United States Department of the Interior

U.S. GEOLOGICAL SURVEY
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IN REPLY REFER TO:

NATIONAL WATER QUALITY LABORATORY TECHNICAL MEMORANDUM 1993.07

March 15, 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 Assistant Regional Hydrologists
District Chiefs
Regional Water-Quality Specialists
Area Assistant Regional Hydrologists for NAWQA
District Water-Quality Specialists
Chiefs, NAWQA Study-Units
Chief, Ocala Project Office
Chief, Yucca Mtn. QA Group
Chief, Branch of Quality Assurance
Employees, National Water Quality Laboratory

From: Chief, National Water Quality Laboratory

Subject: Problems with Laboratory pH analytical determinations

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Revision: No

SCOPE

This tech memo addresses problems associated with the determination of regular pH (Lab Code 68) for low conductivity samples. Both long- and short-term problems exist with this analysis. District input is requested in order to help us best meet the needs of users of these data.

Several problems have been noted by the National Water Quality Laborarory (NWQL) concerning pH values on low conductivity samples determined by the automated pH/conductance analytical line (Lab Code (LC) 68, WATSTORE code 403A). The long-term problem concerns samples submitted for regular pH which have conductivities less than 100 microsiemens per centimeter (µS/cm). The short-term problem concerned samples submitted for regular pH with conductivities less than 1200 µS/cm.

Long-term problem.- When the automated system was set up at the NWQL in 1982, it was known that the pH determination for samples with conductivities less than 100 µS/cm were not accurate due to insufficient electrode stabilization time (this system operates at 70 samples per hour, sample residence time at electrode is 40 seconds). It was a requirement at that time that all samples with conductivities less than 100 µS/cm be analyzed separately by hand to allow for a longer stabilization time. For reasons unknown, this requirement was not passed on when the analysis was shifted from the Log-in area to the Majors Unit in 1987. As a result, all pH determinations for LC 68 since 1987 have been performed only on the automated system with no hand determination of pH for samples with conductivities less than 100 µS/cm.

In 1987, the NWQL set up the Low Ionic-Strength (LIS) Unit specifically to handle samples with conductivities of less than 100 µS/cm, including a low conductance pH method (Lab Code 1268). This method is time-consuming (approximately 13 minutes per sample), resulting in low sample throughput per day. Lab policy dictated that the LIS Unit would only analyze samples specifically requesting LC 1268; i.e., low conductivity samples requesting LC 68 are not automatically done by the LIS method. These developments have resulted in a problem in reported data for pH determination on low conductivity samples.

Short-term problem.- It was recently noted that for standard reference water samples (SRWS) with conductivities less than 1200 µS/cm, pH (LC 68) determinations were increasingly unacceptable. The problem was traced to a slow responding electrode. Because electrode response is even slower in low conductivity samples, the automated system did not have sufficient time to reach a stable reading in samples with conductivities less than about 1200 uS/cm in many cases and resulted in potentially inaccurate results for the samples of this conductivity range run during the month of November to December 14, 1992.

Data Implications.-

Short Term

1. As of December 14, 1992, all pH samples submitted for LC 68 that had conductivities of 1200 µS/cm or less were done by hand to verify the values obtained by the automated system. If a difference existed between the hand and automated value, the hand value was entered to LIMS. This policy continued until new electrodes were received and the system was determined to be back to original specifications on December 21, 1992.

2. It will continue to be the policy of the NWQL to hand-pH all samples with conductivities less than 100 µS/cm requesting Lab Code 68. Because of the instability of samples with respect to pH, the NWQL has deemed it not prudent to rerun old samples. There is no consistent way to correct old data due to the variability shown by samples for this parameter.

Long Term

A recent survey of 1991 data shows that about 10 percent of samples submitted for pH (Lab Code 68) have specific conductances of 100 or less. In order to better serve the needs of the users of these data, the NWQL would like to elicit comments and suggestions from our users on the best way to proceed in resolving this problem. In my opinion, the best solution to this long-term problem is to continue conducting lab pH measurements using the automated equipment used for Lab Code 68 except for samples which have conductivities less than 100 µS/cm. For those samples, pH would be

determined by hand but reported by the same lab code. The 1991 survey indicated this procedure might be applied to about 10% of the samples submitted. Clearly these would actually cost more than the price charged, and these costs would have to be calculated into the price of the determination on a yearly basis.

During the course of our deliberations about these issues, several others came to mind. Some of these are:

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.

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

3. Should all low conductivity (100 uS/cm) samples submitted for pH be done at the level of the LIS determination (LC 1268) with automatic increase in cost to the user?

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

Please let us know if this proposed solution will be consistent with your needs. Also, do you have any input to us about these five issues or any others that we should consider before taking our actions?

Please provide your comments and suggestions April 1, 1993, to either Merle Shockey, Inorganic Program Chief; or to Nancy Driver, Chief, Quality Management Group. Thank you for your assistance on this matter.

/signed/

Peter F. Rogerson

Supersedes: None

Key Words: Method, pH, low conductivity

Distribution: See above plus QWTALK