



IN REPLY REFER TO:

# United States Department of the Interior

U.S. GEOLOGICAL SURVEY

Box 25046 M.S. 407

Denver Federal Center

Denver, Colorado 80225

## NATIONAL WATER QUALITY LABORATORY TECHNICAL MEMORANDUM 1993.02

October 5, 1992

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  
Employees, National Water Quality Laboratory

From: Chief, National Water Quality Laboratory

Subject: Review process for samples analyzed at the National Water Quality Laboratory (NWQL)

Author: Dariel Blackburn, Quality Management Group, (303) 467-8042

Revision: No

### Purpose

The purpose of this memorandum is to assist the District personnel in understanding the Quality Control (QC) review process that samples presently undergo at the NWQL prior to release. As the tools become available to implement major changes in the procedure, the Quality Management Group (QMG) will coordinate with District personnel and chemists to improve the data review process.

The review process is explained for the inorganic and radiochemical samples. The organic review process will be explained in a future memorandum.

## DATA REVIEW OF INORGANIC SAMPLES

After the inorganic sample has been analyzed for all requested constituents and has passed all the analytical line QC checks, the sample data go through at least one, and sometimes two or three, different data review QC checks. Data first go through a QC computer program which flags any failures. Samples which pass this check are immediately released. Samples which fail the check are then reviewed manually by a chemist from the Quality Management Group (QMG).

Listed below are the most common QC failure flags generated from the computer program and the criteria which the QMG follows to address these flags.

1. Any parameter which exceeds the EPA drinking water standard is flagged at present.
  - a. If the District does not mark the sample as a drinking water on the Analytical Services Request (ASR) form, parameters which exceed drinking water standards are not rerun and the data are released. An exception might be very high levels of a known toxic substance. In this case we might ask for a rerun, unless we knew that historically the concentrations were high for this particular site.
  - b. If the sample has been marked as a drinking water sample, we will rerun any parameters which exceed the drinking water standards.
2. Sizeable differences between field and lab measurements will be flagged.
  - a. Differences between field and lab values can be an indication of a bottle mixup. QMG checks the bottles to be certain they agree with the ASR form.
  - b. The pH will be rerun if the difference is greater than 1 pH unit. The pH will change slightly from gain or loss of CO<sub>2</sub>. Some waters without any natural buffers may change more than 1.5 pH units.
  - c. Specific conductance may go up or down slightly, generally from the gain or loss of alkalinity. Differences greater than 10% are rerun unless all other data supports the Lab value. If differences are exceptionally high, QMG will do a bottle check. This means they will check all the sample bottles logged in for a particular Lab I.D. to be sure the information on the bottles matches the ASR form.
  - d. Alkalinity will be rerun if there is a greater than 10% difference from the field measurement, unless all other data support the Lab value. Normally, there will be some loss or gain of alkalinity from the absorption or loss of CO<sub>2</sub>.
3. A cation and anion balance which is not within the allowable range will be flagged and then reviewed by a chemist
  - a. If the actual difference is less than or equal to 4% ( $[(\text{cation} - \text{anion meq/l}) / (\text{cation} + \text{anion meq/l})] \times 100$ ), the sample may be released at the reviewer's discretion.
  - b. If the cations exceed the anions by greater than 4%, QMG checks to see if NO<sub>2</sub>+NO<sub>3</sub> was run on the sample and if the addition would reduce the difference to less than 4%. If so, the sample is released. There are other contributors to anion balance, but NO<sub>2</sub>+N<sub>3</sub> is usually the only major contributor.
  - c. If the anions exceed the cations by greater than 4%, QMG checks to see if the addition of NH<sub>4</sub>, Fe-dissolved, Mn-dissolved, or H<sup>+</sup> ion will reduce the difference to less than 4%. If so, the sample is released. There are other contributors to cation balance, but these are the major contributors we always check for.
  - d. A large difference between the cation and anion sums may indicate a bottle mixup. QMG will do a bottle check, if necessary, before requesting any reruns.

- e. If one set of ions exceeds the other by greater than 4%, the suspect group (cation or anion, or possibly both) will be rerun. However, as the conductance of the sample approaches zero, the percent difference allowed becomes larger and larger.
  - f. All samples that have been rerun and still remain "out of balance" are commented by the QMG. Some districts are still having problems receiving QMG comments. These comments are important to your understanding the history of the analysis; so if you are not receiving them, please contact DENADP.
4. When something is missing for ion balance, a chemist reviews the data. For instance, alkalinity or other major ions that are needed to check the sample balance may not have been requested--and no field value was provided.
    - a. QMG checks any confirming data; i.e., a pH of 8.2 indicates a significant alkalinity content.
    - b. A partial cation or anion sum should be lower than the specific conductance/100.
    - c. QMG will rerun any obvious errors; but, if there are not enough data to make a judgment about the ion concentrations, the sample will be released.

