Techniques of Water-Resources Investigations of the United States Geological Survey

Chapter A6

QUALITY ASSURANCE PRACTICES FOR THE CHEMICAL AND BIOLOGICAL ANALYSES OF WATER AND FLUVIAL SEDIMENTS

By Linda C. Friedman and David E. Erdmann
Quality Assurance Monitoring

In this and the preceding section, the term "quality control" is used when considering the effort made within a laboratory or analytical section of a laboratory to control the quality of the analytical data produced. The phrase "quality assurance monitoring," on the other hand, is considered here not only to involve practices employed by an outside source to assure the quality of the laboratory, but also encompasses practices used by the heads of large laboratories to assure the quality of their laboratory.

Quality assurance efforts should constitute a minimum of about 15 percent of the workload for any determination. This percentage should approach 30 percent for rarely used methods or rarely determined constituents.

Analytical Data Review and Quality Assurance

1. Application or scope

1.1 This practice describes data quality assurance checks made by a computer to aid the quality assurance staff of the Central Laboratories System. Quality control techniques, largely developed prior to 1940 (Howard, 1933; Durum, 1978), plus results from several years of analyses made by the Central Laboratories were used to develop the computer program. All checks described in this practice may also be made by a reviewer using a simple, desk-top calculator.

1.2 The completed analytical report for each sample should be reviewed to determine the acceptability of the analytical data prior to its release outside of the laboratory. Although the quality assurance checks are a guide, the reviewer must judge whether there is a reason for the data to have "failed" a check. This practice details many possible reasons which must be considered for such "errors."

1.3 After receiving the analytical report, the requestor(s) of the analyses must review it. Because the requestor is expected to be familiar with the sampling site (which the analyst is unlikely to be), he may spot questionable values which were not apparent in the laboratory data review.

2. Practice

2.1 Computerized data review

2.1.1 A check is made to determine if bicarbonate, calcium, magnesium, potassium, silica, sodium, sulfate, specific conductance, or calculated solids have been reported as present in the sample. If any of them are reported as present, their corresponding values are checked; if any values have been reported as zero, a warning message so indicating is printed.

2.1.2 A check is made to determine if sodium and potassium are present in the analysis. If they are, the values are compared. If sodium is less than potassium and potassium is greater than 10, a warning message stating that sodium is less than (<) potassium is printed.

2.1.3 A check is made on the pH value and if it is less than 4.5, or greater than 9.0, a warning message so indicating is printed.

2.1.4 A check is made to see if calcium, magnesium, and sodium are in the analysis. If this minimum number of major cations plus specific conductance have been reported to be present, then the total milliequivalents of all cations is computed and used to calculate a total cation/0.01 conductance ratio. If the ratio falls outside the range of 0.92 to 1.24, a warning message is printed.
2.1.5 A check is made to see if bicarbonate, carbonate, chloride, and sulfate are in the analysis. If this minimum number of anions plus specific conductance are present, then the total milliequivalents of all major anions are computed and used to calculate a total anion/0.01 conductance ratio. If the ratio falls outside the range of 0.92 to 1.24, a warning message is printed.

2.1.6 A check is made to see if calculated dissolved solids and specific conductance have been reported for the sample. If they are, then a calculated solids/conductance ratio is computed. If the ratio is outside the range of 0.55 to 0.81, a warning message is printed.

2.1.7 A check is made to see if dissolved solids (residue on evaporation at 180°C) and specific conductance are in the analysis. If they are, then a dissolved solids/conductance ratio is computed. If the ratio is outside the range 0.55 to 0.86, a warning message is printed.

2.1.8 A check is made to see if the dissolved solids (residue on evaporation at 180°C) and calculated solids are in the analysis. If they are, then a dissolved solids/calculated solids ratio is computed. If the ratio is outside the range 0.90 to 1.12 a warning message is printed.

2.1.9 A check is made to see if a percent difference can be computed using the sums of the milliequivalents of major cations and anions. If a check can be, it is computed and compared to the curve shown in figure 15. If the percent difference is in the rejection zone, a warning message is printed.

2.1.10 A check is made to compare selected dissolved and total (or total recoverable) constituent concentrations if they were reported (table 8). If the total or total recoverable concentration for a constituent is not equal to or greater than the dissolved concentration for that constituent (within specified limits), a warning message so indicating is printed.

2.1.11 A check is made of certain dissolved, suspended, and total solids concentrations (table 9). If a dissolved and (or) suspended concentration exceeds the total concentration, a warning message is printed.

2.1.12 A check is made to see if reported concentrations for any constituent listed in table 10 exceed the tabulated value. If the tabulated value is exceeded, a warning message is printed indicating that the value increases the milliequivalent sum.

2.2 Data review by laboratory quality assurance staff

2.2.1 In the Central Laboratories, each analytical report is accompanied by a sheet listing all applicable computer messages (fig. 16). The laboratory's quality assurance staff must review this information and examine each analytical report for anomalies.

2.2.2 Because extremely low values should be reported by the analyst as "less than" the appropriate detection level, the reviewer should be aware that a "zero" concentration usually indicates an error.

2.2.3 The reviewer should realize that, although "concentrations of potassium more than a few tens of milligrams per liter . . . are . . . unusual" (Hem, 1970) and that although the concentration of sodium in ambient water is usually greater than the concentration of potassium, neither of these relationships is always true. Similarly, the reviewer should be aware that, although the concentration of calcium is usually greater than magnesium, the two ions
may be nearly equal (as in waters from a dolomitic formation, for instance) or magnesium may be the predominant ion (in some brines, for instance).

2.2.4 When large percent differences between the milliequivalents of cations and milliequivalents of anions are observed, the reviewer must consider the following:

2.2.4a If not all the major ionic species have been determined, the sum of milliequivalent values may be in error.

2.2.4b If an analytical determination includes undissociated as well as dissociated species, the corresponding milliequivalent value may be “too large.” Published dissociation constants may aid in evaluating the analysis.

2.2.4c In acidic samples, the calculations of milliequivalents of hydrogen ion from the pH may be in error because of the effect of other ions on hydrogen ion activity.

2.2.4d Because alkalinity (and acidity) are determined by titration, weak-acid radicals other than carbonate species (such as phosphate or borate) may be included twice in the summation of anion milliequivalents (once as part of the titration and again as part of the specific constituent analysis).

2.2.5 When large differences between the calculated dissolved solids and the dissolved solids determined by residue on evaporation are observed, the reviewer must consider the following:

2.2.5a The residue may contain organic and inorganic materials which were not specifically determined in the analysis. The measured residue will appear high.

2.2.5b The residue may contain water of hydration (for example, if high in calcium sulfate). The measured residue will appear high.

