



STATE OF NEVADA

Department of Conservation & Natural Resources

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DIVISION OF ENVIRONMENTAL PROTECTION

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Re. **BMI Plant Sites and Common Areas Projects, Henderson, Nevada**
Cation-Anion Balance – Updated Guidance

Dear Sirs and Madam:

All of the parties listed above shall be referred to as “the Companies” for the purposes of this letter. The NDEP’s May 21, 2007 guidance on cation-anion balances has been expanded and clarified. This updated guidance is attached as Attachment A.

Please contact me with any questions (tel: 702-486-2850 x247; e-mail: brakvica@ndep.nv.gov).

Sincerely,

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Attachment A

Evaluation of Inorganic Chemical Analysis

NDEP prepared this technical memorandum to guide checking major ion chemistry to support the development of groundwater chemical datasets suitable for hydrogeologic evaluation at the BMI Complex and Common Areas in Henderson, Nevada. This guidance replaces the NDEP (2007) letter to the Companies entitled *Additional Guidance on Completion of Quality Checks for Cation-Anion Balance, Attachment A*. Please note that Basic Remediation Company, Montrose Chemical Corp of CA, Pioneer Companies, Inc., Stauffer Management Co, LLC, Titanium Metals Corporation, and Tronox, LLC are referred to herein collectively as “the Companies.”

During reviews of cation-anion balances (CAB), total dissolved solids (TDS) data, and electrical conductivity (EC) data the NDEP has noted several issues that need to be addressed. These issues are addressed below.

In addition, the NDEP reiterates its request that the Companies submit results from the checks on chemical analysis in a “live” spreadsheet format, including equations for all calculated values, to facilitate review and checking results.

Cation-Anion Balance

The cation and anion sums expressed in milliequivalents per liter (meq/L) must balance because aqueous solutions are electrically neutral (Hem, 1992; Standard Methods, 1999). The cation-anion balance may be either positive or negative depending on whether cations or anions are more abundant. If the cation sum as meq/L is not within a few percent of the anion sum as meq/L, then there is a problem with either the laboratory analysis or ionic species not identified in the analysis (Fetter, 2001). Given that the NDEP-required inorganic analysis at the BMI Industrial Complex and Common Areas provides for major cations and anions the latter condition (*i.e.*, missing ionic species) is unlikely.

The cation-anion balance will be calculated as recommended by Standard Methods (1999) using the equation:

$$\text{CAB \% Difference} = \frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}}$$

The acceptance criteria are as follows (Standard Methods, 1999).

Anion Sum (meq/L)	Acceptable % Difference
0 – 3.0	± 0.2 meq/L
3.0 – 10.0	± 2%
10.0 - 800	± 2 – 5%

The Companies should note that the acceptable percent difference varies with regard to the anion sum. The NDEP has adopted the use of 5% for the anion sum range 10.0 to 800 meq/L.

The anion-cation balance check should include the following major cations and anions:

1. calcium,
2. magnesium,
3. sodium,
4. potassium,
5. alkalinity,
 - a. bicarbonate,
 - b. carbonate,
 - c. hydroxide (for pH > 10.0),
6. chloride,
7. sulfate,
8. fluoride,
9. nitrate, and
10. perchlorate.

Hydroxide alkalinity, although uncommon in natural groundwater (Hem, 1992, p. 64), was added because high pH values have been reported and apparently associated with reportable levels of the hydroxide anion. Fluoride, nitrate, and perchlorate are included in the anion-cation balance calculation for completeness based on site history. The latter anion contributions to the cation-anion balance are typically small because their percentages are less than one percent of total anions. However, it is recognized that at specific locations at the BMI Complex and Common Areas these anions may contribute to the cation-anion balance.

Typically trace metals are not included in the calculations based on the rationale that analytes measured in the microgram per liter ($\mu\text{g/L}$) range are not likely to significantly affect the balance outcome. However, any trace metals reported greater than 1,000 $\mu\text{g/L}$ will be included as they may affect the balance calculation. The Companies may include trace metals analyses reported less than 1,000 $\mu\text{g/L}$ in the cation-anion balance; however, it is not required.

Calculating Milliequivalents per Liter

The concentration of the ionic species in milligrams per liter (mg/L) is divided by the equivalent weight of the ion; the result is expressed as milliequivalents per liter (meq/L) (Hem, 1992 and Fetter, 2001). The equivalent weight of a dissolved ionic species is the formula weight divided by the electrical charge. The formula weight can be calculated by looking up the atomic weights for the individual element(s) in the Periodic Table. The current standard for reporting atomic weights is the 2005 International Union of Pure and Applied Chemistry (IUPAC) Recommendations (Royal Society of Chemistry, 2005). Atomic weights are reported to five significant figures. Follow the rules for significant figures when reporting results from the calculations.

