Total Kjeldahl Nitrogen for NPDES/SDS Reporting

It has come to the attention of the Minnesota Pollution Control Agency (MPCA) that there have been instances where the Total Kjeldahl Nitrogen (TKN) result is less than the Ammonia-Nitrogen (NH_3-N) result for the same sample.

Since the "Kjeldahl nitrogen" is the sum of organic and ammonia nitrogen, when the TKN result is significantly lower than the NH_3-N result, one of the results is inaccurate. In cases where the TKN result is less than the NH_3-N result, laboratories should not report either result without evaluation. To help ensure the results are usable and defensible, laboratories must compare the results by evaluating the difference between the TKN and NH_3-N values using the applicable method, laboratory, or precision control limits. When results are at or near the reporting level, wider limits may apply. If the difference exceeds the expected precision, the laboratory needs to investigate the cause. Both the TKN and the NH_3-N preparation and analytical data should be reviewed. If it is determined that either of the results are suspect, the sample should be re-prepared and re-analyzed.

The approved analytical methods for the Clean Water Act for analysis of TKN include potential interferences from nitrate levels above 10 mg/L, and/or levels that are 10 X more than the TKN level. It is important to note that the methods state it as *nitrate*, not *nitrate as N*. When the TKN result is significantly lower than the NH_3-N result, one thing that could be occurring during the Kjeldahl digestion is nitrate in excess of 10 mg/L can oxidize a portion of the ammonia released from the digested organic nitrogen, producing N_2O and resulting in a negative interference (APHA 1992, p4-94).

The approved methods [EPA 351.2 (1993), SM4500 N org (1997), and USGS I-4515-91] do not include a proven way to eliminate the nitrate interference. Therefore, to reduce the effect of this interference or other unknown interferences, dilution may be required (EPA 351.2, 1993). If dilution is used, it is important that the laboratory consider the impact of an elevated reporting limit on data usability.

Additional considerations:

- For the TKN analysis, consider using an organic nitrogen standard (nicotinic acid, $C_6H_5NO_2$) to test for the completion of digestion (SM 4500-Norg 1997).
- For both the NH_3-N and TKN preparation batches, check that the samples are correctly matrix-matched to the calibration blank and standards. The colorimetric tests are pH dependent; therefore it may be best for the calibration blank and each of the calibration standards to be distilled/digested (check the requirements of the approved reference method).
- Review any changes the laboratory has made to the preparation or analytical equipment and procedures for either the TKN or NH_3-N analyses.

This information is also being communicated to permittees. If a facility has questions, they can contact their MPCA permit writer, compliance and enforcement staff, or the MPCA's Environmental Data Quality Unit.

References:

American Public Health Association, 1992, Standard methods for the examination of water and wastewater (18th ed.): Washington, D.C., American Public Health Association Inc., p. 4–94.

EPA Method 351.2, Determination of Total Kjeldahl Nitrogen by Semiautomated Colorimetry (Rev 2.0 1993): Office of Research and Development, US EPA Cincinnati Ohio.

SM 4500-Norg, Nitrogen (Organic) (1997) Standards Methods for the Examination of Water and Wastewater.

USGS I-4515-91, Determination of Ammonium Plus Organic Nitrogen by Kjeldahl Digestion Method and an Automated Photometric Finish that Includes Digest Cleanup by Gas Diffusion (2000): U.S. Geological Survey, Denver Colorado.

EPA Code of Federal Regulations 40, Part 136, Table IB. May 18, 2012.