operating properly, the extraction procedure provided no bias, and the method is in control. The LFB/LFBD must be analyzed with the same batch as the LFM/LFMD for ADEQ to accept the LFB/LFBD results. The LCS/LCSD samples must be extracted and analyzed with the same batch as the LFM/LFMD samples for ADEQ to accept the results of the LCS/LCSD samples. The laboratory shall include the numerical values established by the laboratory for the QC acceptance criteria whenever the method has not provided any.

Another option is the dilution technique. The dilution technique is particularly well suited for demonstrating matrix effects in the LFM samples for analyses that don't require extraction procedures. Laboratories performing analytical work for ADEQ that suspect matrix interference in LFM samples may dilute that sample such that all suspected matrix effects are diluted out as well prior to spiking. Once the matrix effects have been diluted out, recovery of the matrix spikes and surrogates should fall within the acceptable recovery criteria established by the method, or the lab if none are given in the method. The dilution of samples suspected of having matrix interference such that interference is no longer a factor strongly suggests that there may have been matrix effectsin the sample and the recovery of the spiked analytes within the acceptance range demonstrates the instrumentation and method are in control. ADEQ will accept use of the dilution technique to demonstrate matrix effects in LFM and LFMD samples because notevery sample is matrix spiked and it cannot be assumed that the matrix effects observed in one sample are representative of the entire sample batch.

Because the dilution technique raises the reporting level of an analyte, it may not be a suitable technique to demonstrate matrix interference if the resulting reporting level exceeds the regulatory (trigger) or action level. The method of standard additions would be a preferred technique to help correct for positive or negative bias in the samples because this technique is unlikely to raise the reporting level of regulated contaminants that may be present in the sample. The method of standard additions usually employs aliquots of a digested or extracted sample which are spiked with at least three different concentrations of astandard. The standard additions are chosen to bracket the unknown sample concentration and the response of the instrument must be linear.

Those samples whose matrix spikes or surrogate recoveries continue to fall outside the acceptance criteria after any of the above three techniques, or an alternate method pre-approved by the ADEQ QA Unit have been employed, shall be reviewed by ADEQ on a case-by-case basis. Any results reported which are affected by matrix interference shall be flagged as an estimated quantitation.