



IN REPLY REFER TO:

United States Department of the Interior

U.S. GEOLOGICAL SURVEY

Box 25046 M.S. 407

Denver Federal Center

Denver, Colorado 80225

NATIONAL WATER QUALITY LABORATORY TECHNICAL MEMORANDUM 1994.07

February 10, 1994

To: Assistant Chief Hydrologist for PC&TS
Regional Hydrologists
Chief, Office of Water Quality
Assistant Chief, Office of Water Quality
Deputy ACH for PC&TS for NAWQA
Area Hydrologists
District Chiefs
Regional Water-Quality Specialists
Assistant Regional Hydrologists for NAWQA
District Water-Quality Specialists
Chiefs, NAWQA Study-Units
Chief, Ocala Project Office
Chief, Yucca Mountain HIP
Chief, Branch of Quality Assurance
Employees, National Water Quality Laboratory

From: Peter F. Rogerson, Chief
National Water Quality Laboratory
Branch of Analytical Services

Subject: Description and use by districts of Laboratory QC sample information in organic determinations

Author: Mark Sandstrom (303) 467-8086 (SANDSTRO)

Revision: None

PURPOSE

This memo describes the laboratory quality-control (QC) sample information available for district use in interpreting the results of determinations of organic substances in environmental samples. The general quality-assurance (QA) practices for analytical activities used by the National Water Quality Laboratory (NWQL) are outlined in Pritt and Raese (1992). Friedman and Erdmann (1982) describe more general QA practices for chemical and biological analyses of water and sediment samples. This memo provides more specific information about the type, purpose, and frequency of

laboratory QC samples in organic analyses, and it provides some examples of their use by districts in interpreting results of environmental samples.

BACKGROUND

The NWQL began releasing some organic QC data to users of selected organic analyses in May 1993. These data included surrogate recovery for each environmental sample, blank data for each sample set, and reagent spike and surrogate recoveries.

LABORATORY QUALITY-CONTROL SAMPLES

The data from QC samples are used to estimate the quality of the analytical data, determine the need for internal laboratory corrective action in response to identified deficiencies, and interpret results after corrective action procedures are implemented (U.S. Environmental Protection Agency, 1992). The requirements for QC samples and corrective action procedures are specified in the NWQL methods of analysis. The data from QC samples are internally reviewed by the analysts to ensure the requirements are met to satisfy criteria for acceptable data quality. In addition, some of the data from QC samples are internally reviewed by the Quality Management Program (QMP) and externally reviewed by the Branch of Quality Assurance (BQA). District users of the NWQL need to understand how these different types of QC samples are used in interpreting their data. It is important to note that the quality of results for a particular sample needs to be evaluated in the context of all available QA/QC information. It is generally not appropriate to reject data on the basis of failure of one aspect of QA/QC data.

The types of laboratory QC samples discussed in this memo are method blanks, reagent spikes, laboratory matrix spikes, surrogate compounds, and replicate samples. These laboratory QC samples are listed in table 1. Other routinely analyzed laboratory QC samples include calibration solutions, tuning solutions, performance check solutions, and calibration check solutions. The results from these solutions are not discussed here because they are always required to be within specifications before data can be released. In addition, Standard Reference Materials and U.S. Environmental Protection Agency audit solutions are routinely analyzed but not discussed in this memo because they generally are not needed to interpret environmental sample data. These QC samples are used to monitor laboratory performance, and are reported separately in periodic memos from the NWQL Quality Management Program (Pritt and Raese, 1992).

Table 1 describes the number per sample set of laboratory QC samples. This number is typical for most organic analytical methods at the NWQL, but differences occur for specific methods. For example, surrogates are not used in dissolved organic carbon methods or suspended organic carbon methods. Exceptions to these generalizations are described in the appropriate sections below.

Method Blank

Description.- A method blank is an analyte-free matrix carried through the entire sample preparation and analytical procedure. All reagents are added in the same volumes or same proportions as for the environmental samples. For most water samples, analyte-free water is the synthetic matrix used as the method blank. An exception is the determination of organochlorine compounds by gas chromatography with electron capture detection. In this case, it is difficult to prepare interference-free water, so the method blank consists of the extraction solvent and reagents placed into a sample bottle. For tissue and sediment samples, sodium sulfate is used as the synthetic matrix blank.

