

# Quality Control Summary Report Nitrate-N Isotope Analysis: May- June 2018

Prepared for Eastern Research Group Prime Contract #EP-W-15-006

**Daniel Snow, University of Nebraska Water Sciences Laboratory Lincoln, NE 68583-0844**

## Introduction

Eighty-seven (87) water samples were received at the University of Nebraska Water Sciences Laboratory over a four-day period from May 1 through May 4<sup>th</sup>, 2018. These arrived in good condition in coolers with dry ice and were promptly logged in by our Separations Chemist, David Cassada following our sample receipt and login SOP. Quality controls include laboratory duplicates (LD1 and LD2), laboratory reagent blanks (LRB) and laboratory fortified blanks (LFB) were each assigned at a rate of at least 1 for every 20 field samples (5%). LRBs were not run for isotopes because of insufficient nitrate-N concentrations.

Scanned copies of the eight chain of custody forms are available in Appendix I. All samples were scheduled for both nitrate+nitrite-N concentration measurement by protocol #02\_03\_01 and Nitrogen and Oxygen Isotopes using azide reduction by protocol #12\_02\_11\_01 (Table 1). Nitrate+nitrite-N analysis was conducted on 05/07/2018 and 05/09/2018. Stable isotope analysis was conducted on 05/14/2018, 06/06/2018 and 06/07/2018 on samples with nitrate+nitrite-N concentrations greater than 0.10 mg/L.

**Table 1. Listing of sample batches, assigned methods, receipt and analysis dates.**

Protocols	Description	Received	Batch	Analyzed	Samples/Batch
02_03_01	Nitrate_Nitrite Cd-Reduction EPA 353.2	05/01/2018	W18196	05/07/2018	22
02_03_01	Nitrate_Nitrite Cd-Reduction EPA 353.2	05/02/2018	W18199	05/07/2018	26
02_03_01	Nitrate_Nitrite Cd-Reduction EPA 353.2	05/03/2018	W18205	05/09/2018	28
02_03_01	Nitrate_Nitrite Cd-Reduction EPA 353.2	05/04/2018	W18215	05/09/2018	11
Subtotal:					87
Protocols	Description	Received	Batch	Analyzed	Samples/Batch
12_02_11_01	Nitrogen and Oxygen Isotopes using azide reduction and Tracegas Preconcentrator Method	05/01/2018	W18197	05/14/2018	13
12_02_11_01	Nitrogen and Oxygen Isotopes using azide reduction and Tracegas Preconcentrator Method	05/02/2018	W18200	06/06/2018	19
12_02_11_01	Nitrogen and Oxygen Isotopes using azide reduction and Tracegas Preconcentrator Method	05/03/2018	W18206	06/06/2018	28
12_02_11_01	Nitrogen and Oxygen Isotopes using azide reduction and Tracegas Preconcentrator Method	05/04/2018	W18216	06/07/2018	11
Subtotal:					71

## Data Summaries

A copy of each laboratory method and standard operating procedure (SOP) is available in the appendices. Each sample with sufficient nitrate-N concentration (>0.050 mg/L) was analyzed in duplicate for nitrate-N isotopes and the average reported as the final result (Table 2). Copies of final reports and method details are included in the appendices. Results for laboratory reagent blanks (LRB) and laboratory fortified blanks (LFB) and reference standards are listed individually and averaged in each summary table. Result for laboratory fortified blank is recorded as percent recovery (=100 x measured/known) prepared at the midrange of the calibration curve. All other results are expressed in concentration. For isotope measurements, the stable isotope abundance of the sample is expressed relative to an international standard as a delta ( $\delta$ ), with units of “‰” or “per mil” using the following equation:

$$\delta(\text{‰}) = \frac{R_{\text{Standard}} - R_{\text{Sample}}}{R_{\text{Standard}}} \times 1000$$

Where “R” is the measured isotope ratio (minor/major) of the sample and standard or reference material. For nitrogen isotope measurements, the  $R_{\text{Standard}}$  abundance ratio ( $^{15}\text{N}/^{14}\text{N}$ ) of atmospheric nitrogen gas is 0.0036765 and for oxygen isotope measurements, the  $R_{\text{Standard}}$  abundance ratio ( $^{18}\text{O}/^{16}\text{O}$ ) of standard mean

ocean water is 0.0020052. The delta measurement allows evaluation of small differences in minor isotope abundance.

*Nitrate-Nitrite Cd-Reduction Colorimetric Method EPA 353.2:* Samples were processed and analyzed using AQ2 method EPA-127-A- Rev. 8 Nitrate-N + Nitrite-N in Drinking and Surface Waters, Domestic and Industrial Wastes (Seal Analytical, Mequon, Wisconsin).

**Table 2. Summary of nitrate-N concentrations together with quality control results.**

Lab_ID	Sample_ID	Collection_Date	NO3+NO2-N	Batch	Analysis Date	Protocol	Project
18-1774	A1A	4/30/2018	0.000	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1775	A1B	4/30/2018	0.052	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1776	A1B LD2	4/30/2018	0.070	W18196	5/7/2018	02_03_01	QA/QC
18-1777	A2A	4/30/2018	0.000	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1778	A2B	4/30/2018	0.006	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1779	A3A	4/30/2018	0.021	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1780	A3B	4/30/2018	0.047	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1781	A4A	4/30/2018	0.568	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1782	A4B	4/30/2018	0.124	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1783	B1A	4/30/2018	0.018	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1784	B1B	4/30/2018	0.043	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1785	B2A	4/30/2018	0.000	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1786	B2B	4/30/2018	0.082	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1787	B3A	4/30/2018	1.284	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1788	B3B	4/30/2018	0.000	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1789	B4A	4/30/2018	17.473	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1790	B4B	4/30/2018	8.807	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1791	C3A	4/30/2018	9.083	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1792	C3B	4/30/2018	0.440	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1793	C1A	4/30/2018	0.000	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1794	C1B	4/30/2018	0.045	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1795	C2A	4/30/2018	22.807	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1796	C2B	4/30/2018	0.866	W18196	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1799	FB	4/30/2018	99.000	W18196	5/7/2018	02_03_01	QA/QC
18-1800	LRB	4/30/2018	0.010	W18196	5/7/2018	02_03_01	QA/QC
18-1806	C12A	5/1/2018	0.000	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1807	C12A LD2	5/1/2018	0.000	W18199	5/7/2018	02_03_01	QA/QC
18-1808	C12B	5/1/2018	0.000	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1809	C13A	5/1/2018	0.000	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1810	C13B	5/1/2018	0.000	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1811	D1A	5/1/2018	0.000	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1812	D1B	5/1/2018	0.000	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1813	D2A	5/1/2018	1.652	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1814	D2B	5/1/2018	13.455	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1815	D3A	5/1/2018	8.983	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1816	D3B	5/1/2018	13.142	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1817	D4A	5/1/2018	10.238	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1818	D4B	5/1/2018	17.697	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1819	C5AA	5/1/2018	13.147	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1820	C5AB	5/1/2018	22.042	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1821	C6A	5/1/2018	15.132	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1822	C6B	5/1/2018	11.703	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1823	C7A	5/1/2018	19.503	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1824	C7B	5/1/2018	14.692	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1825	C8A	5/1/2018	6.636	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1826	C8B	5/1/2018	2.392	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING

Lab_ID	Sample_ID	Collection_Date	NO3+NO2-N	Batch	Analysis_Date	Protocol	Project
18-1827	C9A	5/1/2018	2.470	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1828	C9B	5/1/2018	0.646	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1829	C10A	5/1/2018	7.760	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1830	C10B	5/1/2018	15.606	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1831	C11A	5/1/2018	0.000	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1832	C11B	5/1/2018	0.119	W18199	5/7/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1835	LFB	5/1/2018	98.000	W18199	5/7/2018	02_03_01	QA/QC
18-1836	LRB	5/1/2018	0.000	W18199	5/7/2018	02_03_01	QA/QC
18-1863	LFB	5/1/2018	96.000	W18203	5/7/2018	02_03_01	QA/QC
18-1864	LRB	5/1/2018	0.000	W18203	5/7/2018	02_03_01	QA/QC
18-1865	D5A	5/2/2018	0.451	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1866	D5A LD2	5/2/2018	0.452	W18205	5/9/2018	02_03_01	QA/QC
18-1867	D5B	5/2/2018	1.175	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1868	D6A	5/2/2018	41.140	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1869	D6B	5/2/2018	24.537	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1870	D7A	5/2/2018	30.701	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1871	D7B	5/2/2018	32.208	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1872	D8A	5/2/2018	48.759	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1873	D8B	5/2/2018	39.010	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1874	D9A	5/2/2018	30.252	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1875	D9B	5/2/2018	1.521	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1876	D10A	5/2/2018	8.794	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1877	D10B	5/2/2018	8.403	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1878	D11A	5/2/2018	28.038	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1879	D11B	5/2/2018	14.492	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1880	E1A	5/2/2018	11.656	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1881	E1B	5/2/2018	11.808	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1882	E2A	5/2/2018	0.995	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1883	E2B	5/2/2018	2.579	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1884	E3A	5/2/2018	3.831	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1885	E3B	5/2/2018	6.140	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1886	E4A	5/2/2018	26.056	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1887	E4B	5/2/2018	19.956	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1888	E5A	5/2/2018	28.326	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1889	E5B	5/2/2018	17.491	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1890	E6A	5/2/2018	0.149	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1891	E6B	5/2/2018	0.093	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1892	E7A	5/2/2018	16.130	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1893	E7B	5/2/2018	13.811	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1895	LFB	5/2/2018	96.100	W18205	5/9/2018	02_03_01	QA/QC
18-1896	LFB	5/2/2018	99.500	W18205	5/9/2018	02_03_01	QA/QC
18-1897	LRB	5/2/2018	0.000	W18205	5/9/2018	02_03_01	QA/QC
18-1870	D7A	5/2/2018	30.701	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1871	D7B	5/2/2018	32.208	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1872	D8A	5/2/2018	48.759	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1873	D8B	5/2/2018	39.010	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1874	D9A	5/2/2018	30.252	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1875	D9B	5/2/2018	1.521	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1876	D10A	5/2/2018	8.794	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1877	D10B	5/2/2018	8.403	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1878	D11A	5/2/2018	28.038	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1879	D11B	5/2/2018	14.492	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1880	E1A	5/2/2018	11.656	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1881	E1B	5/2/2018	11.808	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1882	E2A	5/2/2018	0.995	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING

Lab ID	Sample ID	Collection Date	NO3+NO2-N	Batch	Analysis Date	Protocol	Project
18-1883	E2B	5/2/2018	2.579	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1884	E3A	5/2/2018	3.831	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1885	E3B	5/2/2018	6.140	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1886	E4A	5/2/2018	26.056	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1887	E4B	5/2/2018	19.956	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1888	E5A	5/2/2018	28.326	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1889	E5B	5/2/2018	17.491	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1890	E6A	5/2/2018	0.149	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1891	E6B	5/2/2018	0.093	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1892	E7A	5/2/2018	16.130	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1893	E7B	5/2/2018	13.811	W18205	5/9/2018	02_03_01	ERG CSD GROUNDWATER SAMPLING
18-1895	LFB	5/2/2018	96.100	W18205	5/9/2018	02_03_01	QA/QC
18-1896	LFB	5/2/2018	99.500	W18205	5/9/2018	02_03_01	QA/QC
18-1897	LRB	5/2/2018	0.000	W18205	5/9/2018	02_03_01	QA/QC
Laboratory Duplicates	Collection Date	NO3+NO2-N	Batch	Range	Analysis Date	Protocol	Project
18-1775	A1B	4/30/2018	0.052	W18196		5/7/2018	02_03_01
18-1776	A1B LD2	4/30/2018	0.070	W18196	0.018	5/7/2018	02_03_01
18-1806	C12A	5/1/2018	0.000	W18199		5/7/2018	02_03_01
18-1807	C12A LD2	5/1/2018	0.000	W18199	0.000	5/7/2018	02_03_01
18-1865	D5A	5/2/2018	0.451	W18205		5/9/2018	02_03_01
18-1866	D5A LD2	5/2/2018	0.452	W18205	0.001	5/9/2018	02_03_01
18-1806	C12A	5/1/2018	0.000	W18199		5/7/2018	02_03_01
18-1807	C12A LD2	5/1/2018	0.000	W18199	0.000	5/7/2018	02_03_01
18-1865	D5A	5/2/2018	0.451	W18205		5/9/2018	02_03_01
18-1866	D5A LD2	5/2/2018	0.452	W18205	0.001	5/9/2018	02_03_01
		Average Range	0.004	mg/L			
		Average range since 1/1/2018	0.225	mg/L	4.21%		N=47 sets of duplicates
Laboratory Fortified Blanks	Collection Date	NO3+NO2-N	Batch	Analysis Date	Protocol	Project	Project
18-1799	LFB	4/30/2018	99.0	W18196	5/7/2018	02_03_01	QA/QC
18-1835	LFB	5/1/2018	98.0	W18199	5/7/2018	02_03_01	QA/QC
18-1863	LFB	5/1/2018	96.0	W18203	5/7/2018	02_03_01	QA/QC
18-1895	LFB	5/2/2018	96.1	W18205	5/9/2018	02_03_01	QA/QC
18-1896	LFB	5/2/2018	99.5	W18205	5/9/2018	02_03_01	QA/QC
		Average (%)	97.7				Prepared at 1.00 mg/L NO <sub>3</sub> N
		Standard Dev (%)	±1.6				
		Average recovery since 1/1/2018	97.09	±5.04%			N=51 fortified blanks since 1/1/2018
Laboratory Reagent Blanks	Collection Date	NO3+NO2-N	Batch	Analysis Date	Protocol	Project	Project
18-1800	LRB	4/30/2018	0.010	W18196	5/7/2018	02_03_01	QA/QC
18-1836	LRB	5/1/2018	0.000	W18199	5/7/2018	02_03_01	QA/QC
18-1864	LRB	5/1/2018	0.000	W18203	5/7/2018	02_03_01	QA/QC
18-1897	LRB	5/2/2018	0.000	W18205	5/9/2018	02_03_01	QA/QC
		Average (mg/L)	0.003				
		Standard Deviation (mg/L)	0.005				
		Average LRB since 1/1/2018	0.006				N=50 reagent blanks since 1/1/2018

***IRMS DI Nitrate 15N and 18O by Azide reduction.*** Using the nitrate-N plus nitrite-N concentrations measured by the Cd-reduction method described above, 71 samples were processed and analyzed for <sup>15</sup>N-NO<sub>3</sub> and <sup>18</sup>O-NO<sub>3</sub> using an automated method first described by McIllivin and Altabet (2005). The method involves reduction of nitrate to nitrite using a high surface area cadmium and subsequent

reduction of nitrite to nitrous oxide (N<sub>2</sub>O) in sealed helium purge vials. The nitrous oxide is cryogenically trapped on a Tracegas pre-concentrator system and then released for gas chromatographic separation and isotope ratio analysis of <sup>15</sup>N-N<sub>2</sub>O and <sup>18</sup>O-N<sub>2</sub>O on an Isoprime isotope ratio mass spectrometer in continuous flow mode. The reaction chemistry and calibration details are fully described in McIllivin and Altabet (2005). A step-by-step processing protocol is included as a standard operating procedure in the appendix. A summary of the results for samples and quality controls are listed in Table 3. Negative (-) results correspond to a depletion of the minor isotope relative to the reference standard and positive results correspond to enrichment of the minor isotope relative to the reference standard.

