

## USEPA Approves On-line Monitoring of Chlorine Residuals

A new method for the use of on-line chlorine analyses for compliance monitoring is determined to be equally effective as other approved methods. **BY NANCY E. MCTIGUE**

**M**ONITORING CHLORINE residuals in finished water is an important part of complying with several regulations governing drinking water, including the Safe Drinking Water Act and the Ground Water Act. For operations personnel, residual chlorine is the most important operational parameter to monitor, because it verifies that finished water has been sufficiently disinfected to protect public health. Many utilities use on-line instruments to monitor disinfection continuously. Although there are numerous laboratory methods previously approved by the US Environmental Protection Agency for analyzing chlorine residuals in drinking water, none of them specifically addressed the use of on-line monitors to perform the analysis.

### AN APPROVED METHOD

On Nov. 10, 2009, USEPA published Method 334.0, Determination of Residual Chlorine in Drinking Water Using an On-line Chlorine Analyzer. Now utilities have an approved method specifically for on-line chlorine residual monitoring. On-line instruments operated according to the method will produce analytical results comparable to other approved methods and are suitable for compliance reporting

under federal regulations. The method incorporates several quality assurance measures that utilities must incorporate in their standard operating procedures. This development is particularly important for utilities using on-line amperometric chlorine analyzers, which have historically been used for process control. Data resulting from on-line amperometric chlorine analyzers used for compliance have been handled differently by various states.

Using the expedited method-approval process initiated in 2007, USEPA approved Method 334.0 through publication in the *Federal Register*, rather than through a traditional rule-making process. The streamlined process made the method available for utilities to use in time for Ground Water Rule monitoring that some systems were required to begin by Dec. 1, 2009. The method is available online at [http://epa.gov/safewater/methods/analyticalmethods\\_ogwdw.html](http://epa.gov/safewater/methods/analyticalmethods_ogwdw.html).

USEPA determined that chlorine residual data obtained from on-line instruments using Method 334.0 were comparable to data collected from instruments using previously approved methods. In making this determination, USEPA cited a recent study that assessed historical data collected from 38 utilities that used amperometric on-line

instruments and grab samples. The analysis—based on six months to two years of chlorine residual data from all 38 utilities—reflected a cross-section of source waters and treatments typical of drinking water treatment in the United States. The study found that in most cases the data from both methods were well within 0.1 mg/L.

Method 334.0 quality assurance elements are pertinent to amperometric and N,N-diethyl-p-phenylenediamine (DPD) on-line instruments. Key quality assurance and control procedures include the following:

- The on-line instrument is calibrated using aqueous standards or the results from paired grab samples collected at the same point and time.
- The grab samples are analyzed for chlorine using a method approved for drinking water compliance monitoring.
- The on-line analyzer's accuracy is periodically verified and adjusted based on grab sample analysis results.
- The analyst demonstrates competency in using the method.

Because Method 334.0 relies on analysis of a grab sample by an approved method to verify the on-line instrument's accuracy, the method contains requirements for the grab samples and the instrument itself.



An analyst measures chlorine residual using a spectrophotometer. Now utilities have a USEPA-approved method for monitoring disinfection continuously using on-line instruments (Inset).

### GRAB SAMPLE ANALYSIS

Only methods listed in the table on page 16 can be used to analyze grab samples for chlorine concentration verification. Utilities must also adhere to specific guidelines:

**Competence.** Any person responsible for verifying free or total chlorine concentration for compliance demonstration must perform an initial demonstration of capability (IDC) with the approved method used to analyze chlorine in the grab sample. The IDC is meant to demonstrate the field or plant sampler's ability to perform the chlorine residual test with accuracy and precision.

To perform this test, a sample of reagent water and five duplicate independent reference samples are analyzed using a DPD method with a bench or handheld spectrophotometer, amperometric titration, or any other method shown in the accompanying table. Accuracy is demonstrated if the average concentration obtained for the five samples is within 15 percent of the actual value of the reference sample. Precision is demonstrated if the standard deviation of the results of the five reference samples is within 15 percent. Each sampler must perform the IDC using the grab sample method before collecting compliance data. Laboratory personnel are allowed to prepare reference samples for the IDC.

**Quality Assurance and Control.** Method 334.0 specifies startup procedures and ongoing quality assurance protocols. Startup procedures include

- Preparing and verifying a calibration curve by demonstrating that the results of at least three aqueous calibration standards, which are in the expected range of the samples, are within 15 percent of the expected value. The calibration curve must span the expected concentration range of the grab samples and include a standard at 0.2 mg/L or less.
- Checking calibration curves quarterly with a known aqueous sample, with the results agreeing within 10 percent.

### ON-LINE ANALYZER

Method 334.0 requires that online chlorine monitors be appropriate for the chosen location, calibrated, periodically checked for accuracy within a certain range, and subject to routine checks and maintenance.

