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NATIONAL WATER QUALITY LABORATORY TECHNICAL MEMORANDUM 1999.03

October 14, 1998

Subject: Analysis of Total Phenols

Effective date
of changes: October 15, 1998

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Revision: None

PURPOSE AND SCOPE

A new method will be used to analyze water samples for total recoverable phenol at the National Water Quality Laboratory (NWQL). The method is entitled "Phenols," the method number is 5530, and it is published by the American Public Health Association (APHA) (1995). This method offers improved preservation and analytical procedures. The preliminary Method Detection Limit (MDL) will be 2 micrograms per liter ($\mu\text{g/L}$) and the Minimum Reporting Level (MRL) will be 4 $\mu\text{g/L}$.

The sampling requirements for this method are different than the previous method. Samples will be collected in amber, 500-milliliter (mL) baked glass bottles filled to the shoulder. One mL of concentrated sulfuric acid will be added to the sample water in each bottle, to reduce the pH to less than 2. This preservation procedure is good for 28 days. If residual chlorine or other oxidants are expected in the sample, 100 milligrams of ferrous sulfate will be added to the acidified sample. Samples will be stored at 4 degrees Celsius in the field and shipped to the NWQL on ice, in the proper shipping coolers. The samples must be received in the NWQL within 7 days of the sampling date so that the analysis can be completed within 28 days of the sampling date. The sample bottles, 1-mL ampoules of sulfuric acid and ferrous sulfate, can be procured from the Quality of Water Service Unit in Ocala, Florida (e-mail ocalaman). The ferrous sulfate along with instructions can be procured from the Ocala laboratory.

The new lab code will be 2322 and the new method code will be B. The WATSTORE code will not be changed. The method change will be effective October 15, 1998.

BACKGROUND

Since 1983 the NWQL analyzed water samples for phenol using method number O-3110-83, "Phenols, Total Recoverable, Colorimetric, 4-aminoantipyrine" (Wershaw and others, 1987, p. 55).

The NWQL periodically reviews the analytical methods in use to identify any problems. During the review of the phenol method, the following problems were identified:

- 1) Reproducibility at the MRL was about +/- 4 µg/L, which is excessive considering that the MRL is 1 µg/L.
- 2) A literature review indicated that the preservation technique used is only good for 24 hours (American Public Health Association, 1980).
- 3) Reproducibility of the instrument readings was impaired by occluded water in the chloroform extract.
- 4) Samples that were reanalyzed after 20 to 30 days generally had results that were appreciably lower than the original analysis.

A literature review indicated that a different phenol method was available, and it addressed most of the problems encountered with the present method.

Implementation of the APHA method required a demonstration of proficiency, including the following:

- 1) That the analyst can perform the method by successfully analyzing seven replicates of reagent-water samples, spiked near the middle of the method range.
- 2) That method blanks can be maintained at or less than the method-reporting limit.
- 3) That the preliminary MDL is determined.

Also during this study, the NWQL established:

- 1) Bias and variability for the APHA method at three concentrations in reagent water.
- 2) The quality-control limits that will be used to evaluate process control during the analysis of phenol samples.
- 3) The effectiveness of the preservation technique used in the APHA method.

A technical paper, containing all of the data used in this evaluation, will be made available on the NWQL homepage at <http://www.nwql.cr.usgs.gov/USGS>. The paper should be available by January 1, 1999.

DISCUSSION

Bias and Variability

Three sets of reagent water, containing more than ten replicates each, were spiked at 2, 4, and 20 µg/L phenol. These samples were analyzed to demonstrate the analyst's ability to perform the method, and to describe the bias and variability of the method.

Phenol recoveries greater than 84 percent, and Relative Standard Deviations (RSD) of less than 10 percent were obtained from samples containing at least 4 u/L. Phenol recoveries from samples containing less than 4 ug/L were only 72 percent with an RSD of 31 percent.

Method Detection Limit

The data from the analysis of samples spiked at 2 µg/L were used to calculate the preliminary MDL by the U.S. Environmental Protection Agency (1992) procedure. The preliminary MDL is 2 µg/L and the MRL will be set at 4 ug/L.

Quality-Control Limits for Reagent-Water Spiked Samples

The data from the analyses of reagent-water samples spiked at 20 µg/L were used to calculate the preliminary quality-control limits. The mean and standard deviation (SD) were calculated, then the quality-control limits were calculated as the mean plus or minus 3 SD. The preliminary control limits range from 68 to 110 percent recovery.

Sample Preservation and Holding Time

Reagent-water samples (spiked at 1, 5, and 20 µg/L) were analyzed four times over 28 days to evaluate the effectiveness of the preservation technique used in the APHA phenol method and to determine a reasonable holding time. A blank sample was also analyzed along with the spiked samples to evaluate blank variability over time because a reagent-water blank sample is used to calibrate the instrument. Blank variability relates directly to variation in the intercept, of the calibration equation, over time.

There appeared to be a trend of decreasing phenol concentrations, but this decrease was probably caused by the variability of the blank. The magnitude of the range of variation in the blank analysis was about 3.1 ug/L. The apparent losses in the spiked samples were either equal to or less than this variation. The blank variation also affected the reproducibility of the sample spiked at 1 µg/L.

The blanks that were prepared and analyzed on the same day that the spiked samples were analyzed (method blanks) were stable, and none were greater than the MRL of 4 µg/L.

CONCLUSIONS

- 1) The APHA phenol method provides accurate and precise data when compared to the USGS method. The APHA method removes occluded water by filtering the extract through sodium sulfate, which will improve the reproducibility of instrument readings.
- 2) The APHA method is acceptable for samples containing 4 ug/L or more of phenol, but the bias and variability are unacceptable for samples containing less than 4 µg/L phenol. The USEPA Lifetime Health Advisory Limit is 4 mg/L (U.S Environmental Protection Agency, 1996), which is about 1,000 times greater than the MRL of 4 µg/L. Therefore, the improved version of the method is adequate for the analysis of drinking-water samples.
- 3) The preservation method used in the APHA method will preserve samples containing at least 4 µg/L phenol for 28 days, as long as the samples are stored at about 4 degrees Celsius, or below, until analysis is started.

4) Although blanks vary if held over an extended period, method blanks, which are prepared and analyzed on the same day as the instrument calibration standards, are acceptable.

EFFECTS ON THE DATA BASE

The implementation of the APHA method will not have an impact on samples from sites containing 4 µg/L, or more, of phenol. However, sites that have historic data of between 1 and 4 µg/L will be impacted as the MRL is being raised from 1 to 4 µg/L. Concentrations less than 4 µg/L will no longer be reported. This method change will improve data quality because there is a strong possibility that previously reported detections less than 4 µg/L were false positives caused by blank variability.

REFERENCES

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/signed/

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