2.2.5c Certain constituents may be volatilized in the determination of the residue; for example, waters which are high in magnesium chloride may show a loss of chloride, and waters high in nitrate may show a loss of nitrate. The measured residue will appear low.

2.2.5d Weak-acid radicals other than carbonate species (such as phosphate, borate, and silica) may be included in the alkalinity value and also specifically be determined. The calculated value will appear high.

2.2.6 When ratios of dissolved solids to specific conductance which fall outside of the allowable range are observed, the reviewer must consider the following:

2.2.6a Waters which are high in silica or saturated with respect to gypsum may give ratios as high as 1.0.

2.2.6b The dissolved solids/specific conductance ratios for very dilute waters, such as precipitation samples, or for waters which are high (over 30,000 mg/L) in dissolved solids show great variability and are not a useful check on the analysis.

2.2.7 The quality assurance staff must request redetermination of any constituent in which an error is suspected to have been made.

2.2.8 The quality assurance staff evaluates results from reanalyses and, if it is judged that an error (or errors) was made in analysis (or in transcribing results, and so forth), the new value(s) is entered into the data file and a revised analytical report is generated.

2.3. Review by requestor of analyses

2.3.1 After computer and laboratory quality assurance staff data review and approval of the analysis, the analytical report is released to the individuals who requested the analyses.

2.3.2 In the Central Laboratories, all samples are retained for two weeks after approval of the analysis by the laboratory quality assurance staff. During this time, the individuals responsible for requesting the analysis (district or project personnel) must review the analytical report.

2.3.3 Such individuals are expected to be familiar with the site where the sample was collected. Using this knowledge plus historical records, they determine whether any values appear “unreasonable.”

2.3.4 If, during the 2-week limit, the “outside” reviewers feel that an error may have been made, they inform the laboratory’s quality assurance staff and request that the laboratory reanalyze the sample (for a stable constituent). The quality assurance staff reports the value from reanalysis directly to the requesting reviewers.
<table>
<thead>
<tr>
<th>WATSTORE code</th>
<th>Constituent</th>
<th>Computer check</th>
<th>WATSTORE code</th>
<th>Constituent</th>
</tr>
</thead>
<tbody>
<tr>
<td>01105</td>
<td>Aluminum, total recoverable</td>
<td>&gt;</td>
<td>01106</td>
<td>Aluminum, dissolved</td>
</tr>
<tr>
<td>01030</td>
<td>Chromium, dissolved</td>
<td>&gt;</td>
<td>01030</td>
<td>Chromium, hexavalent</td>
</tr>
<tr>
<td>01045</td>
<td>Iron, total recoverable</td>
<td>&gt;</td>
<td>01046</td>
<td>Iron, dissolved</td>
</tr>
<tr>
<td>01055</td>
<td>Manganese, total recoverable</td>
<td>&gt;</td>
<td>01056</td>
<td>Manganese, dissolved</td>
</tr>
<tr>
<td>00625</td>
<td>Nitrogen, ammonia plus organic as N, total</td>
<td>&gt;</td>
<td>00623</td>
<td>Nitrogen, ammonia plus organic as N, dissolved</td>
</tr>
<tr>
<td>00625</td>
<td>Nitrogen, ammonia plus organic as N, total</td>
<td>&gt;</td>
<td>00608</td>
<td>Nitrogen, ammonia as N, dissolved</td>
</tr>
<tr>
<td>00745</td>
<td>Sulfide, total</td>
<td>&gt;</td>
<td>00746</td>
<td>Sulfide, dissolved</td>
</tr>
<tr>
<td>00680</td>
<td>Carbon, organic, total</td>
<td>&gt;</td>
<td>00681</td>
<td>Carbon, organic, dissolved</td>
</tr>
<tr>
<td>00610</td>
<td>Nitrogen ammonia as N, total</td>
<td>&gt;</td>
<td>00608</td>
<td>Nitrogen ammonia as N, dissolved</td>
</tr>
<tr>
<td>00666</td>
<td>Phosphorus as P, dissolved</td>
<td>&gt;</td>
<td>00671</td>
<td>Phosphorus, orthophosphate as P, dissolved</td>
</tr>
<tr>
<td>00665</td>
<td>Phosphorus as P, total</td>
<td>&gt;</td>
<td>00666</td>
<td>Phosphorus as P, dissolved</td>
</tr>
<tr>
<td>00665</td>
<td>Phosphorus as P, total</td>
<td>&gt;</td>
<td>00671</td>
<td>Phosphorus, orthophosphate as P, dissolved</td>
</tr>
<tr>
<td>00665</td>
<td>Phosphorus as P, total</td>
<td>&gt;</td>
<td>70507</td>
<td>Phosphorus, orthophosphate, as P, total</td>
</tr>
<tr>
<td>00300</td>
<td>Solids, residue at 105°-110°C, total</td>
<td>&gt;</td>
<td>70300</td>
<td>Solids, residue at 105°C, dissolved</td>
</tr>
<tr>
<td>71900</td>
<td>Mercury, total</td>
<td>&gt;</td>
<td>71890</td>
<td>Mercury, dissolved</td>
</tr>
<tr>
<td>00631</td>
<td>Nitrogen, nitrite plus nitrate as N, dissolved</td>
<td>&gt;</td>
<td>00613</td>
<td>Nitrogen, nitrite as N, dissolved</td>
</tr>
<tr>
<td>01002</td>
<td>Arsenic, total</td>
<td>&gt;</td>
<td>01000</td>
<td>Arsenic, dissolved</td>
</tr>
<tr>
<td>01007</td>
<td>Barium, total</td>
<td>&gt;</td>
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<td>Barium, dissolved</td>
</tr>
<tr>
<td>01012</td>
<td>Beryllium, total</td>
<td>&gt;</td>
<td>01010</td>
<td>Beryllium, dissolved</td>
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<tr>
<td>01027</td>
<td>Cadmium, total</td>
<td>&gt;</td>
<td>01025</td>
<td>Cadmium, dissolved</td>
</tr>
<tr>
<td>00916</td>
<td>Calcium, total</td>
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<td>00913</td>
<td>Calcium, dissolved</td>
</tr>
<tr>
<td>01034</td>
<td>Chromium, total</td>
<td>&gt;</td>
<td>01030</td>
<td>Chromium, dissolved</td>
</tr>
<tr>
<td>01037</td>
<td>Cobalt, total</td>
<td>&gt;</td>
<td>01035</td>
<td>Cobalt, dissolved</td>
</tr>
<tr>
<td>01042</td>
<td>Copper, total</td>
<td>&gt;</td>
<td>01040</td>
<td>Copper, dissolved</td>
</tr>
<tr>
<td>01051</td>
<td>Lead, total</td>
<td>&gt;</td>
<td>01049</td>
<td>Lead, dissolved</td>
</tr>
<tr>
<td>00927</td>
<td>Magnesium, total</td>
<td>&gt;</td>
<td>00925</td>
<td>Magnesium, dissolved</td>
</tr>
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</table>
Table 8.—Computerized comparison of dissolved and total or total recoverable constituents—Continued

