Protocol for Improving the Quality Control (QC) for Drinking Water Quality Regulation Compliance Monitoring Samples

In 1999, the California Department of Health Services (DHS) established a workgroup [Reporting Level Workgroup (RLWG)] of representatives from a number of commercial laboratories throughout the state and staff from the Sanitation and Radiation Laboratory and the Division of Drinking Water and Environmental Management. The objective was to develop a procedure for setting inorganic chemical (IOC) reporting levels [officially known as Detection Levels for Purposes of Reporting (DLRs)] for regulated drinking water contaminants. The RLWG conducted an interlaboratory study of 55 volunteer commercial laboratories to obtain data to support their efforts and set new scientifically-based DLRs for various metal IOCs.

The IOCs evaluated in the interlaboratory study were: aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium (total), copper, iron, manganese, nickel, lead, selenium, silver, thallium, and zinc. The goal of the study was to derive scientifically-based DLRs by determining the concentration level for each test element at which the interlaboratory measurement precision was 20% or better, and where at least 80% of qualified laboratories could achieve results within ±30% of the true concentration. The data analysis indicated that the DLRs for aluminum, antimony, barium, cadmium, chromium, manganese, and silver should be changed, and that the DLRs for the other elements in the study would not require revisions. The table below lists the DLR changes DHS will propose.

DLRs for the primary drinking water contaminants aluminum, antimony, barium, and cadmium exist in regulation. To officially change the regulatory DLRs for those elements, amendments to the regulations must be adopted, which is a lengthy process; DHS intends to start the regulatory adoption process in the near future. Chromium, also a primary drinking water contaminant, is not included in the table below because a revised MCL will be proposed within the next year or so, along with an amended DLR.

Changing the DLRs for the secondary drinking water contaminants manganese and silver is a simpler process, requiring only that the laboratory reporting forms and the Writeon® program be revised; this is in the works.
Proposed DLR Revisions

<table>
<thead>
<tr>
<th>Element</th>
<th>MCL (mg/L)</th>
<th>Current DLR (mg/L)</th>
<th>Proposed DLR (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Primary Drinking Water Contaminants</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>1</td>
<td>0.05</td>
<td>0.1</td>
</tr>
<tr>
<td>Antimony</td>
<td>0.006</td>
<td>0.006</td>
<td>0.002</td>
</tr>
<tr>
<td>Barium</td>
<td>1</td>
<td>0.1</td>
<td>0.01</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.005</td>
<td>0.001</td>
<td>0.0005</td>
</tr>
<tr>
<td><strong>Secondary Drinking Water Contaminants</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manganese</td>
<td>0.05</td>
<td>0.02</td>
<td>0.005</td>
</tr>
<tr>
<td>Silver</td>
<td>0.1</td>
<td>0.01</td>
<td>0.005</td>
</tr>
</tbody>
</table>

The RLWG concluded from its study that some laboratories would have difficulties in achieving adequate data quality at or near the DLR with certain metal IOCs and methods, even though those methods are presently approved by EPA. Since the RLWG preferred to not eliminate any of the EPA-approved methods as options, it decided to develop a QC protocol to assist laboratories in determining their performance at or near the DLR and improve the quality of analytical data for metal IOCs. The recommended protocol is to be used in addition to protocols prescribed by the EPA-approved methods. However, there should be little or no incremental cost impact.

**QC Protocol**

The QC protocol has two components (A and B): Component A applies to all methods and analytes and is to be performed with every batch of samples to assure adequate data quality for analyte concentrations at or near the DLR. Component B applies to method/analyte combinations for which there is evidence that they may give marginal performance at or near the DLR. It is to be performed at least once annually to evaluate a laboratory’s basic capability to reliably quantitate an analyte at the DLR level by a given method. The method/analyte combinations currently affected are:
Method | Analytes
---|---
EPA 200.7 | Al, As, Cd
EPA 200.9 | Tl, Sb*
SM 3111B | Ag, Cu, Mn, Ni
SM 3111D | Al, Ba
SM 3120B | Al, As
SM 3113B | Sb*
ASTM D-3697-92 | Sb*
ASTM D-2972-93B | As

*Sb is included in this table due to its proposed DLR of 0.002 mg/L, not its current one of 0.006 mg/L.

**Component A – Check Standard:**

After an instrument is calibrated for IOC analysis, a check standard containing the analyte(s) of interest at the DLR level(s) is analyzed as a QC sample. The acceptance criterion for the result is:

\[
\text{Measured concentration} = \text{Concentration of DLR check standard} \pm 40%.
\]

Failure of this test may indicate a systematic problem with the way the calibration curve was constructed. Remedial action should be taken at this point. This may include the use of weighted linear regression, or limiting the concentration range of the calibration curve.

The check standard is analyzed again with every batch of 20 or fewer samples and at the end of an analytical sequence. The acceptance criterion for these subsequent measurements is the same as above.

The ability to pass this test consistently throughout an analytical sequence demonstrates that the analysis remains in control and that adequate data quality can be achieved at or near the DLR level.

In addition to the DLR check standard, a laboratory reagent blank is analyzed with each batch of 20 samples or less and at the end of an analytical sequence. The analyte concentration measured for this blank should be less than or equal to 40% of the DLR concentration.
Component B – Fortified Concentration Test:

The laboratory prepares a solution fortified with the analyte(s) of interest at or below the DLR level. The test matrix is appropriately acidified reagent water. The test solution is analyzed seven times over the course of three non-consecutive days. The results are averaged and compared to the fortified value(s). The acceptance criteria for this test are:

- RSD is less than or equal to 20%
- Average result = Fortified concentration ± 20%

This test should be performed at the same frequency as the MDL determinations required for a given analyte and method (i.e., at least once annually, when a new analyst begins work, or whenever a change in analytical performance caused by either a change in instrument hardware or operating conditions dictates a redetermination). In cases in which the MDL is close to the DLR, it may be possible to select the same test concentrations for the MDL determination and the DLR performance test and do the two tests simultaneously.

Rationale for Selection of Acceptance Criteria

The general data quality objectives for measurements by a single laboratory at the DLR include the expectation that the precision is 20% (RSD) or better and that the accuracy is true value ± 30% or better.

In the Component A test, the accuracy acceptance criteria are set at ± 40%, since with a sample standard deviation of 0.2 x DLR, about 95% of all measurements should fall in the range DLR ± 40%.

In the Component B test, seven replicate measurements are performed at the DLR level. If the sample standard deviation $s$ is 20% of the DLR, the mean of seven measurements should be in the range DLR ± $t(s/\sqrt{n})$, where $n = 7$. The t-value for a two-tailed test with 6 degrees of freedom and a confidence level of 95% is 2.45. Thus, the term $t(s/\sqrt{n})$ corresponds to 18.5% of the DLR. This value is rounded up to give an acceptance range of ± 20%.

If the result for the laboratory reagent blank exceeds 40% of the DLR level, it is unlikely that acceptable accuracy at the DLR concentration can be achieved.