Charge Balance Error

For analyses where the anion sum is greater than 800 meq/L the charge balance error (CBE) will be used to check the analysis by the following equation (Fetter, 2001):

$$CBE = \frac{\sum z \times m_c - \sum z \times m_a}{\sum z \times m_c + \sum z \times m_a} \times 100$$

where

- z is the charge of an ion,
- m_c is the molality of a cation, and
- m_a is the molality of an anion.

As with the cation-anion balance calculation, the charge balance error may be either positive or negative depending on ion abundance. The limit for accepting an analysis by the charge balance error calculation will be $\pm 5\%$.

TDS Measured to Calculated Check

TDS for the samples will be calculated using the formula:

$$TDS \text{ Calculated} = \text{cation sum} + 0.6 \times \text{alkalinity} + \text{anion sum}$$

The measured TDS to calculated TDS ratio will be calculated and should fall within the range (Standard Methods, 1999):

$$1.0 < \frac{\text{measured TDS}}{\text{calculated TDS}} < 1.2$$

Measured TDS to EC Ratio

Hem (1992) provides a detailed analysis and discussion on the relationship of conductivity to TDS. Hem plotted TDS versus EC data that ranged from about 500 to 3000 mg/L and observed that the data set fit a straight line of regression with a slope of 0.59. Further, Hem (1992) indicated that the slope of the line of regression would be steeper for lower EC values, *i.e.*, that the slope of the line of regression is not constant over a wide range of dissolved solids concentration. Hem (1992) stated that for the range of natural water evaluated the range for the ratio of TDS:EC was 0.54 to 0.96.

Recommended Ranges for Evaluating TDS:EC Ratio

NDEP reviewed the Basic Remediation Company (BRC) 5th Round, April 2009, groundwater monitoring dataset for TDS:EC evaluation. The BRC dataset was selected because it encompasses a wide range in TDS values from 570 to 215,000 mg/L. Figure 1 shows data from the 5th Round. The plot shows two groups of data; a low range with TDS less than 10,000 mg/L; a high range with TDS greater than 10,000 mg/L; and data points identified as outliers. Figure 2 shows a plot of the low range data with a line of regression slope of 1.05 and an R² value of 0.88 for the subset of data. Figure 3 shows a plot of the high range data with a line of regression slope of 0.57 and an R² value of 0.92 for the subset of data. These graphs appear consistent with the observations of Hem (1992). NDEP thus recommends using a range in TDS:EC ratio of 0.55 to 1.0 for groundwater samples collected at the BMI Industrial Complex and Common Areas.

NDEP notes that the TDS:EC relationship is influenced by the chemical composition of the groundwater. In future evaluations of the TDS:EC ratio NDEP will look at groundwater impacted by various site-related chemicals.

Data Flags for Analytical Results

Based on the numerous instances in which the correctness of the analyses has not met the Standard Methods (1999) criteria it is recommended that the laboratories performing these analyses also perform the correctness test. When the correctness test is violated, the laboratory should follow the Standard Methods (1999) recommendations and evaluate the data for error and, if necessary, re-analyze the samples.

If the results of any corrective action are not sufficient, then the data that does not meet these quality checks will be qualified. For example, based on cation-anion balance, TDS measured/sum, and TDS:EC ratio checks there are four potential outcomes.

1. Cation-anion balance checks; TDS measured/sum checks, and TDS:EC ratio is within the acceptable range.
2. Cation-anion balance checks; either TDS measured/sum or TDS:EC ratio does not check.
3. Cation-anion balance does not check; TDS measured/sum and TDS:EC ratio checks.
4. Cation-anion balance does not check; TDS measured/sum and TDS:EC ratio does not check.

When the quality checks result in outcome number 1 the analysis is not flagged. When the quality checks result in outcome number 2 the analysis is considered estimated and flagged – J-TDS. When the quality checks result in outcome 3 the analysis is considered estimated and flagged – J-CAB. When the quality checks result in outcome number 4, the analysis is considered unusable and flagged – R-CAB&TDS.

Rules for Significant Figures

Some data tables have reported calculation results with far more significant figures than appropriate. The NDEP recommends the follow rules for determining significant figures.

1. When you multiply or divide, round off to the same number of figures as in the measurement with the least number of significant figures. In this case, count the significant figures in each measurement not the number of decimal places.
2. When adding or subtracting, the answer can contain no more decimal places than the least accurate measurement.
3. Zeroes
 - a. Zeros within a number are always significant. Both 1,502 and 40.08 contain four significant figures.
 - b. Zeros that do nothing but set the decimal point are not significant. Thus, 470,000 has two significant figures.
 - c. Trailing zeros that are not needed to hold the decimal point are significant. For example, 4.00 has three significant figures.

4. If a calculation involves multiple steps, keep additional digits through the intermediate results and round off at the end. If intermediate results need to be reported, round off to the appropriate number of significant figures when you report it; but, go back and pick up the discarded figures when proceeding further with the calculation.

References

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Hem, J. D., 1992. Study and Interpretation of the Chemical Characteristics of Natural Water. U.S. Geological Survey Water-Supply Paper 2254.

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