Application.- The method blank is used to identify contamination from the laboratory during sample preparation and analysis. For a blank to be acceptable, the concentration of each analyte should be less than the method detection limit (MDL). If an analyte is detected in the method blank, an attempt is made to identify the source of contamination and to take corrective action. If an analyte is detected in the method blank and in every sample in the sample set, the reporting limit for that sample set is raised to the concentration of analyte in the blank.

The concentration of analytes in the method blank is not used to correct the environmental sample data unless the source of contamination is known and can be quantified. This is rare; more often, the source of contamination is random and of unknown quantity, and the environmental sample data cannot be corrected using the concentration of analytes in the method blank. Similarly, if an analyte is detected in the method blank, but only in some samples because of random contamination, only those samples having the contamination will have the reporting limit raised to the concentration of analyte in the method blank. The reporting limit for the rest of the samples in the set remains at the initial MDL.

Environmental sample data must be reviewed by project personnel and compared to concentrations of analytes detected in the method blank according to the data-quality objectives established at the beginning of the project. For example, for data to be acceptable using U.S. Environmental Protection Agency (1992) SW-846 methods, concentrations of analytes detected in the method blank need to be less than either the MDL or 5 percent of the concentration measured in the environmental sample. In all cases, the concentrations of the analytes in the method blank need to be reported with the environmental sample data.

Reagent Spike

Description.- A reagent spike is a synthetic matrix fortified with known concentrations of all, or a representative selection of, the method analytes. The synthetic matrix usually is the same as the method blank, for example, organic-free water or sodium sulfate.

Application.- The reagent spike is used to verify the method performance accuracy of each sample set. Over time, analysis of many reagent spike QC samples also provides method performance precision. Accuracy of the reagent spike reflects the best results that can be expected at the time the samples were analyzed, as opposed to recovery data which reflect bias from an environmental sample matrix (see below). The accuracy data for the reagent spike is compared first with the accuracy data for the published method and, then, with the laboratory matrix spike recovery data to determine whether the analytical process is in control. Control charts of reagent spike data are used by the NWQL to indicate trends, variability, and precision of analyses and to identify potential problems that might require corrective action (Pritt and Raese, 1992; Friedman and Erdmann, 1982). Currently (1994), the NWQL prepares control charts of a representative selection of analytes in the reagent spike for most organic analyses.

Environmental sample data must be reviewed by project personnel in relation to the reagent spike for each sample set according to the data-quality objectives established at the beginning of the project. Acceptable ranges of the accuracy of analytes are provided in the control charts (warning limits) or tables provided by the NWQL. If the accuracy of any analyte falls outside the acceptable range, the environmental sample data for that analyte in that set might need to be qualified.

Acceptance criteria for accuracy vary for different analytes. Initially these are reported in the published method and later updated in analytical control charts prepared by the NWQL (Pritt and

Raese, 1992). Generally, acceptable ranges for analyses to be in control are plus or minus three standard deviations of the average accuracy (Friedman and Erdmann, 1982). Warning limits are set at plus or minus two standard deviations of the average accuracy and are used to indicate that there might be a problem for investigation by the analyst.

Sample concentrations reported by U.S. Geological Survey laboratories are not corrected for percentage of analyte recovered in reagent spikes (Wershaw and others, 1987). Interpretive and data reports might need to include a statement or table that summarizes the recovery data of reagent spikes. This statement would be used to document in the report the method performance at the time the samples were analyzed.

Laboratory Matrix Spike

Description.- A laboratory matrix spike is an environmental sample fortified in the laboratory with known concentrations of all, or a representative selection of, the method analytes. The spikes are added in the laboratory immediately before sample preparation and analysis.