\*\* It is important for the Districts to realize that a sample cannot be properly QC'ed unless all the major cations and anions are requested for analysis.

5. If the ratio of specific conductance to the milliequivalents of cations or anions is less than 0.92 or greater than 1.12, a chemist reviews the data. On the basis of water type, QMG sometimes will use a range of .85 to 1.12—even lower if sulfate values of > 1000 mg/L are present.
  - a. QMG will have the cations or anions rerun--whichever has the skewed ratio--if the conductance agrees with the dissolved solids.
  - b. QMG will have the conductance rerun if there is disagreement with the field value and with the conductance/ion ratios.
6. If the ratio of dissolved solids to specific conductance is below .55 or above .86, a chemist reviews the data. On the basis of water type, QMG will usually release samples with a ratio of .53 to .88.
  - a. If the specific conductance is in agreement with other values, QMG will rerun the dissolved solids. The following are exceptions.
    - 1) The specific conductance is less than 100 uS/cm; normal ratios do not apply at this low range. Generally, the lower the conductance, the greater the variance.
    - 2) The dissolved solids are greater than 1000 mg/L. Higher dissolved solids depress the conductance, especially if the sulfate concentration is high. The ratio, in this case, may be 1 or more.
    - 3) Samples that have a relatively low concentration of chloride may also have a depressed specific conductance.
7. If the pH is less than 4 or greater than 9 and does not agree with the field pH, then QMG will have it rerun. Most natural waters fall within this pH range. The pH values that fall outside these ranges can be released without rerun for the following reasons:
  - a. If the pH is less than 4 and there is a comment by the sampler that indicates an unusually acid situation, such as "acid mine drainage."
  - b. If the pH is greater than 9 and there is a comment by the sampler that indicates an unusually alkaline situation, such as "alkali deposits."
8. If the dissolved concentration of a particular metal species is greater than the total concentration, a chemist reviews the data.

- a. Since the minimum reporting unit of a total metal is often significantly within this difference. If so, the sample may be released. For most metals, the acceptable difference for dissolved > totals is 3 times the detection limit of the total species, but if the sample has to be diluted, the acceptable difference must be multiplied by the dilution factor.
- b. If the reporting units do not account for the difference, QMG will rerun both the dissolved and total species.

9. Nutrients are QC'ed by the analytical chemist at the instrument. An NWQL Technical Memorandum is being written to describe this process.

## **Data Review of Radiochemical, Stable Isotopes, and Radon Samples**

### **Radiochemical**

There is no automatic computer data review of radiochemical samples. Each sample is individually reviewed. Depending on the analysis requested, the following are the criteria that the Radiochemical Unit checks for:

1. Are the two gross alpha (U and Th-230) results in agreement (call Radiochemical Unit for specifics)?
2. Are the two gross beta (Cs-137 and Sr-90/Y-90) results in agreement (call Radiochemical Unit for specifics)?
3. Do the isotopic uranium results agree within two standard deviations with the total uranium?
4. Are there any nuclides present (such as Ra-226 or Ra-228) whose progeny could bias the gross alpha or gross beta results?
5. If the two sigma value is high, is there a reasonable explanation (such as small sample volume or counts near background)?
6. If the Ra-226 and uranium results combined do not agree within two standard deviations with the gross alpha, could some of the Ra-226 or uranium have fallen out of solution and adhered to suspended material? (Example – If the dissolved alpha was done on a lab-filtered RU sample, while the Ra-226 and uranium were done on a FA sample.)

In order to answer discrepancies, the Radiochemical unit frequently has to refer to the data sheets from the contracting lab for information such as sample size or date of counting.

The values of the QA samples at the instrument must fall within two standard deviations. If these quality-control checks are met, the data are released to the Districts. If the QA samples fall outside the two standard deviations control limits, further analyses for that parameter are halted until the problem is corrected.

### **Stable Isotopes/Tritium**

Data are not released to the Districts until the QC sample results are reviewed. The results must fall within the limits defined in the specific agreement and are reported as "permil" (permil =  $[\text{isotope 1}/\text{isotope 2}] \times 1000$ ). The limits are as follows:

**ANALYSIS**

Tritium  
C-13/C-12  
S-34/S-32  
N-15/N-14  
O-18/O-16  
D/H

**LIMIT**

2 Standard Deviations  
0.3 permil  
0.5 permil  
0.2 permil  
0.2 permil  
2.0 permil

If the QC samples indicate there is a problem, further analyses are halted until the problem is corrected.

**Radon**

Radon data are not released to the Districts until the results are reviewed. Each radon sample is run in duplicate. If the duplicate radon results do not fall within two standard deviations of each other, the appropriate District personnel are notified before the result is released.

/signed/

Peter F. Rogerson

Key Words: Data review, QC, cation/anion balance

Distribution: See above plus QWTALK