Table 3. Table of nitrate isotope measurement together with quality control results.

Lab ID	Sample ID	Collection Date	15N(‰)	18O(‰)	Batch	Analysis	Project
18-1775	A1B	4/30/2018	-4.94	9.19	W18197	5/14/2018	ERG CSD GROUNDWATER
18-1776	A1B LD2	4/30/2018	-4.60	7.74	W18197	5/14/2018	QA/QC
18-1780	A3B	4/30/2018	-4.15	12.52	W18197	5/14/2018	ERG CSD GROUNDWATER
18-1781	A4A	4/30/2018	4.76	5.27	W18197	5/14/2018	ERG CSD GROUNDWATER
18-1782	A4B	4/30/2018	3.23	0.70	W18197	5/14/2018	ERG CSD GROUNDWATER
18-1784	B1B	4/30/2018	-3.89	17.57	W18197	5/14/2018	ERG CSD GROUNDWATER
18-1786	B2B	4/30/2018	-7.73	2.04	W18197	5/14/2018	ERG CSD GROUNDWATER
18-1787	B3A	4/30/2018	-4.83	-3.64	W18197	5/14/2018	ERG CSD GROUNDWATER
18-1790	B4B	4/30/2018	1.41	2.66	W18197	5/14/2018	ERG CSD GROUNDWATER
18-1791	C3A	4/30/2018	3.88	4.41	W18197	5/14/2018	ERG CSD GROUNDWATER
18-1792	C3B	4/30/2018	0.81	-1.22	W18197	5/14/2018	ERG CSD GROUNDWATER
18-1794	C1B	4/30/2018	-11.41	1.50	W18197	5/14/2018	ERG CSD GROUNDWATER
18-1795	C2A	4/30/2018	0.75	2.30	W18197	5/14/2018	ERG CSD GROUNDWATER
18-1796	C2B	4/30/2018	3.22	1.51	W18197	5/14/2018	ERG CSD GROUNDWATER
18-1798	IAEA N3	4/30/2018	4.77	26.13	W18197	5/14/2018	QA/QC
18-1799	WSL KNO3	4/30/2018	0.29	23.38	W18197	5/14/2018	QA/QC
18-1813	D2A	5/1/2018	17.09	8.63	W18200	5/14/2018	ERG CSD GROUNDWATER
18-1814	D2B	5/1/2018	6.94	0.88	W18200	5/14/2018	ERG CSD GROUNDWATER
18-1815	D3A	5/1/2018	1.07	0.47	W18200	5/14/2018	ERG CSD GROUNDWATER
18-1816	D3B	5/1/2018	1.46	1.57	W18200	5/14/2018	ERG CSD GROUNDWATER
18-1817	D4A	5/1/2018	1.33	-0.25	W18200	5/14/2018	ERG CSD GROUNDWATER
18-1818	D4B	5/1/2018	1.64	-1.72	W18200	5/14/2018	ERG CSD GROUNDWATER
18-1819	C5AA	5/1/2018	2.32	-1.91	W18200	5/14/2018	ERG CSD GROUNDWATER
18-1820	C5AB	5/1/2018	3.42	-0.80	W18200	5/14/2018	ERG CSD GROUNDWATER
18-1821	C6A	5/1/2018	2.40	-0.95	W18200	5/14/2018	ERG CSD GROUNDWATER
18-1822	C6B	5/1/2018	1.19	0.79	W18200	6/6/2018	ERG CSD GROUNDWATER
18-1823	C7A	5/1/2018	0.45	-0.85	W18200	5/14/2018	ERG CSD GROUNDWATER
18-1824	C7B	5/1/2018	0.78	2.17	W18200	5/14/2018	ERG CSD GROUNDWATER
18-1825	C8A	5/1/2018	1.99	10.37	W18200	5/14/2018	ERG CSD GROUNDWATER
18-1826	C8B	5/1/2018	6.53	1.34	W18200	5/14/2018	ERG CSD GROUNDWATER
18-1827	C9A	5/1/2018	1.81	3.76	W18200	5/14/2018	ERG CSD GROUNDWATER
18-1828	C9B	5/1/2018	-6.33	4.59	W18200	5/14/2018	ERG CSD GROUNDWATER
18-1829	C10A	5/1/2018	-1.46	5.69	W18200	5/14/2018	ERG CSD GROUNDWATER
18-1830	C10B	5/1/2018	3.03	5.99	W18200	5/14/2018	ERG CSD GROUNDWATER
18-1832	C11B	5/1/2018	6.10	12.32	W18200	5/14/2018	ERG CSD GROUNDWATER
18-1834	IAEA N3	5/1/2018	4.37	25.41	W18200	5/14/2018	QA/QC
18-1835	WSL KNO3	5/1/2018	0.61	22.89	W18200	5/14/2018	QA/QC
18-1865	D5A	5/2/2018	-0.79	4.94	W18206	5/23/2018	ERG CSD GROUNDWATER
18-1866	D5A LD2	5/2/2018	-0.69	4.21	W18206	5/23/2018	QA/QC
18-1867	D5B	5/2/2018	-8.93	-4.10	W18206	6/6/2018	ERG CSD GROUNDWATER
18-1868	D6A	5/2/2018	-0.83	-2.95	W18206	5/23/2018	ERG CSD GROUNDWATER
18-1869	D6B	5/2/2018	-2.70	-0.51	W18206	5/23/2018	ERG CSD GROUNDWATER
18-1870	D7A	5/2/2018	-2.62	1.53	W18206	5/23/2018	ERG CSD GROUNDWATER
18-1871	D7B	5/2/2018	-4.99	-3.17	W18206	5/23/2018	ERG CSD GROUNDWATER
18-1872	D8A	5/2/2018	8.24	4.86	W18206	6/6/2018	ERG CSD GROUNDWATER
18-1873	D8B	5/2/2018	0.23	2.27	W18206	5/23/2018	ERG CSD GROUNDWATER

Lab ID	Sample ID	Collection Date	15N(‰)	18O(‰)	Batch	Analysis	Project
18-1874	D9A	5/2/2018	-1.65	1.23	W18206	5/23/2018	ERG CSD GROUNDWATER
18-1875	D9B	5/2/2018	2.72	1.35	W18206	5/23/2018	ERG CSD GROUNDWATER
18-1876	D10A	5/2/2018	-6.75	-3.01	W18206	6/6/2018	ERG CSD GROUNDWATER
18-1877	D10B	5/2/2018	-1.72	0.08	W18206	5/23/2018	ERG CSD GROUNDWATER
18-1878	D11A	5/2/2018	1.96	5.26	W18206	5/23/2018	ERG CSD GROUNDWATER
18-1879	D11B	5/2/2018	5.06	2.47	W18206	5/24/2018	ERG CSD GROUNDWATER
18-1880	E1A	5/2/2018	3.35	6.17	W18206	5/24/2018	ERG CSD GROUNDWATER
18-1881	E1B	5/2/2018	6.84	5.39	W18206	5/24/2018	ERG CSD GROUNDWATER
18-1882	E2A	5/2/2018	2.63	6.36	W18206	5/24/2018	ERG CSD GROUNDWATER
18-1883	E2B	5/2/2018	1.89	-0.20	W18206	5/24/2018	ERG CSD GROUNDWATER
18-1884	E3A	5/2/2018	-0.03	1.74	W18206	5/24/2018	ERG CSD GROUNDWATER
18-1885	E3B	5/2/2018	0.68	1.59	W18206	5/24/2018	ERG CSD GROUNDWATER
18-1886	E4A	5/2/2018	3.69	5.12	W18206	5/24/2018	ERG CSD GROUNDWATER
18-1887	E4B	5/2/2018	-0.84	4.71	W18206	5/24/2018	ERG CSD GROUNDWATER
18-1888	E5A	5/2/2018	1.29	4.91	W18206	5/24/2018	ERG CSD GROUNDWATER
18-1889	E5B	5/2/2018	2.59	5.44	W18206	5/24/2018	ERG CSD GROUNDWATER
18-1890	E6A	5/2/2018	-6.39	3.20	W18206	5/24/2018	ERG CSD GROUNDWATER
18-1891	E6B	5/2/2018	-2.48	4.47	W18206	5/24/2018	ERG CSD GROUNDWATER
18-1892	E7A	5/2/2018	3.76	7.91	W18206	5/24/2018	ERG CSD GROUNDWATER
18-1893	E7B	5/2/2018	-4.23	-2.39	W18206	5/24/2018	ERG CSD GROUNDWATER
18-1895	IAEA N3	5/2/2018	4.81	25.32	W18206	5/24/2018	QA/QC
18-1896	WSL KNO3	5/2/2018	-0.12	23.15	W18206	5/24/2018	QA/QC
<b>Laboratory Duplicates</b>							
Lab ID	Sample ID	Collection Date	15N	18O	Batch	Analysis	Project
18-1775	A1B	4/30/2018	-4.94	9.19	W18197	5/14/2018	ERG CSD GROUNDWATER
18-1776	A1B LD2	4/30/2018	-4.60	7.74	W18197	5/14/2018	QA/QC
			<b>Range (‰)</b>	<b>0.34</b>	<b>1.45</b>		
18-1865	D5A	5/2/2018	-0.79	4.94	W18206	5/23/2018	ERG CSD GROUNDWATER
18-1866	D5A LD2	5/2/2018	-0.69	4.21	W18206	5/23/2018	QA/QC
			<b>Range (‰)</b>	<b>0.10</b>	<b>0.73</b>		
<b>2018 Average Ranges LD1-LD2 (‰)</b>			<b>0.51</b>	<b>0.34</b>			<b>N=11 Laboratory Duplicates</b>
<b>Fortified Blanks &amp; Reference Samples</b>							
Lab ID	Sample ID	Collection Date	15N	18O	Batch	Analysis	Project
18-1798	IAEA N3 4.7 AND 25.29	4/30/2018	4.77	26.13	W18197	5/14/2018	QA/QC
18-1799	WSL KNO3 0.1 AND	4/30/2018	0.29	23.38	W18197	5/14/2018	QA/QC
18-1834	IAEA N3 4.7 AND 25.29	5/1/2018	4.37	25.41	W18200	5/14/2018	QA/QC
18-1835	WSL KNO3 0.1 AND	5/1/2018	0.61	22.89	W18200	5/14/2018	QA/QC
18-1895	IAEA N3 4.7 AND 25.29	5/2/2018	4.81	25.32	W18206	5/24/2018	QA/QC
18-1896	WSL KNO3 0.1 AND	5/2/2018	-0.12	23.15	W18206	5/24/2018	QA/QC
18-1798	IAEA N3 4.7 AND 25.29	4/30/2018	4.77	26.13	W18197	5/14/2018	QA/QC
<b>Summary Statistics</b>		<b>Expected Value</b>	4.70	25.29			
	IAEA N3 4.7 AND 25.29	Average (‰)	4.65	25.62			
	WSL KNO3 0.1 AND	Average (‰)	0.26	23.14			
	IAEA N3 4.7 AND 25.29	Std Dev (‰)	0.20	0.36			
	WSL KNO3 0.1 AND	Std Dev (‰)	0.30	0.20			

### Narrative and Summary of Quality Controls

The result of the quality control samples indicate that the methods are within control tolerances and consistent with samples, standards and blanks analyzed in 2018. In nitrate+nitrite-N quality controls, laboratory duplicate ranges varied from 0.000 to 0.018 mg/L, compared to a running average of 0.225 mg/L, or 4.21% relative percent difference in 47 sets of duplicates. Laboratory fortified blanks, prepared at 1.00 mg/L ranged from 96.1 to 99.0% recovery compared to a running average recovery of 97.09±5.04% in 51 fortified blanks analyzed in 2018. Nitrate+nitrite-N in laboratory reagent blanks ranged from 0.000 to 0.010 mg/L, and averaged 0.003 mg/L compared to a running average of 0.006 mg/L in 50 reagent blanks analyzed by this method in 2018. All nitrate isotope samples are run in duplicate and the reported result is an average of the duplicates. Laboratory duplicates are split and

analyzed as separate samples recorded in the laboratory information management system (LIMS) for estimation of method range. Two sets of laboratory duplicate results analyzed with this group of samples indicate that the range in  $\delta^{15}\text{N-NO}_3$  varied between 0.34 and 0.51‰ and  $\delta^{18}\text{O-NO}_3$  varied between 0.34 and 1.45‰. These ranges compare to a running average range of 0.51‰  $\delta^{15}\text{N-NO}_3$  and 0.34‰ for  $\delta^{18}\text{O-NO}_3$  in 11 sets of duplicates analyze in 2018. The  $\delta^{15}\text{N-NO}_3$  of reference sample IAEA N3 averaged  $+4.65\pm 0.2\%$  compared to an expected value of  $+4.70\%$ , while the  $\delta^{18}\text{O-NO}_3$  averaged  $+25.62\pm 0.36\%$  compared to an expected value of  $+25.29\%$ . The  $\delta^{15}\text{N-NO}_3$  of the WSL KNO<sub>3</sub> (potassium nitrate) check standard averaged  $0.26\pm 0.30\%$  compared to a running average of  $0.06\pm 0.46\%$  since 2010. The  $\delta^{18}\text{O-NO}_3$  of WSL KNO<sub>3</sub> averaged  $23.14\pm 0.20\%$  compared to a running average of  $23.22\pm 0.32\%$  (N=12).