Matrix spikes generally are considered project-specific QC samples because information about bias from a sample matrix is specific to a particular project, not to the performance of the method. Consequently, laboratory matrix-spike samples need to be submitted by project personnel as part of their QC samples. In addition, most analytical methods for water samples do not routinely include laboratory matrix spikes because the entire sample submitted for analysis is used; generally, no additional sample is available.

Application.- The laboratory matrix spike is used to verify method performance by recovery of analytes in a particular matrix. Recovery reflects the bias from an environmental sample matrix plus normal method performance, as opposed to accuracy data that reflect the best results that can be expected (see Reagent Spike above). This bias can be either positive or negative and causes recoveries greater than or less than 100 percent. Comparison of the matrix spike recoveries with reagent spike accuracy is used to assess whether the analytical process is in control. Poor performance of the method in a number of different sample matrices indicates the method might not be in control, even if reagent spike accuracy is acceptable. For example, interferences from environmental samples might cause bias in the recovery of matrix spike analytes, indicating corrective action might be needed for a clean-up step.

Environmental sample data must be reviewed by the project personnel in relation to the matrix spike for each sample set according to the data-quality objectives determined at the beginning of the project. If the recovery of any analyte in the matrix spike falls outside the acceptable range for the reagent spike, then the environmental sample data for that analyte in that sample matrix might be suspect. It is important to review all blank, surrogate, and other available QC data before such a conclusion is made because it is possible that there is only a problem with the analyte in the matrix spike sample. For example, low recovery of one analyte in the matrix spike might indicate an interference for that particular matrix, not for all samples.

Values reported by U.S. Geological Survey laboratories are not corrected for percentage of analyte recovered in matrix spikes (Wershaw and others, 1987). The number of matrix spikes needed for a particular project varies depending on the data-quality objectives of the project. This needs to be determined at the start of the project.

Surrogate Compounds

Description.- A surrogate is a compound similar in physical and chemical properties to the analytes of interest. A surrogate normally is not found in environmental samples. Surrogates are chosen that behave similarly in the analytical process to at least some of the analytes of interest but do not interfere with any analytes. The number of surrogates used varies with each analytical method but is generally from one to four compounds. Typical surrogates are compounds that are isotopically labeled, fluorinated, or brominated.

Application.- Surrogates are added to all environmental and QC samples immediately before sample preparation. Surrogates are not used in gross, nonchromatographic analytical methods such as oil and grease, total phenols, methylene-blue active substances, DOC, total organic carbon, and SOC. Because surrogates are added to every sample, they provide quality control by monitoring matrix effects and gross sample-processing errors (Wershaw and others, 1987). Surrogates are not used as an internal standard for quantitative measurement. Surrogates do not reflect the behavior of all analytes and should not be used to correct the analyte concentrations on the basis of percentage of the surrogate recovered.

Surrogates in blanks and reagent spikes are plotted in control charts by the NWQL to indicate trends and variability in analyses, and to indicate if there might be a problem with the analyses that requires corrective action. Surrogates in environmental samples are plotted for some analytical methods, but their interpretation is more difficult than surrogates in reagent spikes because it is likely that bias from sample matrix is the cause of poor performance of one or more surrogates, not a problem with the method that needs corrective action. In some cases, especially during implementation of a new method, plotting surrogates in environmental samples is useful because it can indicate whether the method performs as expected in a wider variety of matrices than tested initially.

Recovery of surrogates in environmental samples needs to be reviewed in relation to the acceptance limits for recovery of surrogates in reagent spikes. If the recovery of all surrogates falls outside the acceptance limits, it might indicate a gross processing error or problematic sample matrix. When gross processing errors are known (for example, a spilled sample extract), the values are generally reported with a greater than (>) remark code. The data for a problematic sample matrix or other problem that causes all surrogate recoveries to be outside acceptance limits are generally flagged as estimated (E) in the remark code. Processing errors also might be indicated if the recovery of only one surrogate falls outside acceptance limits because some surrogates are more sensitive to errors during processing than other surrogates. If the recovery of only one or a few surrogates falls outside acceptance limits, it is likely that the sample matrix causes interferences for that particular surrogate or surrogates, but the concentrations of analytes in the sample need not be considered suspect.