<table>
<thead>
<tr>
<th>WATSTORE code</th>
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<th>Computer check</th>
<th>WATSTORE code</th>
<th>Constituent</th>
</tr>
</thead>
<tbody>
<tr>
<td>01062</td>
<td>Molybdenum, total</td>
<td>&gt;</td>
<td>01060</td>
<td>Molybdenum, dissolved</td>
</tr>
<tr>
<td>01067</td>
<td>Nickel, total</td>
<td>&gt;</td>
<td>01065</td>
<td>Nickel, dissolved</td>
</tr>
<tr>
<td>00623</td>
<td>Nitrogen, ammonia plus organic as N, dissolved</td>
<td>&gt;</td>
<td>00608</td>
<td>Nitrogen, ammonia as N, dissolved</td>
</tr>
<tr>
<td>01022</td>
<td>Boron, total</td>
<td>&gt;</td>
<td>01020</td>
<td>Boron, dissolved</td>
</tr>
<tr>
<td>00951</td>
<td>Fluoride, total</td>
<td>&gt;</td>
<td>00950</td>
<td>Fluoride, dissolved</td>
</tr>
<tr>
<td>01139</td>
<td>Lithium, total</td>
<td>&gt;</td>
<td>01130</td>
<td>Lithium, dissolved</td>
</tr>
<tr>
<td>00669</td>
<td>Phosphorus, hydrolyzable as P, total</td>
<td>&gt;</td>
<td>00672</td>
<td>Phosphorus, hydrolyzable as P, dissolved</td>
</tr>
<tr>
<td>01147</td>
<td>Selenium, total</td>
<td>&gt;</td>
<td>01145</td>
<td>Selenium, dissolved</td>
</tr>
<tr>
<td>01077</td>
<td>Silver, total</td>
<td>&gt;</td>
<td>01075</td>
<td>Silver, dissolved</td>
</tr>
<tr>
<td>01082</td>
<td>Strontium, total</td>
<td>&gt;</td>
<td>01080</td>
<td>Strontium, dissolved</td>
</tr>
<tr>
<td>01102</td>
<td>Tin, total</td>
<td>&gt;</td>
<td>None</td>
<td>Tin, dissolved</td>
</tr>
<tr>
<td>01087</td>
<td>Vanadium, total</td>
<td>&gt;</td>
<td>01089</td>
<td>Vanadium, dissolved</td>
</tr>
<tr>
<td>01092</td>
<td>Zinc, total</td>
<td>&gt;</td>
<td>01090</td>
<td>Zinc, dissolved</td>
</tr>
<tr>
<td>70507</td>
<td>Phosphorus, orthophosphate as P, total</td>
<td>&gt;</td>
<td>00671</td>
<td>Phosphorus, orthophosphate as P, dissolved</td>
</tr>
<tr>
<td>00615</td>
<td>Nitrogen, nitrite as N, total</td>
<td>&gt;</td>
<td>00613</td>
<td>Nitrogen, nitrite as N, dissolved</td>
</tr>
<tr>
<td>00630</td>
<td>Nitrogen, nitrite plus nitrate as N, total</td>
<td>&gt;</td>
<td>00613</td>
<td>Nitrogen, nitrite as N, dissolved</td>
</tr>
<tr>
<td>00630</td>
<td>Nitrogen, nitrite plus nitrate as N, total</td>
<td>&gt;</td>
<td>00631</td>
<td>Nitrogen, nitrite plus nitrate as N, dissolved</td>
</tr>
<tr>
<td>00630</td>
<td>Nitrogen, nitrite plus nitrate as N, total</td>
<td>&gt;</td>
<td>00615</td>
<td>Nitrogen, nitrite as N, total</td>
</tr>
<tr>
<td>01097</td>
<td>Antimony, total</td>
<td>&gt;</td>
<td>01085</td>
<td>Antimony, dissolved</td>
</tr>
</tbody>
</table>

Table 9.—Comparison of solids

<table>
<thead>
<tr>
<th>WATSTORE code</th>
<th>Constituent</th>
<th>Computer check</th>
<th>WATSTORE code</th>
<th>Constituent</th>
</tr>
</thead>
<tbody>
<tr>
<td>00500</td>
<td>Solids, residue at 105-110°C, total</td>
<td>&gt;</td>
<td>70299</td>
<td>Solids, residue at 105-110°C, suspended</td>
</tr>
<tr>
<td>00500</td>
<td>Solids, residue at 105-110°C, total</td>
<td>&gt;</td>
<td>00530</td>
<td>Solids, residue at 105-110°C, suspended</td>
</tr>
<tr>
<td>00500</td>
<td>Solids, residue at 105-110°C, total</td>
<td>&gt;</td>
<td>00510</td>
<td>Solids, nonvolatile, total</td>
</tr>
<tr>
<td>00500</td>
<td>Solids, residue at 105-110°C, total</td>
<td>&gt;</td>
<td>00505</td>
<td>Solids, volatile on ignition, total</td>
</tr>
<tr>
<td>00530</td>
<td>Solids, residue at 105-110°C, suspended</td>
<td>&gt;</td>
<td>00540</td>
<td>Solids, nonvolatile, suspended</td>
</tr>
<tr>
<td>00530</td>
<td>Solids, residue at 105-110°C, suspended</td>
<td>&gt;</td>
<td>00535</td>
<td>Solids, volatile on ignition, suspended</td>
</tr>
<tr>
<td>70300</td>
<td>Solids, residue at 180°C, dissolved</td>
<td>&gt;</td>
<td>00520</td>
<td>Solids, volatile on ignition, dissolved</td>
</tr>
</tbody>
</table>
### Table 10.—Trace constituent concentrations which will contribute to milliequivalent

<table>
<thead>
<tr>
<th>WATSTORE Code</th>
<th>Constituent</th>
<th>Concentration[^] (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>01106</td>
<td>Aluminum, dissolved</td>
<td>450</td>
</tr>
<tr>
<td>01046</td>
<td>Iron, dissolved</td>
<td>930</td>
</tr>
<tr>
<td>01130</td>
<td>Lithium, dissolved</td>
<td>350</td>
</tr>
<tr>
<td>01056</td>
<td>Manganese, dissolved</td>
<td>690</td>
</tr>
<tr>
<td>01090</td>
<td>Zinc, dissolved</td>
<td>1630</td>
</tr>
<tr>
<td>01005</td>
<td>Barium, dissolved</td>
<td>3400</td>
</tr>
<tr>
<td>01080</td>
<td>Strontium, dissolved</td>
<td>2200</td>
</tr>
<tr>
<td>01040</td>
<td>Copper, dissolved</td>
<td>1590</td>
</tr>
<tr>
<td>01049</td>
<td>Lead, dissolved</td>
<td>5180</td>
</tr>
<tr>
<td>01060</td>
<td>Molybdenum, dissolved</td>
<td>800</td>
</tr>
</tbody>
</table>

[^]: These concentrations will yield a milliequivalent value which will contribute to the cation milliequivalent value.