## References

McIlvin, M.R., Altabet, M.A., 2005. Chemical Conversion of Nitrate and Nitrite to Nitrous Oxide for Nitrogen and Oxygen Isotopic Analysis in Freshwater and Seawater. *Analytical Chemistry* 77, 5589-5595.

## Appendices

- I. Chain of Custody -Sample Submittal Forms
- II. Standard Operating Procedures
- III. Analytical Reports

ENVIRONMENTAL PROTECTION AGENCY  
Office of Enforcement

REGION 5  
77 West Jackson Boulevard  
Chicago, Illinois 60604

CHAIN OF CUSTODY RECORD

PROJ. NO.	PROJECT NAME	NO. OF CONTAINERS	ANALYTE	TAG NUMBERS	ACTIVITY CODE				
CB022018	CSD GW Sampling	1	Nitrate	18-1774					
SAMPLERS: (Print Name and Sign) Cheryl Burdett Ben Atkinson									
STA. NO.	DATE	TIME	COMP	GRAB	STATION LOCATION	NO. OF CONTAINERS	ANALYTE	TAG NUMBERS	ACTIVITY CODE
A1a	4/30/18	07:19	X	X	1 <sup>st</sup> Street	1	X	Dry Ice	18-1774
A1b		07:32	X	X	1 <sup>st</sup> Street	1	X	Dry Ice	18-1776
A2a		8:15	X	X	2 <sup>nd</sup> Ave N	1	X		
A2b		8:24	X	X	2 <sup>nd</sup> Ave N	1	X		
A3a		9:06	X	X	2 <sup>nd</sup> Street	1	X		
A3b		9:14	X	X	2 <sup>nd</sup> Street	1	X		
A4a		9:58	X	X	Cranberry Rock Rd	1	X		
A4b		10:09	X	X	Cranberry Rock Rd	1	X		
B1a		10:51	X	X	20 <sup>th</sup> Avenue	1	X		
B1b		10:58	X	X	20 <sup>th</sup> Avenue	1	X		
B2a		11:40	X	X	3 <sup>rd</sup> Street	1	X		
B2b		11:48	X	X	3 <sup>rd</sup> Street	1	X		
B3a		12:29	X	X	3 <sup>rd</sup> Street	1	X		
B3b	4/30/18	12:30	X	X	3 <sup>rd</sup> Street	1	X		18-1788

Relinquished by: (Signature) <i>Sam Rogers</i>	Date / Time 4/30/18 5:55 AM	Received by: (Signature)	Date / Time	Ship To: 202 Water Sciences Laboratory 1840 N. 37th St. Lincoln, NE 68583-08
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Date / Time	ATTN: Daniel Snow
Relinquished by: (Signature)	Date / Time	Received for Laboratory by: (Signature) <i>[Signature]</i>	Date / Time 5/1/18 10:00 AM	Airbill Number
				Chain of Custody Seal Numbers



CHAIN OF CUSTODY RECORD

PROJ. NO.		PROJECT NAME		STATION LOCATION		NO. OF CONTAINERS	ANALYTE:	TAG NUMBERS	
PROJ. NO.	PROJECT NAME	STATION LOCATION	STATION LOCATION	NO. OF CONTAINERS	ANALYTE:				
C8022018	CSD Groundwater Samplings								
SAMPLERS: (Print Name and Sign)									
Ben Atkinson									
Andi Hoday									
STA. NO.	DATE	TIME	COMP.	GRAB	STATION LOCATION	NO. OF CONTAINERS	ANALYTE:	TAG NUMBERS	
C12a	5/1/18	1241		X	19th Avenue	1		Dry Ice 18-1906	
C12b		1247		X	19th Avenue	1		18-1808	
C13a		1330		X	4th Street	1			
C13b		<del>1339</del>		X	4th Street	1			
D1a		1419		X	5th Street	1			
D1b		1426		X	5th Street	1			
D2a		1500		X	6th Street	1			
D2b		1506		X	5th Street	1			
D3a		1541		X	5th Street	1			
D3b		1548		X	5th Street	1			
D4a	5/1/18	1619		X	5th Street	1		Dry Ice	
D4b	5/1/18	<del>1625</del>		X	5th Street	1		Dry Ice	
		1626 CD		X	5th Street	1		Dry Ice 18-1818	
Relinquished by: (Signature)		Date / Time		Received by: (Signature)		Date / Time		Ship To:	
		5/1/18 16:45				5/2/18 10:00 AM		202 Water Sciences Laboratory University of Nebraska Laboratory 1540 N. 37th St Lincoln, NE 68583-0844 Dr. Daniel Snow ATTN:	
Relinquished by: (Signature)		Date / Time		Received by: (Signature)		Date / Time		Airbill Number	
						5/2/18 10:00 AM		1Z A49 E01 22 1046 8939	
Relinquished by: (Signature)		Date / Time		Received for Laboratory by: (Signature)		Date / Time		Chain of Custody Seal Numbers	
						5/2/18 10:00 AM			

CHAIN OF CUSTODY RECORD

PROJ. NO.		PROJECT NAME		STATION LOCATION		NO. OF CONTAINERS	ANALYTE	TAG NUMBERS	ACTIVITY CODE
STA. NO.	DATE	TIME	COMR	GRAB					
CB022018		CSD GW SAMPLING							
SAMPLERS: (Print Name and Sign) Ben Atkinson <i>Ben Atkinson</i> Andi Holey <i>Andi Holey</i>									
C5Aa	5/1/18	0629	X	X	CRG (Nelson Road)	1	X	Dry Ice	18-1819
C5Ab		0643	X	X	CRG (Nelson Road)	1	X		
C6a		0706	X	X	CRG (Nelson Road)	1	X		
C6b		0715	X	X	CRG (Nelson Road)	1	X		
C7a		0748	X	X	4th Street	1	X		
C7b		0802	X	X	4th Street	1	X		
C8a		0835	X	X	4th Street	1	X		
C8b		0842	X	X	4th Street	1	X		
C9a		1000	X	X	4th Street	1	X		
C9b		1021	X	X	4th Street	1	X		
C10a		1105	X	X	4th Street	1	X		
C10b		1112	X	X	4th Street	1	X		
C11a		1146	X	X	20th Avenue	1	X		
C11b		5/1/18 1152	X	X	20th Avenue	1	X	Dry Ice	18-1832
Relinquished by: (Signature) <i>Sam Rogers</i> Date / Time 5/1/18 1645 Received by: (Signature) _____ Relinquished by: (Signature) _____ Date / Time _____ Received by: (Signature) _____ Relinquished by: (Signature) _____ Date / Time _____ Received for Laboratory by: (Signature) <i>[Signature]</i> Date / Time 5/2/18 10:00 AM									
Ship To: 202 Water Sciences Laboratory University of Nebraska Laboratory 1840 N. 37th St Lincoln, NE 68583-0844 ATTN: _____ Airbill Number 1Z A49 E01 22 1006 8939 Chain of Custody Seal Numbers _____									



CHAIN OF CUSTODY RECORD

PROJ. NO.		PROJECT NAME		STATION LOCATION		NO. OF CONTAINERS	TAG NUMBERS
STA. NO.	DATE	TIME	COMP	GRAB			
CB022018		CSD Groundwater Sampling					
ANALYSE: N-15 Isotope Nitrate							
SAMPLERS: (Print Name and Sign) Ben Atkinson <i>[Signature]</i> Andi Hoday <i>[Signature]</i>							
E1a	5/2/18	1241	X	X	23rd Avenue	1	Dry Ice 18-1880
E1b		1258	X	X	23rd Avenue	1	
E2a		1328	X	X	Porter Road	1	
E2b		1337	X	X	Porter Road	1	Dry Ice
E2a dup		1328	X	X	Porter Road	CB 5/2/18	
E2b dup		1337	X	X	CB 5/2/18		
E3a		1403	X	X	Porter 7th Street	1	Dry Ice
E3b		1409	X	X	7th Street	1	
E4a		1437	X	X	7th Street	1	
E4b		1443	X	X	7th Street	1	
E5a		1508	X	X	7th Street	1	
E5b		1513	X	X	7th Street	1	
E6a	V	1538	X	X	20th Avenue	1	
E6b	5/2/18	1544	X	X	20th Avenue	1	Dry Ice 18-1891
						CB 5/2/18	
Relinquished by: (Signature)		Date / Time		Received by: (Signature)		Date / Time	
<i>[Signature]</i>		5/2/18 1644					
Relinquished by: (Signature)		Date / Time		Received by: (Signature)		Date / Time	
Relinquished by: (Signature)		Date / Time		Received for Laboratory by: (Signature)		Date / Time	
						5/3/18 10:30 AM	

Ship To: 402-472-7539  
 Dr. Daniel Snow  
 Nebraska Water Sciences Laboratory  
 1840 N. 37th St  
 ATTN: Lincoln, NE 68583-0844  
 Airbill Number  
 12 A49 E01 22 1096 889 5  
 Chain of Custody Seal Numbers

CHAIN OF CUSTODY RECORD

PROJ. NO.	PROJECT NAME	NO. OF CON-TAINERS	ANALYTE	STATION LOCATION	DATE	TIME	COMP	GRAB	TAG NUMBERS
C8028018	CSD Groundwater Sampling	1	NIS-Isotope	5th Street	5/2/18	0638	X	X	Dry Ice 18-1865
	SAMPLERS: (Print Name and Sign) Ben Atkinson Andi Hodge	1		5th Street		0646	X	X	18-1867
		1		5th Street		0717	X	X	
		1		5th Street		0729	X	X	
		1		2300 Avenue		0812	X	X	
		1		2300 Avenue		0819	X	X	
		1		2300 Avenue		0855	X	X	
		1		2300 Avenue		0911	X	X	
		1		2300 Avenue		0945	X	X	
		1		2300 Avenue		0954	X	X	
		1		2300 Avenue		1029	X	X	
		1		2300 Avenue		1041	X	X	
		1		2300 Avenue		1119	X	X	
		1		2300 Avenue		5/2/18 1142	X	X	
		1		2300 Avenue		5/2/18	X	X	Dry Ice 18-1879

Ship To: Peter Snyder  
Dr. Daniel Snyder  
402-7530-4116  
Nebraska Water Sciences Laboratory  
10th Floor  
202 Water Science  
5/2/18 536 S Clark Street Laboratory  
ATTN: Chicago, IL 60605  
1840 N. State St  
Airbill Number  
12-A49 E01 22 1006889 5  
Chain of Custody Seal Numbers  
68588-0844

Relinquished by: (Signature)  
*Sam Rogers*  
Date / Time: 5/2/18 1644  
Received by: (Signature)  
Date / Time:   
Relinquished by: (Signature)  
Date / Time:   
Received for Laboratory by: (Signature)  
Date / Time: 5/2/18 10:32 AM



# Sample Submission

## OVERVIEW

---

Sample submittal and log-in is the process of accepting and documenting field sample receipt and transferal to the Laboratory. All client or student samples must be submitted with a properly completed Sample Submission Form. If necessary, they could instead be accompanied by a Chain of Custody Form, which legally documents transport and submission. Ensuring that these forms are filled out properly and completely will facilitate the movement of the samples through the laboratory workflow.

## WORKFLOW

---

Field samples should be logged-in immediately upon arrival by laboratory personnel. If immediate log-in is not possible, samples may be stored temporarily in coolers, or in Refrigerator 1 next to Room 105, until log-in can be performed.

Clients should provide either a Chain of Custody Form, or a Sample Submission Form. This can be submitted as a paper copy with the samples, or electronically through the WSL webpage. Both forms serve as a record of sample submission, and document the collection date/time, preservation, and requested protocols. Each Sample Submittal Form accommodates up to 20 samples. If more samples are being submitted, additional forms will be required.

### Sample Acceptance

- If the Chain of Custody form or Sample Submission form is not filled out correctly or completely, the samples associated with them will not be accepted. The information that is required on the Sample Submittal form for sample acceptance is:
  1. Sample Field IDs
  2. Date
  3. Contact Information
  4. Matrix Type
  5. Number of Samples
  6. Tests Desired
  7. Extended Sample Storage
  8. Collection Date and Time
  9. Sampled By
  10. An answer to the 'To be billed?' question (see #4 under Sample Submittal Form)

If you have a cost object, this can be provided after sample submission if necessary. For information on how to correctly fill out the Sample Submission form, please see the associated section within this document.

- Under most circumstances, all water and sediment samples received will be accepted and evaluated before analysis. Other types of samples (food, tissue, grain, etc.) are not normally delivered to the Laboratory, therefore special arrangement should be made for the handling of other sample matrices.
- Individual water and sediment samples may be rejected for log-in under the following conditions:
  1. The sample container is damaged and the contents contaminated.
  2. The sample container is empty, or nearly empty, indicating the sample was either lost in transit or never collected.
  3. The sample label is illegible or missing completely, and it is impossible to identify the sample using other means.
  4. The sample temperature indicates the contents may be compromised.

If any of these conditions are met, then the sample is not logged in, and the Laboratory Manager is notified. The Laboratory Manager will attempt to contact the sample collector to determine if additional sample can be collected.

- If sample condition is questionable, it will be noted on the Sample Submission Form under Comments. Samples which are logged in may later be determined to be unsuitable for the type of analysis requested. The analyst assuming the responsibility for sample processing will make this determination using criteria outlined in the appropriate standard operating procedure (SOP).

## **SAMPLE SUBMITTAL FORM**

---

Hard copies of the sample submittal form can be obtained from Laboratory Staff, and the form can also be accessed electronically through the Water Sciences Laboratory webpage. Properly completed Sample Submittal Forms must include the following information:

1. Date: Date (MO/DA/YR) samples were delivered to the Laboratory.
2. Contact Name/Information: Contact information for billing purposes. If a student is bringing in samples, the information listed here should be the principal investigator's information.
3. Project Code: Code associated with the research project the samples are to be analyzed for. If samples are not for a research project, list 'Other' for project name. Contact the Laboratory Director or Manager for additional project codes if necessary.
4. Billing Question/Account Number: A client should answer yes if they don't have a designated cost object. A bill will be sent to the address listed in the 'Billing Address' section. If the client has a designated cost object, it should be listed here.
5. Matrix Type: Matrix of samples. If the matrix is not listed, it may be written to the side.
6. Number of Samples: The total number of samples listed on the sample submittal form. If submitting more than 20 samples, additional forms must be used.
7. Tests Desired: The protocol to be followed when analyzing samples. If protocol code is unknown, they can be found on the price lists on the WSL webpage. A member of staff can also assist you.