Replicate Samples

Description.- Replicate samples are two (or more) aliquots of a composite sample collected at the same time and location under identical circumstances and treated exactly the same throughout field and laboratory procedures. Replicate samples are produced by dividing a composite sample into two (or more) aliquots. These replicate samples are used to address variation in the measurement process, and need to be distinguished from field QC samples collected at different times or places, or both, that are used to address spatial and temporal variation.

Typically, replicate samples are prepared on site by the project personnel and are submitted as QC samples by the project. These project-submitted QC samples need to be included in the project QC

plan. In some cases, replicate samples are produced in the laboratory for use as laboratory QC samples because there is sufficient sample available. Currently (1994), replicate samples are analyzed as part of the suite of laboratory QC samples for biological tissue analysis and volatile organic carbon (VOC) analysis.

For organic compounds, splitting devices need to be constructed of suitable materials that will not introduce contaminants or cause losses of compounds. Information on sources of suitable splitters can be obtained from the NWQL. Samples for VOC analyses should not be split using such splitting devices because of potential volatilization losses.

Application.- Analyses of replicates provide information about the precision associated with sample handling (after splitting), shipping, and storage, as well as laboratory procedures. Replicate samples provide information about analytical precision if analytes are present in the samples. If analytes are not in the samples, or if concentrations are unknown, duplicate matrix spikes should be used to provide precision information. For example, if all analytes in replicate samples are reported as less than the MDL, there is no quantitative information about the precision of the analysis. In this case, matrix spikes added to replicate samples would have provided information about the recovery and precision of the analysis.

Replicate samples also can be sent to two different laboratories for confirmation of analytical accuracy. A number of split samples (approximately 5 percent) produced in the field serve to allow the project coordinator to assess the accuracy of a local laboratory in comparison to NWQL. It should be noted that replicate samples used for this purpose will not provide the precision information discussed above. Additional replicate samples might need to be collected to fulfill both quality-assurance objectives.

Enclosure

Supersedes: none

Key Words: Laboratory QC samples, Method blanks, Reagent spikes, Laboratory matrix spikes, Surrogate compounds, and Replicate.

Distribution: See above plus the continua USGS.labnews & .water quality

References

Friedman, L.C., and Erdmann, D.E., eds., 1982, Quality assurance practices for the chemical and biological analyses of water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A6, 181 p.

Pritt, J.W., and Raese, J.W., eds., 1992, Quality assurance/quality control manual--National Water Quality Laboratory: U.S. Geological Survey Open-File Report 92-495, 33 p.

U.S. Environmental Protection Agency, 1992, Test methods for evaluating solid waste, Physical/chemical methods (SW-846): 3rd edition.

Wershaw, R.L., Fishman, M.J., Grabbe, R.R., and Lowe, L.E., eds., 1987, Methods for the determination of organic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A3, 80 p.

Table 1.- Laboratory quality-control samples analyzed as part of ongoing quality-assurance practices for most organic analytical methods

QC sample	Description	QA addressed	Number per sample set
Method Blank	Sample of organic-free matrix undergoing the sample preparation steps in the lab	Contamination in laboratory during sample preparation and analysis	1
Reagent Spike	Sample of organic-free matrix fortified in the lab with known concentrations of organic compounds	Accuracy of analytes in reagent water; laboratory preparation, instrumental analysis, and data interpretation. Precision from repeated analyses of reagent spikes	1
Laboratory Matrix Spike	Environmental sample fortified in the lab with known concentrations of organic compounds	Recovery of analytes in particular sample matrix; bias from sample matrix (as well as laboratory preparation, instrumental analysis, and data interpretation)	Dependent on project-submitted samples
Surrogate Compounds	Organic compounds similar in physical and chemical properties to analytes but not present in samples	Precision and accuracy of surrogate recovery; check for out-of-control situation in sample-by-sample basis	Every sample
Replicate Sample	Environmental sample split into two or more aliquots	Precision and bias between different laboratories; consistency of analysis for regional interpretation	1 or project-submitted