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**QUALITY CONTROL INFORMATION FOR LAB ID # 334016 RECORD # 30510**

- **CATION/CONDUCTANCE RATIO IS EITHER BELOW 0.92 OR ABOVE 1.24** = 0.873
- **CALCULATED SOLIDS/CONDUCTANCE RATIO IS EITHER BELOW 0.55 OR ABOVE 0.81** = 0.529
- **THE PERCENT DIFFERENCE COMPUTED FOR THE ANALYSIS DOES NOT AGREE WITH THE CURVE VALUE** = 0.690

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**Figure 16.** Example of computer-generated “error” messages.

### References

Reference Material Submitted
by Laboratory Management

1. Application or scope
1.1 This practice describes and documents the Central Laboratories System program in which the chief of each Central Laboratory ensures that reference materials which are unknown to any analyst or section head are submitted daily to the laboratory. Results from analyses of the reference materials are used to aid the laboratory chief in monitoring the quality control program of his laboratory and in assuring data quality.
1.2 The section “Reference material,” should also be referred to.

2. Practice
2.1 Sample submission
2.1.1 A minimum of one reference material for major inorganic constituents (calcium, magnesium, sodium, potassium, chloride, fluoride, sulfate, silica, alkalinity, dissolved solids, and nitrite plus nitrate) are submitted every day.
2.1.2 A minimum of two reference materials for trace inorganic constituents (aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, iron, lithium, manganese, mercury, molybdenum, nickel, selenium, silver, strontium, and zinc) are submitted every week.
2.1.3 A minimum of one natural sample for gross alpha and beta radioactivity and for uranium are submitted every week.
2.1.4 Prior to their submission to the laboratory, the reference materials are rebottled in the type of sample bottles which are routinely received by the laboratory.
2.1.5 Each rebottled reference material is assigned a routine log-in number, and the log-in sheet accompanying the samples is coded to allow computer recognition of the reference material so that the results can be checked automatically as they are produced. Log-in sheets go directly to the automatic data processing (ADP) section and are not seen by the analyst.

2.2 Data processing
2.2.1 The most probable values and associated standard deviations for the reference material constituents are stored in a computerized file. The file is updated as new reference materials become available.
2.2.2 Upon completion of a set of analyses, the analyst submits the data for computer entry. The following morning, the laboratory’s quality assurance staff receives a list of reference sample values which are greater than 1 standard deviation from the most probable value; values which are greater than 1.5 standard deviations from the most probable value are starred (fig. 17).
2.2.3 The quality assurance staff of the laboratory asks the section head to investigate analyses of reference material which showed significant (over 1.5 standard deviations) error.
2.2.4 During his investigation, the section head may require the analyst to perform the analysis again. (This would not be the case for obvious transcribing or data processing errors.) When the reference sample is reanalyzed, several samples throughout the analytical run must also be reanalyzed including samples near the beginning, the end, and on either side of the reference sample.
2.2.5 Once the area in which the error occurred has been defined, analyses throughout the area are repeated and the data are corrected. The section head informs the quality control staff of the reason for the error, describes corrective measures to eliminate the problem, and indicates which samples were reanalyzed.
<table>
<thead>
<tr>
<th>LAB-ID</th>
<th>RECORD #</th>
<th>REF. SAM.</th>
<th>PARAMETER NAME</th>
<th>LAB-CODE</th>
<th>REPORTED VALUE</th>
<th>ACCEPTANCE INTERVAL</th>
<th>MEAN</th>
<th>STANDARD DEV.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>POTASSIUM DISSOLVED</td>
<td>54</td>
<td>8.10 GOOD</td>
<td>7.41 TO 9.13</td>
<td>8.27</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>MERCURY DISSOLVED</td>
<td>226</td>
<td>2.20 GOOD</td>
<td>3.98 TO 5.38</td>
<td>4.68</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CHLORIDE DISSOLVED</td>
<td>15</td>
<td>8.50 GOOD</td>
<td>8.13 TO 9.39</td>
<td>8.76</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SULFATE DISSOLVED</td>
<td>63</td>
<td>63.00 GOOD</td>
<td>55.34 TO 64.06</td>
<td>59.70</td>
<td>4.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>COBALT DISSOLVED</td>
<td>18</td>
<td>17.00</td>
<td>12.68 TO 16.92</td>
<td>14.80</td>
<td>2.12</td>
</tr>
<tr>
<td></td>
<td>1843</td>
<td>63</td>
<td>COPPER DISSOLVED</td>
<td>22</td>
<td>83.00 GOOD</td>
<td>52.67 TO 71.32</td>
<td>62.00</td>
<td>9.32</td>
</tr>
<tr>
<td></td>
<td>1843</td>
<td>63</td>
<td>LEAD DISSOLVED</td>
<td>38</td>
<td>0.00</td>
<td>1.03 TO 8.77</td>
<td>4.90</td>
<td>3.87</td>
</tr>
<tr>
<td></td>
<td>1843</td>
<td>63</td>
<td>MANGANESE DISSOLVED</td>
<td>42</td>
<td>250.00 GOOD</td>
<td>228.50 TO 277.50</td>
<td>253.00</td>
<td>24.50</td>
</tr>
<tr>
<td></td>
<td>1843</td>
<td>63</td>
<td>NICKEL DISSOLVED</td>
<td>44</td>
<td>9.00</td>
<td>4.04 TO 10.76</td>
<td>7.40</td>
<td>3.36</td>
</tr>
<tr>
<td></td>
<td>1843</td>
<td>63</td>
<td>CADMIUM DISSOLVED</td>
<td>73</td>
<td>13.00 GOOD</td>
<td>11.77 TO 18.03</td>
<td>14.90</td>
<td>3.13</td>
</tr>
</tbody>
</table>

Figure 17.—Example of computer messages for reference samples submitted by laboratory management.
Reference Material Submitted from Outside the Laboratory

1. Application or scope
   1.1 This practice describes and documents the Central Laboratories System program in which reference materials that are unknown to anyone in the laboratory system are submitted by Geological Survey district personnel, along with their routine samples, to the laboratories. Data from analysis of the reference materials are used for quality assurance monitoring.
   1.2 The section, “Reference material,” should also be referred to.