8. Extended Sample Storage: Whether samples will be stored for a period beyond the 4 weeks listed in the storage policy, for a small fee. The storage policy can be found on the WSL webpage under 'Client Services'.
9. Billing Address: Address where bill should be sent.
10. Sample Field ID: Sample identification information, assigned at the time of collection.
11. Collection Date/Time: Complete collection date (MO/DA/YR), including the time if given.
12. Sampled By: The name or initials of the person(s) who collected the samples.
13. Preservative: Description of sample preservation, if any.

# Water Sciences Laboratory

University of Nebraska-Lincoln  
watersciences.unl.edu



## Sample Submittal Form

- 1 Date \_\_\_\_\_
- 2 Contact Name \_\_\_\_\_  
Company \_\_\_\_\_  
Address \_\_\_\_\_  
City \_\_\_\_\_ State \_\_\_\_ Zip \_\_\_\_\_  
Email Address \_\_\_\_\_  
Telephone \_\_\_\_\_
- 3 Project Code \_\_\_\_\_
- 4 To be billed? (Y/N) Acct. \_\_\_\_\_
- WSL Batch Number(s) \_\_\_\_\_
- 5 Matrix Type:  Water  Wastewater  Sediments  
(Use a separate form for each matrix)
- 6 Number of Samples \_\_\_\_\_
- Tests Desired**  
(Please refer to protocol code if possible)

7
- 8 Extended sample storage (Y / N) \_\_\_\_\_  
See website under 'Client Services' for storage policy
- 9 Billing Address \_\_\_\_\_

	10	11	12	13	
	Sample Field ID#	Collection Date/Time	Sampled By	Preservative?	Lab ID# (WSL use only)
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					

Comments \_\_\_\_\_  
Date Completed \_\_\_\_\_

Mail or deliver samples and completed form to  
202 Water Sciences Laboratory – 1840 N 37<sup>th</sup> St.  
University of Nebraska-Lincoln, Lincoln, NE 68583-0844  
dsnow1@unl.edu; 402-472-7539

# Nitrate – Nitrite Analysis

## 1 INTRODUCTION

---

The protocol was developed for the AQ2 equipment in lab 203, WSL. This method is adapted from the SEAL Analytical AQ2 method

## 2 SCOPE AND APPLICATION

---

### 2.1 OVERVIEW

This method covers the determination of Nitrate–N + Nitrite–N in sewage and effluents, raw and finished drinking waters and industrial wastes. This method, equivalent to USEPA Method 353.2 Rev. 2.0 (1993), is approved for the Clean Water Act for use in wastewater compliance monitoring, under National Pollutant Discharge Elimination System (NPDES). For NPDES monitoring, this method is also equivalent to Standard Methods 4500-NO<sub>3</sub>F (2000 forward.), ASTM Method D-3867-04A and USGS Method 1-2545-90. This method is also approved for the Safe Drinking Water Act for use in drinking water compliance monitoring, under National Primary Drinking Water Regulations (NPDWR).

### 2.2 METHOD DETECTION LIMIT

By USEPA procedure, MDL = 0.003 mg N/L

### 2.3 ACCEPTABLE RANGES:

0.012 -2.0 mg N/L

### 2.4 TRAINING TIME

4-8 hours

### 2.5 SAMPLE PRESERVATION

Can be preserved with few drops of sulfuric acid

## 3 REQUIRED TRAINING

---

EHS certification, Basic Lab Training, A pass in Basic Lab Exam

## 4 EQUIPMENT AND MATERIALS

---

### 4.1 APPARATUS AND MATERIALS

### 4.2 CHEMICALS

Chemical	CAS Number	Hazards	Location
Cupric (II) Sulfate Pentahydrate	7758-99-8		Cabinet 1 Shelf 1
Ammonium chloride	12125-02-9		Cabinet 1 Shelf 1
Ammonium hydroxide			Room 205
Disodium EDTA dihydrate	6381-92-6		Cabinet 1 Shelf 2
N-(1-naphthyl)-ethylenediamine dihydrochloride			Dessicator below Cabinet 2, in 203
Phosphoric acid, conc.	7664-38-2		Room 205
Sodium nitrate	7631-99-4		Cabinet 2
Sodium nitrite			Cabinet 3 Shelf 2
Sodium hydroxide	1310-73-2		Cabinet 2 Shelf 3
Sulfanilamide	63-74-1		Cabinet 2 Shelf 2
Sulfuric acid, conc.	7664-93-9		Room 205
Triton X-100			Non-flammable organics

## 5 STANDARD SOLUTIONS

---

### 7.1 TRITON® X-100, 7.5% w/v

Triton® X-100 (neat liquid) (nonflammable organics)

15 g

DDI Water

dilute to 200 mL

Weigh 15 g Triton® X-100 (neat liquid) into a small weigh boat or beaker. Set up a 500 mL container with about 150 mL deionized water and a stir bar. While stirring vigorously, add Triton® X-100 slowly. The Triton® X-100 will thicken initially but will dissolve with continued stirring. Immerse the weigh vessel in the stirring mixture to attain complete transfer. Dilute to 200 mL total volume. Filter this reagent, e.g., using filter paper. Store in refrigerator. Discard after six months, or if solids are seen.

### 7.2 COPPER (II) SULFATE, 2% w/v

Cupric (II) sulfate pentahydrate (Cabinet 1, Shelf 1)

31.3 g

DDI water

dilute to 1 L

In a 1 L volumetric flask dissolve 31.3 g copper (II) sulfate pentahydrate in about 800 mL deionized water. Fill to the mark with deionized water and mix well.

### 7.3 AMMONIUM CHLORIDE BUFFER STOCK, pH 8.55

Ammonium chloride, anhydrous, low in nitrate (Cab. 1, S.1)	45 g
Ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA, Cab. 1, S. 2)	0.5 g
* Ammonium hydroxide, concentrated for pH adjustment (Rm 205 shelf)	pH 8.55 *
DDI water	dilute to 250mL

\* Although USEPA method 353.2 specifies ammonium hydroxide for pH adjustment, 10% (w/v) sodium hydroxide (10 g NaOH pellets per 100 mL) is a suitable replacement. Dissolve 45 g ammonium chloride and 0.5 g EDTA in 100 mL deionized water. SEAL recommends product number 6451 from GFS Chemicals. Adjust the pH to  $8.55 \pm 0.05$  using ammonium hydroxide, concentrated and dilute to 250 mL.

NOTE: ACS grade ammonium chloride may contain nitrate contamination. An alternate recipe for the ammonium chloride buffer is:

**\*\*CAUTION--Fumes!\*\*** To a 250mL container add 100mL deionized water. Carefully add 70 mL (83.25 g) hydrochloric acid, concentrated, 56.75 mL (51 g) ammonium hydroxide, concentrated and 0.5 g EDTA. Cool to room temperature. Adjust to  $pH\ 8.55 \pm 0.05$  using ammonium hydroxide, concentrated and dilute to 250 mL.

### 7.4 WORKING BUFFER, 0.0375% surfactant

Ammonium chloride buffer stock (above)	200 mL
7.5% (w/v) Triton® X-100 solution, required (above)	1.0 mL

Add 1.0 mL 7.5% (w/v) Triton® X-100 solution to a 200 mL flask. Add, with swirling, 200 mL ammonium chloride buffer stock and shake well to mix. Prepare fresh every two weeks.

### 7.5 SULFANILAMIDE-NEDD

Phosphoric acid, concentrated (in Acid lab under 1 <sup>st</sup> hood)	20 mL
Sodium hydroxide (Cab. 2, S. 3)	1.0 g
Sulfanilamide (Cab. 2, S. 2)	7.5 g
N-(1-naphthyl)-ethylenediamine dihydrochloride (Dessicator below Cab. 2)	0.375 g
DDI water	dilute to 500 mL

Dissolve 1.0 g sodium hydroxide pellets in about 250 mL deionized water. Carefully add 20 mL phosphoric acid, concentrated (low in nitrite). Add 7.5 g sulfanilamide and 0.375 g N-(1-naphthyl)-ethylenediamine dihydrochloride and stir to dissolve. Dilute to 500 mL with deionized water. Filter this reagent, e.g., using filter paper. This reagent is stable for at least 6 weeks when stored in the dark at 4 °C. As the reagent slowly turns pink, re-filter it as needed. Discard this reagent when background absorbance of analyzed blanks exceeds 0.04 absorbance unit.

### 7.6 SULFURIC ACID, 5 normal

Sulfuric acid, concentrated (Rm 205)	70 mL
DDI water	dilute to 500 mL

Slowly add 70 mL sulfuric acid, concentrated to about 400 mL of deionized water. Caution, the container will become very warm. Cool to room temperature and dilute to 500 mL with deionized water. This reagent is available commercially.

### 7.7 NITRATE-N STOCK STANDARD SOLUTION (500mgNO<sub>3</sub>-N/L)

Sodium nitrate (Cabinet 3, Shelf 2)	0.7585 g
Sulfuric acid, 5 normal (above)	up to 1.25 mL
DDI water	dilute to 250mL

Dissolve 0.7585 g sodium nitrate (dried at 105 °C) in deionized water in a 250 mL volumetric flask. Up to 1.25 mL sulfuric acid, 5 normal, may be added for preservation. Dilute to the mark with deionized water.

### 7.8 NITRITE-N STOCK STANDARD SOLUTION (500 mg NO<sub>2</sub>-N/L)

Sodium nitrite (Cabinet 3, Shelf 2)  
DDI water

0.61575 g  
dilute to 250 mL

Dissolve 0.61575 g sodium nitrite (dried at least 4 hours in a dessicator) in about 100 mL deionized water in a 250mL volumetric flask. Dilute to the mark with deionized water. Do not add acid for preservation. Store up to 1 month in an amber bottle at 4 °C.

#### 7.9 NITRATE-N TOP STANDARD SOLUTION (2.0 mg NO<sub>3</sub>-N/L)

NITRATE-N stock standard (500 mg N/L, above)  
DDI water

1 mL  
dilute to 250 mL

To a 250 mL volumetric flask pipet 1 mL NITRATE-N stock standard (500 mg NO<sub>3</sub>-N/L) and dilute to the mark with deionized water. Prepare every two weeks.

#### 7.10 NITRITE-N TOP STANDARD SOLUTION (2.0 mg NO<sub>2</sub>-N/L)

NITRITE-N stock standard (500 mg N/L, above)  
DDI water

1 mL  
dilute to 250 mL

To a 250 mL volumetric flask pipet 1 mL NITRITE-N stock standard (500 mg NO<sub>2</sub>-N/L) and dilute to the mark with deionized water. Prepare twice weekly.

## 6 PROTOCOL

---

- Turn on AQ2 using 2 power buttons on the back-right, small first then large
- Warm up AQ2 for 20 minutes, check necessary reagents in the mean time
- After 20 minutes go to SETTINGS -> DAILY START-UP -> OKAY to get water baselines. Record these in an Excel file (on desktop) titled "Daily Water Baselines." Make sure results are consistent with previous data. If not, contact the Lab Manager.
- Go to SETTINGS -> MAINTENANCE -> CUVETTE FUNCTIONS -> EXTRA WASH. That finishes when the green bar is full.
- **For Cadmium Coil Regeneration:** Make sure reagent position 13,14 and 15 has the 100ppm Nitrate, Buffer solution and Copper Sulfate Solution respectively. Then under maintenance, go to CADMIUM COIL -> OKAY, finished when green bar is full. DILUTER -> 10 PRIMES -> START PRIMES, finished when green bar is full.
- Label sample cups (located in corner cabinet left of AQ2, with appropriate Lab ID numbers)
- Have the top standard labeled as well
- Lab Fortified Blank (LFB) will be half top half DDI water (1 mL each)
- Place sample cups in tray in order of Lab ID, **putting the TOP in the first position of the sample tray**
- When Maintenance is complete go to SCHEDULING (on the left) -> REAGENT SET 2 -> EMPTY TRAY -> Label as Date\_Batch#\_NO<sub>3</sub>NO<sub>2</sub>. Click OKAY.
- Skip the first line and then start entering Lab ID #'s in each line from the 2<sup>nd</sup> row
- Highlight the third column from the second line to the last one with a Lab ID and select the NO<sub>3</sub>\_NO<sub>2</sub> test at the top of the page
- Click SAVE from the top of the screen
- Place tray in machine
- Click RUN (on the left) and select tray just made
- In the screen that pops up check mark all boxes and replace reaction wells as specified. Click OKAY
- Double check the location of TOP STANDARD and BLANKS. Click OKAY

- Double check the placement of reagents, their expiration dates and how full they are. Replace and add as necessary
- Click OKAY and the machine should begin
- When the test has finished running, click REPORTING -> GENERATE REPORT WITH RAW DATA -> test run -> GENERATE REPORT -> Right click on screen that pops up -> PRINT -> PRINT -> Type in title of test -> Save to AQ2 folder

## 7 QUALITY ASSURANCE

---

This section should include the most recent Instrument Detection Limit (IDL) and Method Detection Limit (MDL) for the method.

Replicate no.	Nitrate standard (mg NO <sub>3</sub> -N/L)	Calculated concentration (mg NO <sub>3</sub> -N/L)
1	0.35	0.367
2	0.35	0.359
3	0.35	0.338
4	0.35	0.348
5	0.35	0.346
6	0.35	0.345
7	0.35	0.343
8	0.35	0.357
STATISTICS		
Average		0.350375
Standard deviation		0.00968
Student's t test		2.998
MDL		0.02902
% RSD		2.762666

## 8 ADDITIONAL READING

---

### Cadmium coil regeneration

1. On the AQ2 the Cadmium coil is the purple coil on the machine. If the AQ2 has not been run for two or more days you must regenerate this coil. Remove the coil by gently pulling out the tubes from each end. Have a 100mL beaker of DDI water prepared and take out the syringe from the second right hand drawer from the AQ2 instrument. Attach the coil to the syringe.



