United States Department of the Interior

U.S. GEOLOGICAL SURVEY
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IN REPLY REFER TO:

NATIONAL WATER QUALITY LABORATORY TECHNICAL MEMORANDUM 1994.02

December 10, 1993

To: Assistant Chief Hydrologist, 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 Mtn. QE Group
Chief, Branch of Quality Assurance
Employees, National Water Quality Laboratory

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

Subject: NWQL Policy on pH Analytical Determinations

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Revision: None

SCOPE

National Water Quality Laboratory (NWQL) Technical Memorandum 93-07 presented a brief history of pH determinations at the NWQL and asked for input to determine if the current procedures are meeting user needs. This memorandum presents a new policy statement for pH determinations based on user responses and technical discussions within the NWQL.

The method for pH determinations (Lab Code 68) at the NWQL is Method I-2587-85 from the Techniques for Water Resources Investigations (TWRI) Book 5, Chapter A-1. This method

specifies an automated system, applicable only for samples which had a specific conductance exceeding 70 microsiemens per centimeter. For low-conductivity samples, the automated system may not provide reliable pH results because of slow electrode response. The pH for many of these low conductivity samples was determined using a manual variation incorporating longer equilibration times. Alternatively, low-conductivity samples can be submitted for a pH determination by Lab Code 1268. Therefore, manual variations to the method will no longer be conducted on samples submitted for pH determinations by Lab Code 68. Projects needing more reliable pH for low-conductivity waters should use Lab Code 1268 performed in the Low Ionic Strength Unit. This is a more laborious and more costly procedure. Keep in mind, even this more precise measurement may be inaccurate when compared to field measurements of pH due to changes in the sample.

For all laboratory determinations of pH, whether by Lab Codes 68 or 1268, NWQL will include the remark code of "E" (estimated). This acknowledges that laboratory measurements of pH, no matter how reproducible, may not accurately reflect the pH of a sample at the time of collection. Finally, because pH is not a stable parameter and because NWQL results are only estimates, we will no longer accept normal rerun requests for pH.

Response to questions presented in NWQL Technical Memorandum 93.07:

NWQL Technical Memorandum 93-07 was sent to all District and Regional Offices from which a total of 9 responses was received. Not all responses replied to each question.

Question 1.- Should the NWQL be performing pH determinations at all? The field values should be the most accurate due to the instability of this determination after collection.

> 78 percent (7 of 9) of the respondents said the NWQL should continue performing pH determinations.

Question 2.- For regular pH determinations, is our current precision and accuracy performance adequate for your needs?

> 67 percent (4 of 6) of the respondents indicated that the current precision and accuracy are adequate.

Question 3.- Should all low-conductivity (100 microsiemens per centimeter (µS/cm)) samples submitted for pH be done at the level of the Low Ionic Strength (LIS) determination (Lab Code (LC) 1268) with automatic increase in cost to the user?

> 71 percent (5 of 7) of the respondents did not want the sample switched to the LIS Unit for more accurate results.

Question 4.- Should all low-conductivity pH results (LC 68) be deleted by the NWQL? This option would result in decreased cost and price for pH determinations but clearly results in incomplete data for some users.

> None of the six respondents thought that the NWQL should delete pH values for samples submitted to the Majors Unit which had conductivities below 100 µS/cm.

In addition to answering the above four questions, most of those users responding to NWQL Technical Memorandum 93-07 stressed that laboratory pH (LC 68) should only be used as a qualitative check or to determine the stability of samples during transit. Office of Water Quality Technical Memorandum 82.06, which states that laboratory pH should be published only as a last resort, serves as the basis for these responses. In addition, the Code of Federal Regulations (CFR 40 136.3) indicates that environmental measurements of pH need to be determined immediately. In essence, this means that laboratory measurements of pH are unacceptable, especially for purposes of litigation.

Technical discussions on the stability of pH by NWQL personnel have raised the following concerns:

1. All samples are susceptible to pH changes that occur when they equilibrate with atmospheric CO2 during analytical determinations. Low- conductivity samples are particularly susceptible to these types of changes.

2. The pH of natural water samples can rapidly change due to various environmental and chemical reactions. Since most samples take at least 2 to 3 days to transport to the NWQL from the field, there is high susceptibility for pH changes during transport.

3. Given the instability of pH, the practice of requesting reruns for pH is considered highly questionable.

Thank you to all Division personnel who have helped us struggle with this issue. We have tried to come up with a policy that is technically sound, fulfills WRD needs, and fits within economic realities.

Supersedes: None

Key Words: pH, reporting limits, conductivity, precision, accuracy

Distribution: See above plus QWTALK