2. Practice
   2.1 Preparation and submission of samples
      2.1.1 Inorganic reference materials are specially prepared by a quality assurance project which is independent of the production laboratory system. Usually two or more Standard Reference Water Samples (SRWS) are combined; for example, 60 percent of SRWS 10 is mixed with 40 percent of SRWS 12.
      2.1.2 Samples are mailed to Geological Survey district offices. Only two quality assurance projects, both independent of the analytical laboratory, are aware of which WRD districts are involved and what the concentrations of the reference materials are; but even they do not know when the samples will be submitted.
      2.1.3 District personnel are requested to submit samples on a weekly basis at times of their choosing. Field personnel know the composition but not the concentrations of the reference material.
      2.1.4 The samples are provided with “unique” station identification numbers (downstream order numbers) which will allow computer recognition of the sample; in all other respects they appear identical to other samples submitted by the district. Thus, samples are “blind” to everyone in the laboratory.

   2.2 Data processing
      2.2.1 The expected analytical result and standard deviation is stored in the computer file under the station identification number assigned to the sample.
      2.2.2 As in the case of the reference material submitted via the laboratory management, there is a 1-day response delay between analysis of the sample and receipt of the results by the laboratory’s quality assurance staff. (This delay will be eliminated with the advent of “on-line” instruments; real-time reference sample monitoring will then be routine.)
      2.2.3 The computer-generated report indicates how close the analysis is to the theoretical (most probable) value and specifically notes values which are significantly (over 1.5 standard deviations) in error. The laboratory is not informed which sample is the reference sample, but only informed of the Julian date (job) when the reference sample was submitted (fig. 18).
      2.2.4 Section heads are required to respond, in writing, to any problems indicated by the results of reference sample analyses. They must describe what the problem was and the corrective action taken. The response is stored in the computer (fig. 19).
THE FOLLOWING PARAMETERS HAVE BEEN DETERMINED ON BLIND SAMPLES SUBMITTED TO YOUR CENTRAL LABORATORY BY DISTRICTS THAT YOU
SERVE. FOR PARAMETER VALUES \( \leq 1.5 \) STANDARD DEVIATIONS, NO RESPONSE IS NECESSARY. HOWEVER, FOR VALUES \( >1.5 \) A RESPONSE IS
MANDATORY. THIS REPORT IS PREPARED TO ASSIST YOU IN TURNING OUT THE HIGHEST QUALITY WORK POSSIBLE.

<table>
<thead>
<tr>
<th>LAB CODE</th>
<th>PARAMETER NAME</th>
<th>LAB JOB</th>
<th># STAN.</th>
<th>COMMENT</th>
<th>RESPONSE KEY</th>
<th>RECORD NO</th>
<th>LAB CODE</th>
<th>EXPLANATION OF PROBLEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>ARSENIC DISSOLVED</td>
<td>3 199</td>
<td>-0.19</td>
<td>LOOKS GOOD</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>69</td>
<td>SP. CONDUCTANCE LAB</td>
<td>2 206</td>
<td>0.86</td>
<td>LOOKS GOOD</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>63</td>
<td>SULFATE DISSOLVED</td>
<td>2 194</td>
<td>5.13</td>
<td><strong>OH OH</strong></td>
<td>77081142 100</td>
<td>63</td>
<td>RESPONSE REQUIRED</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>CHORIDE DISSOLVED</td>
<td>2 194</td>
<td>-2.26</td>
<td><strong>OH OH</strong></td>
<td>77081142 101</td>
<td>15</td>
<td>RESPONSE REQUIRED</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 18.**—Example of computer-generated reference sample report.

**Figure 19.**—Example of section responses to reference sample "errors."
Reference Material Submitted to Cooperator and Contractor Laboratories

1. Application or scope

1.1 This practice provides some guidelines for submitting reference samples to those laboratories that are analyzing samples for the Geological Survey under the terms of a cooperative agreement or contract. Specific quality assurance procedures depend on the type of analyses that are to be performed; because Geological Survey cooperator and contract programs vary, specific requirements should be included with each cooperation agreement or contract.

1.2 Analyses used by the Geological Survey or stored in the WATSTORE computer system should be of known precision and of acceptable accuracy. Analyses performed by cooperator and contractor laboratories must yield data comparable to the Central Laboratories.

1.3 Refer also to the section “Reference Material.”

2. Practice

2.1 Prepared reference material

2.1.1 If reference materials are available for the constituent(s) of interest, submit at least 1 for every 25 samples analyzed (NOTE 1).

NOTE 1. At least three Standard Reference Water Samples must be submitted per year (see 2.1.4, below).

2.1.2 If in any month 10 or more samples are analyzed, submit a reference sample (even though less than 25 samples are analyzed).

2.1.3 If possible, submit samples in such a way that the receiving laboratory will not know they are reference materials. When a cooperating agency both collects and analyzes the sample, such “blind” submission is not possible; however, in no case is the analyzing laboratory or cooperative agency to be informed of concentration values prior to sample analyses.

2.1.4 Standard Reference Water Samples (SRWS) are usually prepared from natural water and are available, on a limited basis, for the following constituents: aluminum, antimony, arsenic, barium, beryllium, bicarbonate alkalinity, boron, cadmium, calcium, chloride, chromium, cobalt, copper, dissolved solids, fluoride, iron, lead, lithium, magnesium, manganese, mercury, molybdenum, nickel, nitrate, nitrite, pH, phosphorus, potassium, selenium, silica, silver, sodium, specific conductance, strontium, sulfate, thallium, and zinc. Semiannually, samples are also available for ammonia, Kjeldahl nitrogen, orthophosphate, and dissolved phosphorus. The most probable concentration of each constituent and the standard deviation of the analysis is determined from interlaboratory analyses.