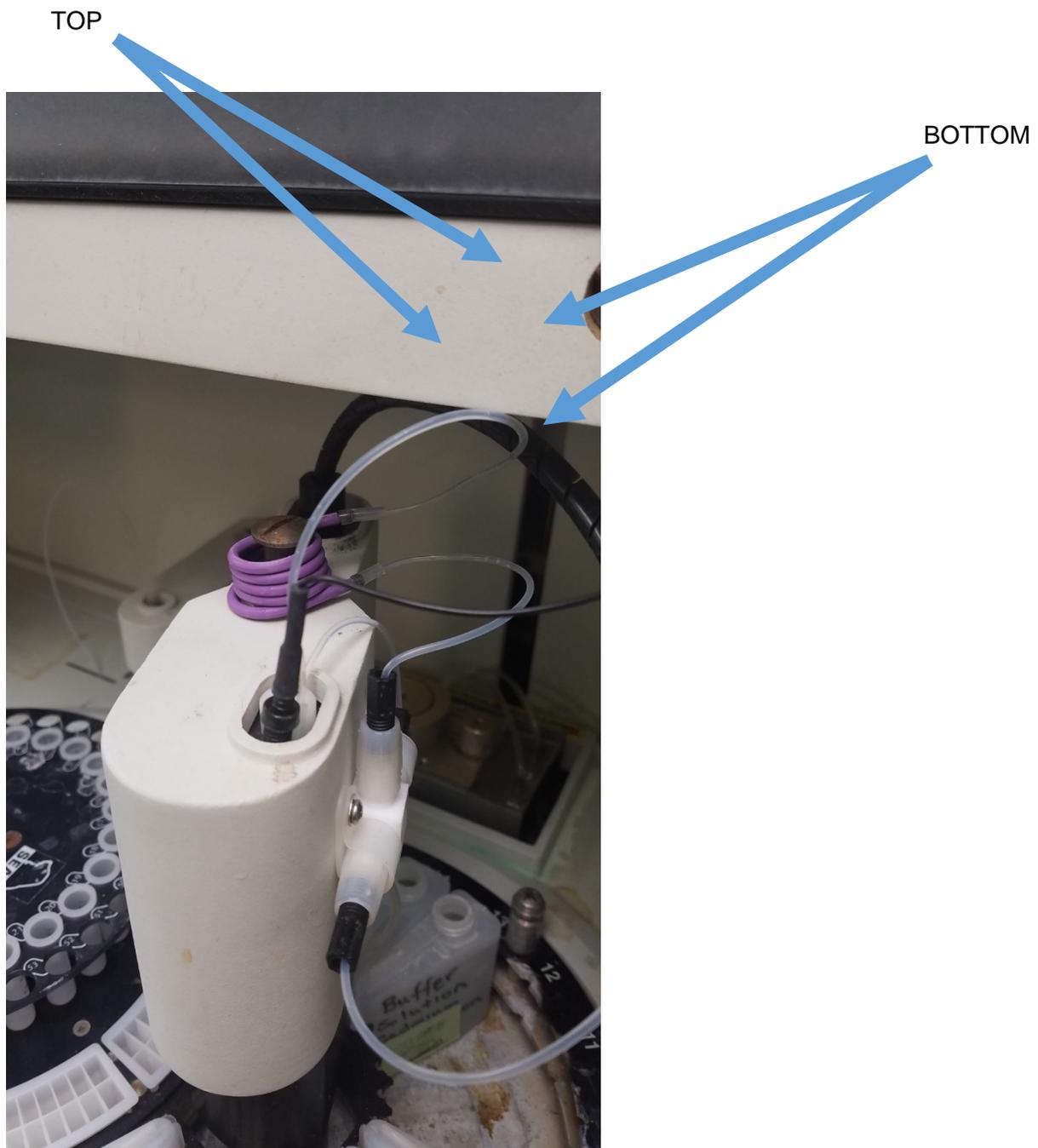
2. Place the coil in the beaker of water and draw in about 5 mL of water.



3. Take the coil out of the water and pull up some air.



4. Repeat this process until the syringe is full and the black specs are gone. Return the coil to the AQ2 with the bottom attaching the tube coming out of the bottom black section and the top attaching to the top section (see image below).



**Write about Cd coil maintenance from the software using CuSO<sub>4</sub> solution**

## 9 PREVIOUS ISSUES AND CHANGES

---

### 9.1 ISSUE CHANGES

August 31, 2004 Rev. 1

- Method format changed to meet EPA standards
- Document tracking information added
- Equivalent methods listed
- Support data added
- Buffer recipe modified
- Method number changed from 2-018-1-H to EPA-126-A
- Test parameters changed
- Alternative buffer recipe added

September 2, 2004 Rev. 2

- Referenced EPA 353.2 (1993)
- Interference and sample preservation sections amended
- Changed wording of NSDWR to NPDWR

October 8, 2004 Rev. 3

- Front page reformatted
- Method Supplement 1 document created and implemented

June 1, 2005, Rev. 4

- Minor adjustments in Test Parameters to improve performance
- Reagent recipes rewritten to accommodate both 10-mm cuvettes

(p/n10031 and p/n5670)

March 3, 2006 Rev. 5

- Increased level of EDTA in pH 8.6 buffer to counteract heavy metal contamination
- Replaced calibration curve

December 29, 2009 Rev. 6

- Minor editorial revisions

December 13, 2010 Rev. 7

- Minor editorial revisions

July 12, 2012 Rev. 8

- Method reworked
- Method document reformatted

March 27, 2018 Rev. 9

- Changed Copper (II) sulfate pentahydrate to Cupric sulfate pentahydrate
- Cut Nitrate and Nitrite Stock amounts into a fourth
- Cut Nitrate and Nitrite Intermediate amounts in half
- Changed Intermediate to Top
- Deleted Working Standards

April 24, 2018 Rev. 10

- Minor editorial revisions

## Nitrate–N + Nitrite–N in Drinking and Surface Waters, Domestic and Industrial Wastes

### 1 SCOPE

---

This method covers the determination of Nitrate–N + Nitrite–N in sewage and effluents, raw and finished drinking waters and industrial wastes.

This method, equivalent to USEPA Method 353.2 Rev. 2.0 (1993), is approved for the Clean Water Act for use in wastewater compliance monitoring, under National Pollutant Discharge Elimination System (NPDES). For NPDES monitoring, this method is also equivalent to Standard Methods 4500-NO<sub>3</sub>F (2000 forward.), ASTM Method D-3867-04A and USGS Method 1-2545-90.

This method is also approved for the Safe Drinking Water Act for use in drinking water compliance monitoring, under National Primary Drinking Water Regulations (NPDWR).

### 2 RANGE OF APPLICATION

---

Range	0.012 – 2.0 mg N/L
-------	--------------------

### 3 METHOD DETECTION LIMIT

---

By USEPA Procedure	MDL = 0.003 mg N/L
--------------------	--------------------

### 4 METHOD PRINCIPLE

---

The sample is mixed with pH buffer and then transferred to a copperized cadmium coil, where nitrate is chemically reduced to nitrite. The chemically-reduced sample is mixed with color reagent, prepared in dilute phosphoric acid. Original nitrite, plus nitrite from chemical reduction, reacts with sulfanilamide to form a diazonium compound. This species couples with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a reddish-purple azo dye that is measured photometrically at 520 nm. Separate results for nitrite are obtained using AQ2 method EPA-115-A. The 115-A method is similarly equivalent to USEPA method 353.2, except that cadmium reduction is omitted.

### 5 REFERENCES

---

Methods for the Determination of Inorganic Substances in Environmental Samples, USEPA 600/R 93/100, August 1993: Method 353.2, Revision 2.0.

Standard Methods for the Examination of Water and Wastewater, APHA/AWWA/WEF, method 4500 NO<sub>3</sub>– F (2000 forward)

#### Water Sciences Lab additions for nitrate sample analysis: (added by David Cassada, 8/16/2017)

1. Due to the high variability and sometimes elevated concentrations of typical nitrate concentrations for samples analyzed by the Laboratory, in addition to the original sample, always analyze a separate diluted aliquot (duplicate) of each sample at a 41x dilution factor (2 mL distilled water to 50 uL of sample). Enter this dilution factor into the Cup Dilution field so that the AQ2 software can calculate the undiluted nitrate concentration.

2. Run two Lab Fortified Blanks (LFB) per batch of samples, one at 0.6 mg-N/L and another at 2.44 mg-N/L (equivalent to 100 mg-N/L when using a 41x dilution factor). Report the recovery of the 41x diluted sample.

3. Validate reduction efficiency of the Cadmium coil at least once during each batch of samples (see Section 8.7)

## 6 INTERFERENCES

---

Samples containing strong oxidants or reductants, such as chlorine or sodium thiosulfate, cause low results by decreasing nitrate reduction efficiency. See Section 11.1 for guidance on sample pretreatment.

Highly alkaline or overly-acidified samples may give low results due to a shift in pH. Neutralize the pH as needed.

Low results might be obtained for samples that contain high concentrations of iron, copper or other metals. EDTA is included to eliminate this interference.

Samples that contain oil and grease may coat the surface of the cadmium. This interference may be eliminated through sample pretreatment with activated carbon or by extracting the sample with an organic solvent.

Bias from sample turbidity or color is correctable, using sample blanking feature of AQ2 software.

## 7 REAGENTS: CHEMICALS REQUIRED AND SAFETY INFORMATION

---

Consult the material safety data sheets (MSDS) for details on safe handling of chemicals.

<u>Chemical</u>	<u>C.A.S. No.</u>	<u>Safety Information</u>
Ammonium chloride, anhydrous	12125-02-9	Irritating to eyes and skin. May cause irritation of respiratory tract.
Ammonium hydroxide, conc.	1336-21-6	Causes severe burns. Toxic if inhaled or swallowed.
Copper (II) sulfate	7758-98-7 7758-99-8	Irritating to eyes, skin, and respiratory tract. Harmful if swallowed.
Disodium EDTA dihydrate	6381-92-6	Irritating to eyes, skin, and respiratory tract.
N-(1-naphthyl)-ethylenediamine dihydrochloride	1465-25-4	Irritating to eyes, skin, and respiratory tract.
Phosphoric acid, conc.	7664-38-2	Causes severe burns. Toxic if inhaled or swallowed.
Sodium nitrate	7631-99-4	Irritating to eyes and skin. Harmful if inhaled or swallowed.
Sodium nitrite	7632-00-0	Irritating to eyes and skin. Harmful if inhaled or swallowed.
Sodium hydroxide	1310-73-2	Causes severe burns. Harmful if inhaled or swallowed.
Sulfanilamide	63-74-1	Irritating to eyes, skin, and respiratory tract. Harmful if swallowed.
Sulfuric acid, conc.	7664-93-9	Causes severe burns. Toxic if inhaled or swallowed
Triton® X-100	9002-93-1	Irritating to eyes, skin, and respiratory tract. Harmful if swallowed.

## 8 REAGENT SOLUTIONS

Use reagent-grade chemicals, certified for analytical or general laboratory use. Reagents of technical or commodity grade must be validated by the user. Use high-purity reagent water, distilled or deionized, and free from organic contamination. Grade 1 (ISO Standard 3696) or better than Type II (ASTM Standard D1193) are suitable.

### 8.1 TRITON® X-100, 7.5% w/v

Triton® X-100 (neat liquid)	15 g
DI Water	dilute to 200 mL

Weigh 15 g Triton® X-100 (neat liquid) into a small weigh boat or beaker. Set up a 500 mL container with about 150 mL deionized water and a stir bar. While stirring vigorously, add Triton® X-100 slowly. The Triton® X-100 will thicken initially but will dissolve with continued stirring. Immerse the weigh vessel in the stirring mixture to attain complete transfer. Dilute to 200 mL total volume. Filter this reagent, e.g., using filter paper. Store in refrigerator. Discard after six months, or if solids are seen.

### 8.2 COPPER (II) SULFATE, 2% w/v

Copper (II) sulfate pentahydrate	31.3 g
or	
Copper (II) sulfate anhydrous	20 g
DI water	dilute to 1 L

In a 1L volumetric flask dissolve 31.3 g copper (II) sulfate pentahydrate or 20 g copper (II) sulfate, anhydrous in about 800 mL deionized water. Fill to the mark with deionized water and mix well.

### 8.3 AMMONIUM CHLORIDE BUFFER STOCK, pH 8.55

Ammonium chloride, anhydrous, low in nitrate	180 g
Ethylenediaminetetraacetic acid disodium salt dihydrate	2.0 g
* Ammonium hydroxide, concentrated for pH adjustment	pH 8.55 *
DI water	dilute to 1 L

\* Although USEPA method 353.2 specifies ammonium hydroxide for pH adjustment, 10% (w/v) sodium hydroxide (10 g NaOH pellets per 100 mL) is a suitable replacement.

Dissolve 180 g ammonium chloride and 2.0 g ethylenediaminetetraacetic acid, disodium salt dihydrate in 800 mL deionized water. SEAL recommends product number 6451 from GFS Chemicals. Adjust the pH to  $8.55 \pm 0.05$  using ammonium hydroxide, concentrated and dilute to 1 L.

NOTE: ACS grade ammonium chloride may contain nitrate contamination. An alternate recipe for the ammonium chloride buffer is:

CAUTION--Fumes! To a 1 L container add 400 mL deionized water. Carefully add 280 mL (333 g) hydrochloric acid, concentrated, 227 mL (204 g) ammonium hydroxide, concentrated and 2.0 g ethylenediaminetetraacetic acid, disodium salt dihydrate. Cool to room temperature. Adjust to pH  $8.55 \pm 0.05$  using ammonium hydroxide, concentrated and dilute to 1 L.

### 8.4 WORKING BUFFER, 0.0375% surfactant

Ammonium chloride buffer stock (above)	200 mL
7.5% (w/v) Triton® X-100 solution, required (above)	1.0 mL

Add 1.0 mL 7.5% (w/v) Triton® X-100 solution to a 200 mL flask. Add, with swirling, 200 mL ammonium chloride buffer stock and shake well to mix. Prepare fresh every two weeks.