**Calibration.** Regardless of the analytical method used by the on-line monitor, the instrument must be calibrated. This must be accomplished by following the manufacturer's instructions and can be done using aqueous standards or results of grab samples analyzed by an approved method. To establish the instrument is calibrated, the readings of the aqueous

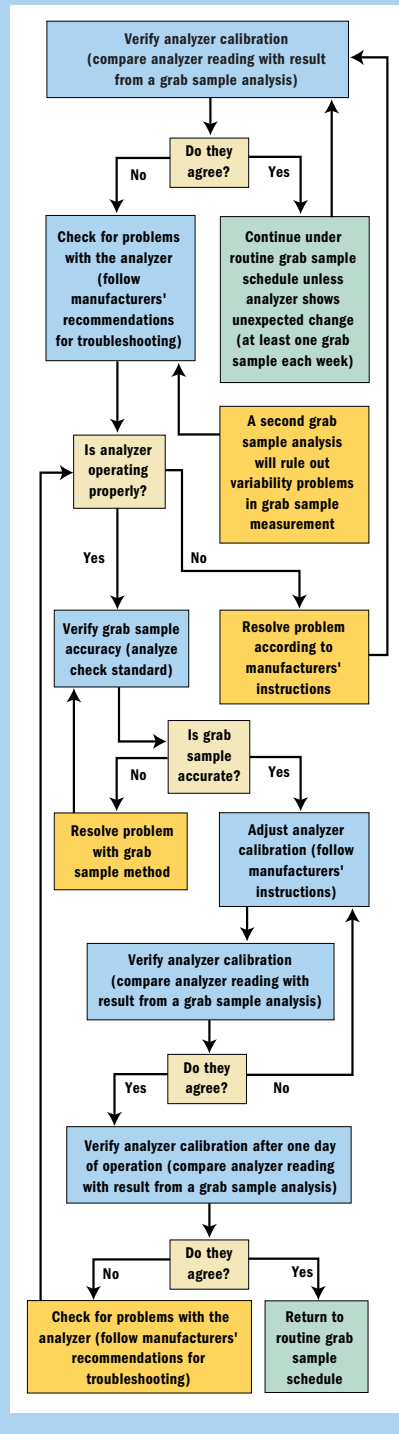
standards or the paired grab samples should be within 15 percent or 0.1 mg/L.

**Demonstrated Capability.** Because some on-line monitors use chemistries that may not be appropriate for use in certain water qualities, Method 334.0 requires that any on-line instrument used for compliance monitoring must demonstrate that its use is appropriate for each situation. After an instrument is calibrated, the instrument must be put in place and data collected and compared with results of a paired grab sample for a minimum of 14 days. This instrument IDC (Section 2.2.2.3) must be completed before any data are used for compliance demonstration. During the IDC, paired grab samples must be collected at least daily, and on-line analyzer results must agree with the grab sample data within 15 percent or 0.1 mg/L, whichever is larger. If, during this time, the data don't agree, the cause of the discrepancy must be determined and corrected. At least 14 days of data showing that the paired data are comparable must be collected and maintained. If data agreement within specified limits can't be attained during a 14-day period, the instrument can't be used for compliance monitoring. The method does allow a utility to use historical data to demonstrate an instrument's IDC and allows for a shortened IDC if the utility uses

Following Method 334.0, utilities can use on-line chlorine monitors to analyze free and combined chlorine residuals.

## Quality Control for On-line Chlorine Analyzer

Compare analyzer readings with grab sample measurements.



## Testing Methods for Disinfectant Residuals

Only approved methods can be used to analyze grab samples for chlorine concentration.

Residual	Methodology		
	Standard Methods <sup>1</sup>	ASTM <sup>2</sup>	Other
<b>Free Chlorine</b>			
Amperometric Titration	4500-Cl D	D 1253-08	
DPD Ferrous Titrimetric	4500-Cl F		
DPD Colorimetric	4500-Cl G		
Syringaldazine (FACTS)	4500-Cl H		
Amperometric Sensor			ChloroSense <sup>3</sup>
On-line Chlorine Analyzer			EPA 334.0 <sup>4</sup>
<b>Combined Chlorine</b>			
Amperometric Titration	4500-Cl D	D 1253-08	
DPD Ferrous Titrimetric	4500-Cl F		
DPD Colorimetric	4500-Cl G		
<b>Total Chlorine</b>			
Amperometric Titration	4500-Cl D	D 1253-08	
Low-level Amperometric Titration	4500-Cl E		
DPD Ferrous Titrimetric	4500-Cl F		
DPD Colorimetric	4500-Cl G		
Iodometric Electrode	4500-Cl I		
Amperometric Sensor			ChloroSense <sup>3</sup>
Online Chlorine Analyzer			EPA 334.0 <sup>4</sup>
Approved Dec. 1, 2009 [40 CFR 141.131(c)(1)]			
<sup>1</sup> Standard Methods for the Examination of Water and Wastewater, 21st edition (2005)			
<sup>2</sup> Available at <a href="http://astm.org">http://astm.org</a>			
<sup>3,4</sup> Approved Nov. 10, 2009			

multiple monitors to measure chlorine in similar water quality conditions (Method 334.0, Section 10.2.2.2).

**Continuous Verification.** Method 334.0 specifies that data from the on-line monitor must be compared with data from a grab sample collected at the same time and location as the on-line sample. The grab sample must also be analyzed using a method previously approved by regulations and collected at a sufficient frequency to detect instrument drift, but at least once every seven days. The method describes procedures to determine optimal frequency (Method 334.0, Appendix A). Data from the on-line monitor and grab sample must agree within 15 percent or 0.1 mg/L, whichever is greater. If the data don't agree, the cause

of the discrepancy must be determined and corrected. All data from these comparisons must be recorded and maintained. Certain conditions, such as instrument repair or unusually high readings, also trigger a requirement for accuracy checks of the on-line instrument by grab sample comparison.

### THE ROAD AHEAD

Following Method 334.0, utilities can use on-line chlorine monitors to analyze free and combined chlorine residuals. For many utilities, the procedures in Method 334.0 are similar to practices they currently use for chlorine monitoring. But for all utility personnel who monitor chlorine residuals for compliance, the method will help ensure accurate results.