2.1.4a Each cooperating or contracting laboratory must analyze a minimum of three SRWS per year for each of the above-named constituents which it determines; two out of the three analyses needed to meet this minimum requirement may be obtained by participation in the program to analyze new SRWS. For inclusion in this program, contact:

Project Chief for Standard Reference Water Sample Program
U.S. Geological Survey
Water Resources Division
Mail Stop 407, Box 25046
Denver Federal Center
Denver, CO 80225

2.1.4b In order to obtain more reference materials for continuing laboratory evaluation, contact:

Project Chief for Laboratory Evaluation
U.S. Geological Survey
Water Resources Division
Mail Stop 407, Box 25046
Denver Federal Center
Denver, CO 80225

2.1.5 Ampouled concentrates of many constituents, prepared in distilled water, are
available; however, Geological Survey district personnel are responsible for quantitatively preparing solutions from the concentrates. If solutions are prepared in a natural-water matrix, submit to the laboratory for analysis both the sample spiked with the concentrate and the unspiked sample. Ampoules should be used to monitor Kjeldahl nitrogen, ammonia, chemical oxygen demand, and carbon analyses.

2.1.5a In order to obtain ampoules, contact the Project Chief for Laboratory Evaluation.

2.1.5b Alternatively, obtain samples from:
U.S. Environmental Protection Agency
Quality Assurance Branch
Environmental Monitoring and Support Laboratory
Cincinnati, OH 45268

As more fully described in the January 1981 edition of the EPA Quality Assurance Newsletter, the following types of Quality Control samples are available, primarily as ampouled concentrates, for use to interested water analyses laboratories:
- Antimony, thallium, and silver
- Chlorine
- Chlorophyll
- Cyanide
- Demand analyses
- Haloethers
- Herbicides
- Linear alkylate sulfonate
- Mercury
- Mineral/physical analyses
- Municipal digested sludge
- Nitrate/fluoride
- Nitrilotriacetic acid
- Nutrients
- Oil and grease
- Pesticides
- Pesticides, organochlorine
- Pesticides, organophosphorus
- Pesticides, urea-based

2.1.6 Reference materials prepared in a natural-water matrix typical of water being analyzed by a laboratory may also be obtained. Matrix water for these samples is generally collected by the district and submitted to the Project Chief for Laboratory Evaluation. This bulk matrix water sample may be split and treated to yield several types of reference material samples which are then returned to the District. These may include: (1) filtered, untreated sample, (2) filtered, untreated sample with known amounts of major constituent additions, (3) filtered, acidified sample, and (4) filtered, acidified sample with known amounts of trace constituent additions.

2.1.6a Direct requests for the preparation of “matrix material samples” to the Project Chief for Laboratory Evaluation.

2.1.6b Submit matrix samples to at least two laboratories; participation by more than two laboratories is desirable. Submit at least four subsamples of any specific prepared sample (over a period of time) to each laboratory (NOTE 2).

NOTE 2. Sufficient water must be collected initially to allow for each participating laboratory to analyze the samples the minimum four times. Preferably, when collecting the water, a minimum of four samples of the natural water should be collected and submitted to each participating laboratory to provide “base level” data.

2.2 Spikes and dilutions: substitution for prepared reference material

2.2.1 For many constituents, prepared reference materials are difficult to obtain or are unavailable. Spiked or diluted samples may often be substituted.

2.2.2 Since these samples are being substituted for reference material (or used in conjunction with reference materials when supplies of the latter are limited), all of the requirements of the previous section also apply.

2.2.3 Because the analyses will yield more information on the quality of a laboratory’s work, spiking with known concentrations of constituents to be determined is preferred over the dilution techniques.

2.2.4 For “spiked samples,” spike every 25th sample collected (or 1 sample per month if between 10 and 25 samples are analyzed in a month) with a known amount of the constituent(s) to be determined. Submit both
spiked and unspiked portions to the laboratory. If possible, select or prepare concentrations of the material to be used as spikes so that the resulting concentration will remain in the analytical range of the method or will need the same dilution as the unspiked sample. Examination of other analyses from the same site, and determination of the specific conductance of the sample, will be helpful in making the dilution. Report concentrations determined in the original (unspiked) sample, the spiked sample, and report the calculated percent recoveries (bias).

2.2.4a If there is a possibility that spiking with more than one constituent may cause interference problems (such as coprecipitation) or if the cooperating agency collects its own samples, provide the material to be used for the spikes directly to the analyzing laboratory and supply directions for adding the material to the samples. In no case should the laboratory or cooperating agency be informed of the concentration of the spike prior to the analysis.

2.2.4b The Project Chief for Laboratory Evaluation can provide some material suitable for use as spikes.

2.2.4c Many organic compounds are available from the Environmental Protection Agency, Research Triangle Park, in 100 mg quantities (Watts, 1980). If obtained by the district directly, it will be the responsibility of the district to ensure that solutions to be used in spiking are quantitatively prepared (NOTE 3).

NOTE 3. CAUTION: Since many of these compounds are extremely hazardous, extreme care must be taken in their handling.

2.2.5 For “diluted samples,” dilute every 25th sample (or 1 sample per month if between 10 and 25 samples are analyzed in a month). Use a one-half dilution (unless it is known that the diluted and undiluted samples will require different treatment to be in the analytical range) and submit both diluted and undiluted portions to the laboratory. If the cooperating agency collects its own samples, submit these dilution “replicates” in addition to the regular samples analyzed. Vary the dilution and do not inform the laboratory or cooperating agency of the dilutions. Obtain the reported concentrations determined in both diluted and undiluted samples. Estimate the bias, using the explanation for figure 14 in the practice, “Quality control charts” as a guide.

2.3 Split samples

2.3.1 Split every 30th sample into a minimum of 8 samples. Send equal numbers (at least four) to the cooperating laboratory and to a central laboratory.

2.3.2 In any month in which 10 or more samples are analyzed, submit the split subsamples to both the cooperating and central laboratory (even though less than 30 samples are done).

2.3.3 If possible, submit samples in such a way that the receiving laboratory will not know that they are splits of a given sample. (For example, disguise the name of the sample.) If the cooperating agency collects its own samples, submit the pair of “splits” to the laboratory in addition to the regular samples analyzed; be sure to also submit a simultaneous pair to a central laboratory (NOTE 4).

NOTE 4. If a cooperator agency collects its own samples, it may be advisable to occasionally dilute one of the “splits” in order to make the split more of an “unknown.”

2.4 Other material

2.4.1 As indicated previously, 1 in every 25 samples analyzed should include a prepared reference material or a spiked or diluted sample. An additional 2 out of every 31 samples should be a split sample. This combination constitutes a quality assurance workload of approximately 10.5 percent. An additional 4.5 percent quality assurance workload is needed to achieve the required 15 percent total (NOTE 5).

NOTE 5. Although initially this “external” quality assurance should comprise 15 percent of the laboratory work, if a laboratory has an active quality control program and if results from the initial quality assurance analyses appear acceptable, the percentage may be decreased. The percentage, however, should never be less than 5 percent of the laboratory work.