**8.5 SULFANILAMIDE-NEDD**

Phosphoric acid, concentrated	20 mL
Sodium hydroxide	1.0 g
Sulfanilamide	7.5 g
N-(1-naphthyl)-ethylenediamine dihydrochloride	0.375 g
DI water	dilute to 500 mL

Dissolve 1.0 g sodium hydroxide pellets in about 250 mL deionized water. Carefully add 20 mL phosphoric acid, concentrated (low in nitrite). Add 7.5 g sulfanilamide and 0.375 g N-(1-naphthyl)-ethylenediamine dihydrochloride and stir to dissolve. Dilute to 500 mL with deionized water. Filter this reagent, e.g., using filter paper. This reagent is stable for at least 6 weeks when stored in the dark at 4°C. As the reagent slowly turns pink, re-filter it as needed. Discard this reagent when background absorbance of analyzed blanks exceeds 0.04 absorbance unit.

**8.6 SULFURIC ACID, 5 normal**

Sulfuric acid, concentrated	70 mL
DI water	dilute to 500 mL

Slowly add 70 mL sulfuric acid, concentrated to about 400 mL of deionized water. Caution, the container will become very warm. Cool to room temperature and dilute to 500 mL with deionized water. This reagent is available commercially.

## 8.7 OPEN TUBULAR CADMIUM REACTOR COIL (OTCR)

The OTCR is a 14" coiled cadmium tube having a purple cladding. Within the OTCR, nitrate is chemically reduced to nitrite. The exposed ends are sleeved with Tygon® tubing, p/n 5719. The tee connector on the rotating sampler arm connects to a 15 cm piece of 1/16" o.d. PTFE tubing. Moisten the free end of this tube and insert it into the OTCR inlet sleeve, leaving 1 mm gap from the cadmium. Locate the 1/16" o.d. dilutor transfer line, which passes beneath the sampler arm cosmetic cover. Insert the end of this tube into the other sleeve at the outlet of the OTCR. Important: Avoid making crimps or kinks to these 1/16" o.d. tubes.

### **SEAL Analytical recommendations to prepare the OTCR for nitrate analyses**

Under MAINTENANCE, locate the icon for automated copperization and activation of the OTCR. To launch this utility, click this icon and follow the instructions that appear.

#### Daily start-up, when the coil is fluidically installed and has been used recently:

- From MAINTENANCE, prime the syringe dilutor.
- Run the regeneration utility once, without using 2% CuSO<sub>4</sub>. This means replace the reagent container in position 15, used for 2% CuSO<sub>4</sub>, with deionized water.

#### Coil regeneration and start-up, when the coil has sat idle for 3 to 7 days:

- Remove the coil by gently sliding the soft sleeve tubes off the cadmium ends.
- Use a 6" piece of Tygon® tubing to connect the male luer of a 50 mL syringe to the coil. SEAL recommends tubing p/n 116-0536-18, having 0.11" i.d.
- Using the syringe, rapidly draw deionized water into the coil, while purposely drawing air in alternation. Done vigorously, this technique expels the previous activated coating, seen as fine black flakes.
- Re-attach the coil to its sleeve connectors. From MAINTENANCE, prime the syringe.
- Run the regeneration utility twice, both times using 2% CuSO<sub>4</sub> in position 15.

#### Acid-stripping of the coil, with regeneration, to correct low nitrate reduction efficiency:

- Remove the coil by gently sliding the soft sleeve tubes off the cadmium ends.
- Attach the coil to the syringe as described above. Draw 6 N hydrochloric acid into the coil and stand for 2–5 minutes. Rapidly draw deionized water into the coil, alternating with air as described above. Repeat this technique to expel all debris.
- Re-install the coil, prime the syringe and run the utility twice, using 2% CuSO<sub>4</sub>.

### **Validate reduction efficiency**

The experienced SEAL AQ user can judge >85% nitrate reduction efficiency for the cadmium coil, by comparing the nitrate absorbance change observed over the current calibrated range to the corresponding absorbance change from previous nitrate calibrations.

To measure reduction efficiency, run duplicates of a nitrite–N standard, having the same mid-range concentration as the periodically-analyzed nitrate–N QC standard. Assuming the nitrate+nitrite test has been calibrated, reduction efficiency is calculated as follows:

$$\text{Percent Reduction Efficiency} = \frac{\text{NO}_3\text{-N Result}}{\text{NO}_2\text{-N Result}} \times 100$$

Refer to SEAL Analytical AQ Technical Tips series, Cd Coil Regeneration, for more information.

## 9 STANDARD SOLUTIONS

---

### 9.1 NITRATE-N STOCK STANDARD SOLUTION (500 mg NO<sub>3</sub>-N/L)

Sodium nitrate	3.034 g
Sulfuric acid, 5 normal (above)	up to 7 mL
DI water	dilute to 1 L

Dissolve 3.034 g sodium nitrate (dried at 105°C) in deionized water in a 1 Liter volumetric flask. Up to 7 mL sulfuric acid, 5 normal, may be added for preservation. Dilute to the mark with deionized water.

### 9.2 NITRITE-N STOCK STANDARD SOLUTION (500 mg NO<sub>2</sub>-N/L)

Sodium nitrite	2.463 g
DI water	dilute to 1 L

Dissolve 2.463 g sodium nitrite (dried at least 4 hours in a dessicator) in about 800 mL deionized water in a 1 Liter volumetric flask. Dilute to the mark with deionized water. Do not add acid for preservation. Store up to 1 month in an amber bottle at 4°C.

### 9.3 NITRATE-N INTERMEDIATE STANDARD SOLUTION (2.0 mg NO<sub>3</sub>-N/L)

NITRATE-N stock standard (500 mg N/L, above)	2 mL
DI water	dilute to 500 mL

To a 500 mL volumetric flask pipet 2 mL NITRATE-N stock standard (500 mg NO<sub>3</sub>-N/L) and dilute to the mark with deionized water. Prepare every two weeks.

### 9.4 NITRITE-N INTERMEDIATE STANDARD SOLUTION (2.0 mg NO<sub>2</sub>-N/L)

NITRITE-N stock standard (500 mg N/L, above)	2 mL
DI water	dilute to 500 mL

To a 500 mL volumetric flask pipet 2 mL NITRITE-N stock standard (500 mg NO<sub>2</sub>-N/L) and dilute to the mark with deionized water. Prepare twice weekly.

### 9.5 NITRATE-N WORKING STANDARD SOLUTIONS (prepare weekly)

Concentration, mg NO <sub>3</sub> -N/L	0	0.01	0.02	0.05	0.1	0.4	1.0	1.6	2.0
Volume (mL) Intermediate nitrate-N standard solution diluted as indicated with deionized water	--	1	2	5	5	20	50	80	100
Final Volume, mL	100	200	200	200	100	100	100	100	100

### 9.6 NITRITE-N WORKING STANDARD SOLUTIONS

Concentration, mg NO <sub>2</sub> -N/L	0.04	0.4	2.0
Volume (mL) Intermediate nitrite-N standard solution diluted to 100 mL with deionized water	2	20	100

Use nitrite-N working standards to test nitrate reduction efficiency. Prepare twice weekly.

## 10 SAMPLE PRESERVATION AND STORAGE

---

Samples may be collected into plastic or glass containers.

Sample preservation and holding time requirements are as follows, for samples to be reported for drinking water compliance monitoring under the Safe Drinking Water Act:

- For nitrate: Preserve the sample by cooling to 4°C and analyze within 48 hours. If the sample is chlorinated, preserve by cooling to 4°C and analyze within 14 days.
- For nitrite: Preserve the sample by cooling to 4°C and analyze within 48 hours.
- For nitrate+nitrite (combined): Preserve the sample by cooling to 4°C and acidifying to pH < 2 with sulfuric acid, concentrated, up to 2 mL sulfuric acid per liter. Analyze within 28 days.

Sample preservation and holding time requirements are as follows, for samples to be reported for wastewater compliance monitoring under the Clean Water Act:

- For nitrate: Preserve the sample by cooling to 4°C and analyze the sample within 48 hours.
- For nitrite: Preserve the sample by cooling to 4°C and analyze within 48 hours.
- For nitrate+nitrite (combined): Preserve the sample by cooling to 4°C and acidifying to pH < 2 with sulfuric acid, concentrated, up to 2 mL sulfuric acid per liter. Analyze within 28 days.

## 11 PROCEDURE

---

Prepare standards and reagents as described in Sections 8 and 9. Any reagents having visible particulates should be filtered.

Pour calibration standards, quality control solutions and samples into sample cups and 45 mL reagent wedges, according to the user-defined worklist.

Before running the analysis batch, check the analyzer for sufficient reagent water, fresh reaction segments, correct location of reagent vessels and a waste collection bottle in place.

### 11.1 CHEMISTRY TROUBLESHOOTING TIPS

Typically, calibration standards do not require matrix matching to account for field sample preservation, up to 2 mL/L of sulfuric acid. To verify, add 5 mL typical preserved field sample to an equal volume of working buffer. Similarly, mix equal volumes of a calibration standard with the working buffer. The measured pH values should agree within 0.25 pH unit, within the pH range 8.2 to 8.6.

Samples containing more than about 1 ppm residual chlorine require pre-treatment to prevent loss of nitrate reduction efficiency. Studies for nitrate reduction efficiency on AQ2 indicated that two drops of 1% (w/v) sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) effectively dechlorinated a 25 mL sample containing 5 ppm residual chlorine. Studies further indicated that adding 1% (w/v) sodium sulfite in excess of full dechlorination, between 1% and 6% volume-basis excess of the aliquot volume, caused negative bias but did not cause persistent loss of coil reduction efficiency. In contrast, adding excess sodium thiosulfate, as suggested by USEPA Method 353.2, caused persistent loss of coil reduction efficiency.

## 12 REFERENCES, supplementary

---

- 1) U.S. EPA, 40 CFR, Part 136, Appendix B and Part 136.3 Tables IB and II, and Part 141.23.
- 2) 2003 NELAC Standard, National Environmental Laboratory Accreditation Conference, June 5, 2003, EPA-600/R-04/003, <http://www.epa.gov/nerlesd1/land-sci/nelac/index.html>
- 3) "Methods Update Rule", Vol. 72 Federal Register No. 47 (12 March 2007) Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; National Primary Drinking Water Regulations and National Secondary Drinking Water Regulations.
- 4) Manual for the Certification of Laboratories Analyzing Drinking Water, 4th ed., USEPA 815/B-97/001, March 1997.

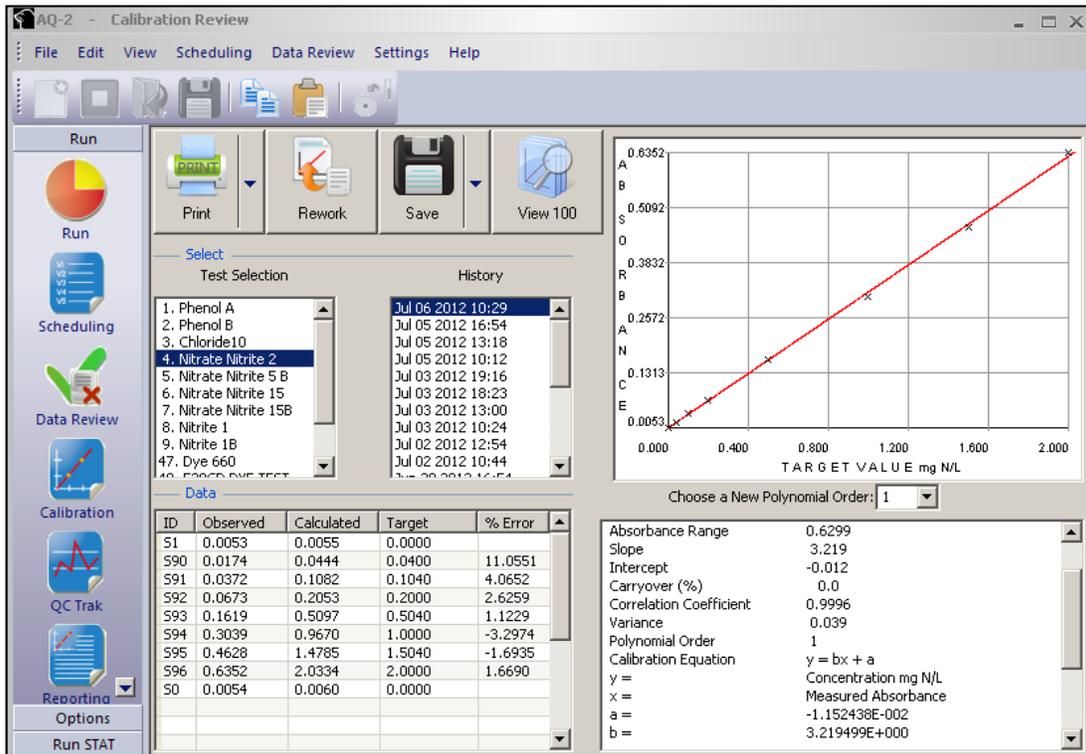
## 13 TEST PARAMETERS

PARAMETER	AQ2 SETTING
Test name	NO3_NO2 2
Units	mg N/L
Decimals	3
Test type	Cadmium reduction
Sample volume ( $\mu\text{L}$ )	500
Water volume ( $\mu\text{L}$ )	0
Number of mixes	2
Cuvette primes	1
Cuvette washes	2
Reduction time (seconds)	25
Cadmium flush volume	310
Reaction time (seconds)	480
Wavelength (nm)	520
Polynomial order	1
Number of reagents	2
1. Working buffer ( $\mu\text{L}$ )	265
2. Sulfanilamide–NEDD ( $\mu\text{L}$ )	350
Advanced Test Parameters	<input checked="" type="checkbox"/> Eliminate Air from Test Transfer <input checked="" type="checkbox"/> Eliminate Air from Cuvette Wash <input checked="" type="checkbox"/> Extra Debubbling Action

**DEFINITIONS:**

Test Name:	Name which appears on the final report
Decimals:	Number of decimal places in the reported result
Units:	Concentration units appearing against the reported result
Number of mixes:	Number of mixes of the sample + reagent in the reaction well
Reaction time:	Time (in seconds) between addition of sample + reagent and measurement of the reaction mixture
Sample volume:	Volume (in microliters) of the sample used in the test
Number of reagents:	Number of reagents defined for the test
Reagent volume:	Volume (in microliters) of the reagent used in the test
Wavelength:	Interference filter wavelength to be used in the test
Cuvette primes:	Number of times the cuvette is flushed with reagent (no sample) prior to sampling
Cuvette wash:	Number of washes of the cuvette between aspirations of finished reaction liquid
Baseline on Wash:	Water baseline measured between aspirations to provide drift correction
Polynomial order:	Polynomial order to be used when fitting the standard points to the standard graph (1 = linear)

## 14 STANDARDIZATION



### DEFINITIONS:

Abs. Range: Difference between the absorbance of the highest standard and the absorbance of the blank

Variance: Calculated as follows:

$$\text{Variance} = \frac{\sum (\text{Deviations, i.e., errors})^2}{\sum (\text{Observed values})^2} \times 100$$

Carryover(%): Calculated as follows:

$$\text{Carryover}(\%) = 100 \times \frac{(A - B)}{C}$$

Where, A = absorbance of carryover blank (S0)

B = absorbance of blank (S1)

C = calibration absorbance range

## 15 PERFORMANCE VALIDATION DATA

### 15.1 DETECTION LIMIT STUDY

Replicates of 0.008 mg N/L nitrate standard in reagent water\*\*\*

	Concentration (mg N/L)		
	0.002	0.010	0.009
	0.004	0.010	0.009
	0.007	0.011	0.009
	0.003	0.010	0.010
	0.003	0.010	0.009
	0.006	0.009	0.010
	0.004	0.011	0.010
	0.005	0.010	0.010
	0.006	0.011	0.009
	0.004	0.011	0.011
	0.005	0.012	0.010
	0.007	0.012	0.010
	0.003	0.011	0.010
	0.007	0.010	0.009
	0.003	0.010	0.010
Statistics			
Mean	0.004	0.011	0.010
Std. Deviation	0.0017	0.0008	0.0006
MDL*	0.005	0.002	0.002

### 15.2 PERFORMANCE STUDY

Replicates of 0.02 mg N/L nitrate standard in reagent water\*\*\*

	Concentration (mg N/L)			
	0.021	0.023	0.021	0.026
	0.018	0.023	0.024	0.025
	0.019	0.023	0.025	0.025
	0.019	0.023	0.021	0.024
	0.019	0.023	0.022	0.024
	0.019	0.024	0.024	0.022
	0.019	0.023	0.023	0.026
	0.019	0.022	0.021	0.021
	0.021	0.023	0.023	0.023
	0.021	0.023	0.022	0.022
	0.020	0.022	0.023	0.023
	0.019	0.024	0.025	0.022
	0.020	0.023	0.030	0.022
	0.020	0.024	0.021	0.023
	0.018	0.024	0.024	0.021
Statistics				
Mean	0.020	0.023	0.023	0.023
Std. Deviation	0.0011	0.0007	0.0023	0.0016
% RSD**	5.5	3.0	10.0	6.9
% Recovery	95.8	113.7	114.6	115.9

\* MDL is calculated by multiplying the Standard Deviation by the Student-t value for the number of replicates run.

\*\* %RSD is calculated by dividing the Standard Deviation by the mean, then multiplying by 100.

### 15.3 PRECISION STUDY

Replicates of 1.0 mg N/L nitrate standard in reagent water\*\*\*

Concentration (mg N/L)

Statistics					
Mean	1.06	1.05	1.08	1.13	1.10
% Recovery	106.2	105.1	107.6	112.6	109.9
Std. Deviation	0.024	0.049	0.030	0.036	0.036
% RSD**	2.2	4.7	2.8	3.2	3.3
Maximum	1.11	1.15	1.12	1.17	1.17
Minimum	1.02	0.98	1.03	1.04	1.05

Replicates of 2.0 mg N/L nitrate standard in reagent water\*\*\*

Concentration (mg N/L)

Statistics					
Mean	2.16	2.06	1.99	2.00	2.06
% Recovery	108.1	102.8	99.5	100.1	103.1
Std. Deviation	0.058	0.047	0.074	0.029	0.048
% RSD**	2.7	2.3	3.7	1.5	2.3
Maximum	2.31	2.13	2.01	2.02	2.14
Minimum	2.11	1.97	1.81	1.94	1.99

\*\*\* To prepare these standards, refer to Section 9.

## 16 REVISIONS

---

August 31, 2004 Rev. 1	Method format changed to meet EPA standards Document tracking information added Equivalent methods listed Support data added Buffer recipe modified Method number changed from 2-018-1-H to EPA-126-A Test parameters changed Alternative buffer recipe added
September 2, 2004 Rev. 2	Referenced EPA 353.2 (1993) Interference and sample preservation sections amended Changed wording of NSDWR to NPDWR
October 8, 2004 Rev. 3	Front page reformatted Method Supplement 1 document created and implemented
June 1, 2005, Rev. 4	Minor adjustments in Test Parameters to improve performance Reagent recipes rewritten to accommodate both 10-mm cuvettes (p/n 10031 and p/n 5670)
March 3, 2006 Rev. 5	Increased level of EDTA in pH 8.6 buffer to counteract heavy metal contamination Replaced calibration curve
December 29, 2009 Rev. 6	Minor editorial revisions
December 13, 2010 Rev. 7	Minor editorial revisions
July 12, 2012 Rev. 8	Method reworked Method document reformatted

## **Oxygen and Nitrogen Isotopes in Dissolved Nitrate (NO<sub>3</sub>) by Azide Reduction**

Protocol 12\_02\_11\_01

### **1 INTRODUCTION**

---

This method has been developed at the University of Nebraska for the rapid and precise analysis of oxygen and nitrogen isotopes in dissolved NO<sub>3</sub>N in ground and surface water samples.

### **2 SCOPE AND APPLICATION**

---

#### **2.1 OVERVIEW**

This method generally follows a published method for conversion of nitrate to nitrous oxide for stable isotope analysis (McIlvin and Altabet, 2005) with the following changes: 1) 4ml of sample is reacted with high purity Cd powder for the cadmium reduction step, 2) 1ml of reduced sample is reacted with 0.25ml of azide solution in the azide reduction step. Samples with previously measured NO<sub>3</sub>N concentrations are diluted to a final concentration of 0.25ug/ml and NO<sub>3</sub><sup>-</sup> is converted to NO<sub>2</sub><sup>-</sup> by reaction with cadmium, with further reduction to nitrous oxide (N<sub>2</sub>O) using sodium azide in an acetic acid buffer with resulting N<sub>2</sub>O is then cryogenically separated and analysed on a Trace Gas Isoprime IRMS instrument for <sup>15</sup>N and <sup>18</sup>O. Isotope calibration uses known standards (USGS 32, USGS34, USGS35 and IAEA N3).

#### **2.2 METHOD DETECTION LIMIT**

Validation of the method was determined running 11 replicates of WSL KNO<sub>3</sub> at a concentration of 0.05mg/L. IDL was calculated as 0.5 nA. 16 replicates of WSL KNO<sub>3</sub> at a concentration of 0.25mg/l resulted in standard deviations of 0.144‰ on 15N and 0.242‰ on 18O.

#### **2.3 ACCEPTABLE RANGES**

Samples should be diluted to a constant concentration to help reduce variation due to linearity effects. Based on tests run in 2017 the most consistent results were with 0.25mg/l samples.

## 2.4 TRAINING TIME

## 2.5 SAMPLE PRESERVATION

Samples for N and O isotope analysis are shipped frozen in 100ml wide mouth Nalgene bottles. Upon arrival, samples should be thawed and subsampled, 10ml each into two 14ml centrifuge bottles. One is for isotope analysis and should be placed in a rack labeled with batch number then placed in Freezer 3. The other is for AQ2 analysis of nitrate+nitrite-N concentration and should have concentrated sulfuric acid added to preserve it and should also be placed in a rack labeled with batch number then placed in Refrigerator 2.

## 3 REQUIRED TRAINING

---

List the protocols that are required to complete this protocol. These must be recorded in staff or student training file. Link to **training table**

**Balance**

**Pipette**

**Sonicator**

## 4 EQUIPMENT AND MATERIALS

---

### 4.1 APPARATUS AND MATERIALS

- Two 1 ml gas tight syringes
- Balance (Mettler PM480)
- Sonicator Bath 5.7L Fisher
- Pipettes Finnpiptette II (1-5ml, 100-1000ul, 20-200ul)
- Exetainer sample vials 12ml
- Exetainer sample vials 4.5ml
- 4.5ml autosampler tray
- 12ml autosampler tray

### 4.2 REAGENTS

1. Sodium Chloride, lab grade, precombusted
2. Cadmium powder 325 mesh 99.5% (Acros, #AA1189136 or equivalent)
3. 1M Imidazole solution
4. 20% acetic acid
5. 2.0M sodium azide ( $\text{NaN}_3$ )
6. 6M sodium hydroxide
7. Vacutainer sample vials 12ml and 4.5ml

### 4.3 CHEMICALS

Populate this table from the **chemical database**

<b>Chemical</b>	<b>CAS Number</b>	<b>Hazards</b>	<b>Location</b>
Sodium Chloride	7647-14-5	General/Poison	Cabinet 2
Cadmium	7440-43-9	Poison, Inhalation hazard, Flammable	WSL103C
Imidazole	288-32-4	Danger Corrosive	Cabinet 2
Acetic acid	64-19-7	Corrosive, Organic, toxic	WSL 205
Sodium azide	26628-22-8	POISON	Cabinet 2
Sodium Hydroxide	1310-73-2	Corrosive base	Cabinet 2

---

## 5 SAFETY PRECAUTIONS

Reagents used in this method are acidic and poisonous!! Required use of gloves, eye protection, closed toe shoes, and labcoats. Warning: sodium azide can become an explosive hazard if exposed to metal. Keep all sodium azide in the fume hood and do not make more than needed.

---

## 6 SOLUTIONS AND REAGENTS

### 6.1 IMIDAZOLE SOLUTION 1 MOLAR

Imidazole	FW	6.8077g
DDI H2O	FW	Fill to 0.1L

**Protocol:** mass imidazole and place into 100ml volumetric flask. Add ~50ml of DDI H2O and shake to dissolve. Add DDI H2O to 100ml.

**Storage:** Room Temperature

**Disposal:**

### 6.2 AZIDE SOLUTION 2 MOLAR

Sodium Azide	FW	13.06g
DDI H2O	FW	Fill to 0.1L

**Protocol:** mass azide and place into 100ml volumetric flask. Add ~50ml of DDI H2O and shake to dissolve. Add DDI H2O to 100ml.

**Storage:** Room Temperature for no more than 2 weeks

**Disposal:** decant into used sodium azide chemical container. When container is filled to near the neck of the bottle, remove EHS label and send to EHS.

### 6.3 SODIUM AZIDE SOLUTION

Sodium azide 2M	FW	5ml
Acetic Acid 20%	FW	5ml

**Protocol: combine equal amounts of 2M azide solution and 20% acetic acid**

**Storage: prepared daily and disposed of daily**

**Disposal: decant into used sodium azide chemical container. When container is filled to near the neck of the bottle, remove EHS label and send to EHS.**

## 7 STANDARD SOLUTIONS

## 8 PROTOCOL

### Cadmium reduction

---

1. Dilute samples to 0.25ug/ml NO<sub>3</sub><sup>-</sup> as N.
2. For samples under 0.25mg/L, 4 ml of undiluted sample will be used.
3. Place 500mg cadmium powder into a 4.5ml Exetainer tube.
4. Next add 0.121g of precombusted NaCl to vial.
5. Then pipette 4 ml of sample/standard into vial
6. Finally add 200ul of 1M Imidazole solution to buffer.
7. This will be repeated for 4 calibration standards, 3 drift standards, 1 LD2 and 25 samples.
8. Cap and place in a tray in heated sonicator at ~40°C for 2 hours then let sit over night at room temperature.

### Azide reduction

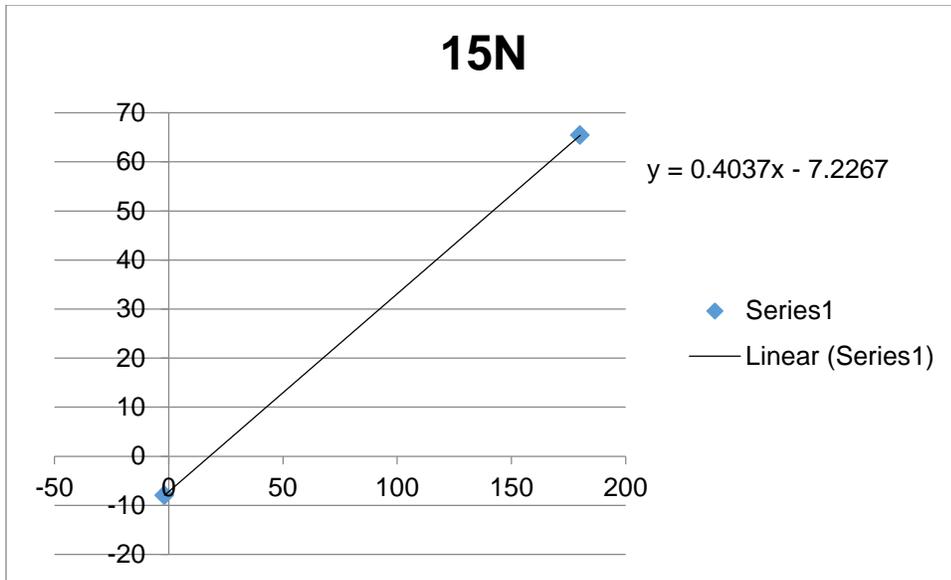
1. Centrifuge the 4.5ml exetainers at 2500rpm for 10 min to separate cadmium from sample.
2. For diluted samples: Pipette 1ml of sample (which should now be converted to NO<sub>2</sub>) from the cadmium containing vial and into each of 2 12ml exetainers.
3. For samples with less than 0.25mg/L NO<sub>3</sub><sup>-</sup> as N: pipette a volume of sample to result in 0.2ug of N, up to 4ml.
4. Samples and standards are then injected with 0.2ml of the azide solution using a gas tight syringe.
5. Vials are shaken vigorously and after 15 minutes the reaction is halted by injection of 0.1ml of 6M NaOH using a second gas tight syringe.
6. Clean tops of vials of any NaOH residue. This residue can clog the needle on the Tracegas autosampler analyser.