2.4.2 Unless the District obtains and submits more reference materials, data must be obtained from each laboratory showing results from any other reference samples which are run (as part of a state program for example), spiked or duplicate samples run as part of a quality
control program, etc. Quality control charts should be obtained if available. This data must be sufficient to show that, when combined with data from district submitted samples, there is a total quality assurance–quality control workload of at least 15 percent (NOTE 6).

NOTE 6. If less than 30 samples are analyzed for a constituent in a month, the percentage of district-submitted “split” samples must be increased, and if there is less than 25 samples analyzed for a constituent in a month, the percentage of district-submitted reference materials (on spiked or diluted substitutes) must be increased. If additional information is available, it is recommended that it be obtained; however, this additional information is required only if the quality assurance workload from the above-mentioned district-submitted samples is less than 15 percent.

References

Reference Material Use in Monitoring Field pH and Specific Conductance Measurements

1. Application or scope

1.1 This practice describes and documents the Geological Survey field proficiency testing program. Significant amounts of Geological Survey water-quality data are obtained by field measurements made by large numbers of personnel using a wide variety of instrumentation and equipment; the program described in this practice is used to document acceptability of data obtained by field measurements.

1.2 More specifically, this practice describes the use of reference sample test solutions for pH and specific conductance in the program.

2. Practice

2.1 Preliminary information required

2.1.1 Approximately 1 month prior to shipment of the test solutions, each district is requested to supply a list detailing the make, model, serial number, and location (if in a field or subdistrict office) of each pH and specific conductance meter in the district.

2.1.2 Each district also lists the names of the individual(s) assigned to each instrument for purposes of the test.

2.1.3 Every person performing pH or specific conductance measurements and every instrument in use must be included in the tabulation. This requirement may make it necessary to assign more than one person to an instrument or more than one pH and (or) specific conductance instrument to a person.

2.2 Reference material assignment

2.2.1 A number of different quality assurance pH and specific conductance test solutions are prepared under the direction of the Project Chief for Laboratory Evaluation. Each reference material is assigned to a specific instrument analyst combination so that, insofar as possible, each combination in any one field office is sent a set (pH and specific conductance) of reference materials which is unique.

2.2.2 Sample numbers are designed to identify the district, instrument-analyst combination, and the test sample type. Each sample number begins with two letters identifying the district. The third symbol in the sample number is coded P for a pH test sample or C for a specific conductance test sample. The next two symbols are the test sample sequence numbers assigned to each instrument analyst combination given on the inventory sheets submitted by the respective district. The sixth symbol is a letter A, B, or C, and so forth, to represent the first, second, third, or other sample assigned to each instrument. Thus, the six symbols comprising the sample number identify the district and sample type and provide a sequence number which, when used with a computerized cross-reference list, identifies the instrument make, model, and serial number, the analyst, and the theoretical value of each sample.

2.3 Measurement and data submission

2.3.1 Prior to making measurement on any of the pH or specific conductance test solutions supplied for this effort, instruments should be calibrated in the usual manner. The section, "Instrumental Techniques," should be referred to for specific calibration procedures.

2.3.2 Data should be reported for all samples sent to a field office. If no data are reported for a sample, an unsatisfactory (U) rating will be listed in the final report for each district. Consequently, in case of absences, alternate analysts should be assigned and changes noted. Similarly if the test solution samples are used for meters other than those initially assigned, the meter identification model and serial number should also be corrected on the computer sheet listing.

2.3.3 Computer-generated listings of the analysts and meters and the corresponding test samples assigned to each combination are in-
cluded with each sample shipment for recording and reporting the analytical data. The data are analyzed and evaluated by a quality assurance project independent of district personnel (see practice "Evaluation of field reference material data," in the section "Review, Summary and Evaluation of Data" for further information).
Quality Assurance and Quality Control Personnel

1. Application or scope

1.1 All laboratory personnel have responsibility for the quality of the laboratory's analyses. In order to increase reliability of the laboratory's analytical data, the laboratory staff must include a portion of laboratory personnel that are involved solely in the effort to define and control the quality of analytical data.

1.2 Additionally, someone outside the laboratory system should monitor laboratory quality control.

2. Practice

2.1 Laboratory chief and quality control staff

2.1.1 The responsibility for the quality of analytical result rests with the laboratory chief. If analytical results are produced in the field, the responsibility rests with the district chief, project chief, or equivalent.

2.1.2 In order to fulfill this responsibility, each laboratory chief should have on his staff at least one person involved in quality assurance/quality control activities. Such a person(s) should not be involved in making analyses. This person should be at an organizational level equivalent to a section chief and should report directly to the laboratory chief.

2.2 Section chiefs and analysts

2.2.1 The section chief has dual quality control and production functions. Although analyses deadlines must be met, the section chief is responsible for the quality of work in his section; the production of greater numbers of analyses is meaningless unless a high degree of quality control also is maintained. The practice "Quality control: section leader duties and responsibilities," in the section on "Laboratory Quality Control" should be referred to for specific requirements.

2.2.2 The analyst also has dual quality control and production functions. Although he may be under pressure to increase the number of analyses made, the analyst must be certain not to compromise the quality of the work. Specific quality control requirements are discussed in the section "Laboratory Quality Control."

2.2.3 Although not directly involved in producing the analytical result, personnel involved in logging in the sample, processing the data and so forth, have equivalent responsibilities.

2.3 Quality assurance overseer

2.3.1 Laboratory quality control should be monitored by someone from outside the laboratory. One person overseeing all quality assurance and possibly all quality control practices may suffice.

2.3.2 This person should be on the organizational level with the laboratory chief and should report to the same person as does the laboratory chief.
Documentation, Summary, and Evaluation of Data

All data relating to the analyses of water and fluvial sediments and to the quality assurance of the analyses must be carefully documented. Thorough records must be kept both by each laboratory doing work in cooperation with or through a contract with the Geological Survey and by the Geological Survey office responsible for the cooperation agreement or contract.

Periodic review of all laboratory records must be made including review of documentation of standard solution preparation, instrument calibration, and reference material analyses. Quality assurance data should be summarized and evaluated semiannually. The documentation, summary, and evaluation of data should ensure that data of a known and comparable quality is being produced.

Required Documentation and Review of Data

1. Application or scope
   1.1 This practice describes records to be kept by field and laboratory personnel. These records must completely document all aspects of sample collection and analysis. Specific practices elsewhere in this chapter should also be referred to.

2. Practice
   2.1 Field data
      2.1.1 At the time a sample is collected, all information pertaining to its identification must be recorded in a "field notebook." All data also must be written on or submitted with the sample bottle. Such information should include, but is not limited to, the date and time of collection, complete site identification information (such as latitude, longitude, and depth of a well), the name of the person or persons collecting the sample, and important environmental facts and observations (such as weather conditions or apparent turbidity of river).

      2.1.2 Data from field measurements (such as temperature, pH, specific conductance, and alkalinity) must also be recorded in the field notebook, along with information pertinent to instrument calibration. Results from such field measurements must be written on or submitted with the sample bottle.

      2.1.3 If an automated monitor is in use at the sampling site, a comparison must be made between observed values and those recorded by the monitor. Discrepancies, such as differences in temperature, dissolved oxygen, or gage height, must be noted in both the field notebook and on the monitor's recorder output. Monitor intake systems should be carefully checked and, if necessary, cleaned. If debris (such as leaves) appears to have caused a problem, this fact should be recorded.

   2.2 Laboratory data
      2.2.1 All analytical methods must be carefully documented and available to the analyst. The analyst should record every deviation from routine procedure. For example, notes should be kept on any interferences and on modifications taken to eliminate them.

      2.2.2 Records should be kept on the method used to analyze each sample and the expected precision of that method should be documented. (In the Geological Survey's Central Laboratories System, results are entered into the computer using "lab codes"; these codes
represent not only the constituent determined, but also the method used.)

2.2.3 Records should be kept on the preparation of all standards. All weights and volumes should be recorded. Records should include not only data related to the preparation of stock solutions, but also data on all intermediate and working standards. The dates of preparation and the name of the preparing analyst should be noted. Date of opening reagents and standards should be recorded on the bottle labels and, if critical, also in a notebook.

2.2.4 Instrument calibration procedures should be documented and readily available to the analyst. The analyst should retain records on instrument calibration, and may use recorder charts to do so (for example, on gas chromatographs.)

2.2.5 All analyses of reference materials should be recorded and kept. The identification of all samples run with individual reference samples should also be recorded.

2.2.6 Careful records must be kept by "cooperator" and "contract" laboratories and by the Geological Survey office responsible for the cooperation agreement or contract. The quality of the data must be comparable to that of the central laboratories, since these data may be entered into the WATSTORE computer system and must be able to be used without qualifications.

2.2.7 Regular review of all laboratory records must be scheduled and made. This includes review of documentation of standard solution preparation, instrument calibration, and reference material analyses.

2.2.8 Data review programs should provide for continual review and evaluation of laboratory performance for all laboratories.

Selected References
Evaluation of Field Reference Material Data

1. Application or scope
1.1 This practice describes computerized data processing techniques that are used to process and analyze the voluminous amount of data produced in conjunction with efforts to evaluate measurements made in the field. (See practice “Reference material use in monitoring field pH and specific conductance” in section “Quality assurance monitoring.”)

2. Practice
2.1 Data evaluation
2.1.1 Measurement results for the reference materials are required to be submitted to the initiating quality assurance project, located at the National Water Quality Laboratory (NWQL), within approximately 30 days of the initial sample distribution dates. Data received at the NWQL within the required time frames are considered “on time,” and are used to calculate the mean, average deviation, percent deviation from the mean, standard deviation, and total range values for each test solution. Outlying values are rejected using the $T$ test described in the practice “Single operator precision” in the section “Analytical Methods Development Procedures.” ($T$ values are listed in table A1.) After deleting outlying observations, the mean of these remaining data is computed and taken to be the most probable value (MPV). The data calculations are made by computer. Each data set is then examined to determine how individual test sample analyses meet a priori evaluation criteria.

2.1.2 Initially, acceptance criteria (expressed as “maximum allowable deviation from the most probable value”) were arbitrary: for pH, values with maximum deviations of 0.1 unit or less were satisfactory (S), values with deviations from 0.1 to 0.2 unit were marginal (M), and values with deviations greater than 0.2 unit were unsatisfactory (U); for specific conductance, values with deviations equal to or less than 4 percent were satisfactory (S), values with deviations from 4 to 5 percent were marginal (M), and values with deviations greater than 5 percent error were unsatisfactory (U). These criteria may be revised as more information from this program becomes available.

2.1.3 Each test sample is identified by a unique number which assigns the sample to a specific district, instrument and analyst. Individual results for each test sample are alphabetically listed by district and analyst on computer generated tabulations. The measured test value for each test sample and the corresponding MPV, obtained as described above, are given in the columns following the test sample number.

2.1.4 Values reported for each test sample are rated as satisfactory (S), marginal (M), unsatisfactory (U) or not rated (N). Comments explaining the assigned ratings are made when applicable.

2.1.5 Scatter diagrams (fig. 20) produced by using a Statistical Analysis System (SAS) computer program (Barr and others, 1976) have been used to illustrate the pH and specific conductance field measurement as reported for each district. The value and the number of measurements are indicated by the location of the plotted letters, A, B, C, and so forth, with an A indicating a single value reported for a field measurement, a B for two values, C for three, and so forth. The “most probable value” for each test solution is indicated by an appropriately plotted slash (/). A letter superimposed over the slash indicates the number of measurements reported that duplicate the most probable value.

2.1.6 Ideally, all points would be superimposed over the respective slash mark representing the most probable value for the respective test solution. An excessive vertical distance of the plotted letters from the respective “slash” value is readily evident and usually indicates
unacceptable measurements or samples outside the range of the measuring instrument.

2.1.7 Most graphs include a statement at the bottom such as, “xx observations hidden.” This statement refers to the fact that the computer plots an “MPV” (slash) for each measured and plotted test sample value (A, B, C, and so forth). Superimposed slashes are not recognizable and are called “hidden observations.” Decimal point or sample identification errors will also result in excessive scatter of the plotted points and can generally be recognized.

2.2 Report preparation and distribution

2.2.1 All results, obtained within the required time frames, are compiled and tabulated. Overall results obtained within a Geological Survey region are then used to compute the relative performance ratings demonstrated by the districts in that region. These ratings are based on the percent of acceptable measurement submitted for the samples tested. Ratings obtained by each district are included in separate evaluation reports prepared for the respective testing period for each region.

2.2.2 If data from more than one round of testing have been obtained, such as during the second half of a testing year, presentation of all data may be useful. This summary can provide a convenient mechanism for identifying areas which have shown improvement or those in need of assistance. Whenever possible, specific problem areas are identified and ways are suggested to correct or reduce them.

2.2.3 After completion of a round of testing which has included all districts in all four regions, a summary report is prepared. These reports include both tabular and narrative evaluations of the results obtained by all districts and personnel participating during each complete round of testing. The combined efforts of all personnel involved provide the information necessary to effect the timely identification and correction of problems which may exist in the determination of field measured water quality data.

References