### **Azide solution**

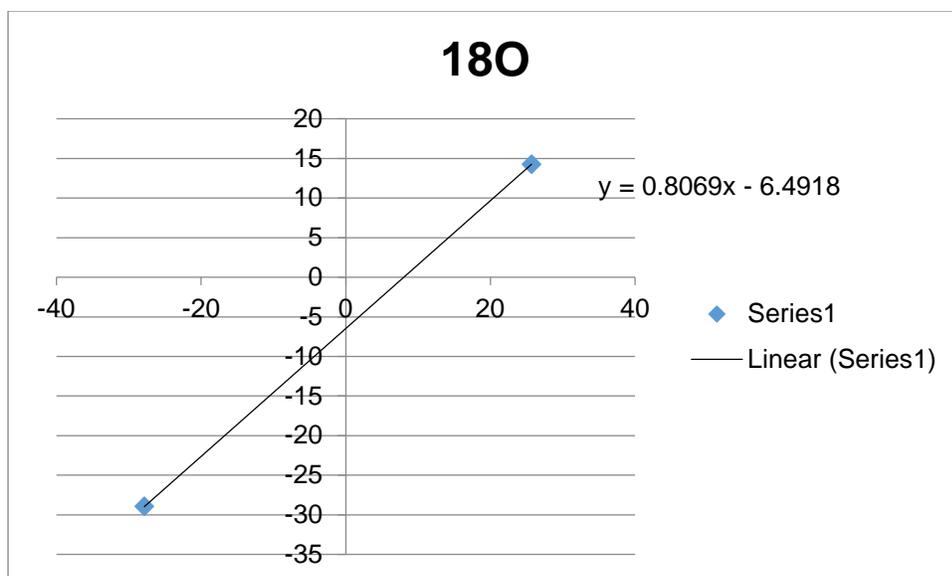
To prepare azide solution for 34 samples/standards (44 exetainer vials):

1. Into an empty exetainer headspace vial add
2. 5ml of acetic acid 20%
3. Then add 5ml of 2M sodium azide





<b>180 Stretch Correction</b>		USGS 34	USGS 32	USGS 35		43.48	56.8		18.28	25.7
		-25.24	18.28	43.48						
						18.28	25.7		-25.24	-27.8
						Diff Measured	Diff accepted		Diff Measured	Diff accepted
	Average	-25.24	18.28	43.48		25.2	31.1		43.52	53.5
	Actual	-27.8	25.7	56.8		stretch factor			stretch factor	
	unstretched	-31.028	22.47197	53.66		1.234126984			1.229319853	
blank	0.00	3.22803	3.140159		3.140159		3.22803309	Shift RM1		
USGS 32	18.28	25.7	25.7		25.7		3.14015873	Shift RM2		
USGS 34	-25.24	-27.8	-28.0092		-28.0092					
USGS 35	43.48	56.6789	56.8		56.8					
WSL TG 5	-7.63	-6.1517	-6.27623		-6.27623					
WSL TG 10	31.65	42.136	42.20028		42.20028					



## 10 QUALITY ASSURANCE

Every time the IRMS/Autosampler is changed to a new method or protocol, or the system is vented to atmosphere, stability/zeros, background scans, linearity, and sensitivity tests are run. This is followed by running 11 standards to check the variability in delta value.

Only after these values are shown to be acceptable are samples/calibrations run. Acceptable background and vacuum pressures are given in the tables below. Peak Center should be done before every analytical run. Stability check should be run at least weekly. If the instrument has been idle for 2 or more days a peak center and stability check are required

### 10.1 QUALITY-CONTROL (QC) SAMPLES

Samples and standards are prepared and analyzed in runs of up to 35 daily. Each run contains approximately eight reference materials and one blank. The first samples of the run are one blank, three Calibration standards (depleted, intermediate, and enriched) followed by a QC. A drift correction standard is analyzed for every 5 or 6 samples, usually in autosampler slots 6, 11, 17, 22, 28 and 33. All of these reference materials can serve as QC samples.

For every run, the analyst,

(1) examines the computer printouts for indications of analytical problems, and reviews the results to determine which samples need to be analyzed a third time to achieve acceptable results (i.e.,  $\Delta\delta \leq 0.2\text{‰}$  for  $^{15}\text{N}$  and  $0.5\text{‰}$  for  $^{18}\text{O}$ ).

(2) determines the daily additive and expansion correction factors by the using the calibration standards, and

(3) applies correction factors to isotopic data.

These values with dates and analysis-number ranges are calculated in an excel workbook with the batch number as the file name in a folder named for the project. The final corrected isotope value (and % element if determined) is recorded manually in the protocol lab book, and entered into LIMS. Each batch of samples will have a LFB (Lab Fortified Blank), REF (reference) and LD2 (Lab Duplicate 2). Any of the QC can be entered as the LFB or REF. The LD2 is used to test sample standard deviation.

## 10.2 ACCEPTANCE CRITERIA FOR ALL QC SAMPLES

Acceptance criteria for QC samples are the same as acceptance criteria for the other samples. The rules are as follows:

- If standard deviation is  $\leq 0.2$  ‰, use mean delta.
- If there are three or more analyses, delete the outlier and recalculate.
- If standard deviation of this recalculation is  $\leq 0.2$  ‰, use mean from this recalculation.
- If none of the above is the case, the result is not accepted, and corrective action is required.

## 10.3 CORRECTIVE ACTION REQUIREMENTS

If the analyst finds any problem with the daily reference-sample data, the analyst contacts the supervisor. This process requires an evaluation and reanalysis of certain samples to ascertain the origin of the problem.

If samples do not give satisfactory results after three or more separate analyses, the analyst averages all the data and reports the mean value. Such analytical results are indicated with a comment, and the customer will be advised by e-mail or other means.

## 10.4 METHOD VALIDATION

The following table summarizes replicate analysis of a low level standard (0.05 mg/L NO<sub>3</sub>N) processed and analyzed using this protocol.

	Peak Height	D15N	d18O	Peak Height	d15Nb
WSL TG 3	4.75	25.95	36.99	0.29	-3.22
WSL TG 3	4.76	25.99	37	0.29	-3.56
WSL TG 3	5.01	25.89	37.05	0.3	-2.99
WSL TG 3	4.86	25.9	37.28	0.29	-4.37
WSL TG 3	4.75	25.96	37.07	0.29	-4.13
WSL TG 3	5.1	25.9	36.82	0.3	-3.44
WSL TG 3	5.31	25.74	37.11	0.32	-2.69
WSL TG 3	5.22	25.83	37.34	0.31	-3.75
WSL TG 3	5.39	25.8	37.46	0.32	-4.18
<b>Average</b>	<b>5.02</b>	<b>25.88</b>	<b>37.12</b>	<b>0.30</b>	<b>-3.59</b>
<b>SD</b>	<b>0.24</b>	<b>0.08</b>	<b>0.19</b>	<b>0.01</b>	<b>0.54</b>

## 11 ADDITIONAL INFORMATION

---

### 11.1 REFERENCES

M. R. McIlvin, M. A. Altabet. Chemical conversion of nitrate and nitrite to nitrous oxide for nitrogen and oxygen isotopic analysis in freshwater and seawater. *Anal. Chem.* 2005, 77, 5589.

Ying Tu, Yunting Fang, Dongwei Liu and Yuepeng Pan. Modifications to the azide method for nitrate isotope analysis. *Rapid Commun. Mass Spectrom.* 2016, 30, 1213–1222

### 11.2 ADDITIONAL READING

### 11.3 INSTRUMENTATION TECHNICAL SUPPORT

### 11.4 COMMENTS

## 12 PREVIOUS ISSUES AND CHANGES

---

Document File Name	Issue	Issue Effective Dates	Author

### 12.1 ISSUE CHANGES

#### 12.1.1 Issue 001:

- Change 1
- Change 2
- Change 3

# Water Sciences Laboratory

## Analytical Report



**Nebraska  
Water Center**

Daugherty Water for Food Global Institute

[Nebraska Water Center](#), a part of the  
[Robert B. Daugherty Water for Food Global Institute at the University of Nebraska](#)  
e: [dsn1@unl.edu](mailto:dsn1@unl.edu) | p: 1 402.472.7539 | f: 1 402.472.9599 | c: 1 402.304.3748

Results Reported To:

Jessica Gray  
Eastern Research Group, Inc.  
14555 Avion Parkway Suite 200  
Chantilly, VA 20151  
(703) 633-1625  
[jessica.gray@erg.com](mailto:jessica.gray@erg.com)

**Project: ERG CSD GROUNDWATER  
SAMPLING**

Sampled By: Juan Rogers  
Received: 05/01/2018  
Received By: David Cassada  
Batch: **W18196**

**Protocol: 02\_03\_01**

Nitrate\_Nitrite Cd-Reduction EPA 353.2

Protocol Reference:

Seal Analytical Nitrate-N + Nitrite-N in  
Drinking and Surface Waters Domestic and  
Industrial Wastes.

### \*\*\* Results of Analysis \*\*\*

Lab ID	Sample ID	Collection Date	NO3+NO2-N (mg/L)	Analysis Date
18-1774	A1A	04/30/2018	*0.000	05/07/2018
18-1775	A1B	04/30/2018	0.052	05/07/2018
18-1777	A2A	04/30/2018	*0.000	05/07/2018
18-1778	A2B	04/30/2018	*0.006	05/07/2018
18-1779	A3A	04/30/2018	0.021	05/07/2018
18-1780	A3B	04/30/2018	0.047	05/07/2018
18-1781	A4A	04/30/2018	0.568	05/07/2018
18-1782	A4B	04/30/2018	0.124	05/07/2018
18-1783	B1A	04/30/2018	0.018	05/07/2018
18-1784	B1B	04/30/2018	0.043	05/07/2018
18-1785	B2A	04/30/2018	*0.000	05/07/2018
18-1786	B2B	04/30/2018	0.082	05/07/2018
18-1787	B3A	04/30/2018	1.28	05/07/2018
18-1788	B3B	04/30/2018	*0.000	05/07/2018
18-1789	B4A	04/30/2018	17.5	05/07/2018
18-1790	B4B	04/30/2018	8.81	05/07/2018
18-1791	C3A	04/30/2018	9.08	05/07/2018
18-1792	C3B	04/30/2018	0.440	05/07/2018
18-1793	C1A	04/30/2018	*0.000	05/07/2018
18-1794	C1B	04/30/2018	0.045	05/07/2018
18-1795	C2A	04/30/2018	22.8	05/07/2018
18-1796	C2B	04/30/2018	0.866	05/07/2018

**Detection Limit:** 0.01

# Water Sciences Laboratory

## Analytical Report



**Nebraska  
Water Center**

Daugherty Water for Food Global Institute

Nebraska Water Center, a part of the  
Robert B. Daugherty Water for Food Global Institute at the University of Nebraska  
e: [dsnow1.unl.edu](mailto:dsnow1.unl.edu) | p: 1 402.472.7539 | f: 1 402.472.9599 | c: 1 402.304.3748

Results Reported To:

Jessica Gray  
Eastern Research Group, Inc.  
14555 Avion Parkway Suite 200  
Chantilly, VA 20151  
(703) 633-1625  
[jessica.gray@erg.com](mailto:jessica.gray@erg.com)

**Project: ERG CSD GROUNDWATER  
SAMPLING**

Sampled By: Cheryl Burdett  
Received: 05/02/2018  
Received By: David Cassada  
Batch: **W18199**

**Protocol: 02\_03\_01**

Nitrate\_Nitrite Cd-Reduction EPA 353.2

Protocol Reference:

Seal Analytical Nitrate-N + Nitrite-N in  
Drinking and Surface Waters Domestic and  
Industrial Wastes.

### \*\*\*\* Results of Analysis \*\*\*\*

Lab ID	Sample ID	Collection Date	NO <sub>3</sub> +NO <sub>2</sub> -N (mg/L)	Analysis Date
18-1806	C12A	05/01/2018	*0.000	05/07/2018
18-1808	C12B	05/01/2018	*0.000	05/07/2018
18-1809	C13A	05/01/2018	*0.000	05/07/2018
18-1810	C13B	05/01/2018	*0.000	05/07/2018
18-1811	D1A	05/01/2018	*0.000	05/07/2018
18-1812	D1B	05/01/2018	*0.000	05/07/2018
18-1813	D2A	05/01/2018	1.65	05/07/2018
18-1814	D2B	05/01/2018	13.5	05/07/2018
18-1815	D3A	05/01/2018	8.98	05/07/2018
18-1816	D3B	05/01/2018	13.1	05/07/2018
18-1817	D4A	05/01/2018	10.2	05/07/2018
18-1818	D4B	05/01/2018	17.7	05/07/2018
18-1819	C5AA	05/01/2018	13.1	05/07/2018
18-1820	C5AB	05/01/2018	22.0	05/07/2018
18-1821	C6A	05/01/2018	15.1	05/07/2018
18-1822	C6B	05/01/2018	11.7	05/07/2018
18-1823	C7A	05/01/2018	19.5	05/07/2018
18-1824	C7B	05/01/2018	14.7	05/07/2018
18-1825	C8A	05/01/2018	6.64	05/07/2018
18-1826	C8B	05/01/2018	2.39	05/07/2018
18-1827	C9A	05/01/2018	2.47	05/07/2018
18-1828	C9B	05/01/2018	0.646	05/07/2018
18-1829	C10A	05/01/2018	7.76	05/07/2018
18-1830	C10B	05/01/2018	15.6	05/07/2018
18-1831	C11A	05/01/2018	*0.000	05/07/2018
18-1832	C11B	05/01/2018	0.119	05/07/2018

**Detection Limit:** 0.01

# Water Sciences Laboratory

## Analytical Report



**Nebraska  
Water Center**

Daugherty Water for Food Global Institute

[Nebraska Water Center](#), a part of the  
[Robert B. Daugherty Water for Food Global Institute at the University of Nebraska](#)  
e: [dsn1@unl.edu](mailto:dsn1@unl.edu) | p: 1 402.472.7539 | f: 1 402.472.9599 | c: 1 402.304.3748

Results Reported To:

Jessica Gray  
Eastern Research Group, Inc.  
14555 Avion Parkway Suite 200  
Chantilly, VA 20151  
(703) 633-1625  
jessica.gray@erg.com

**Project: ERG CSD GROUNDWATER  
SAMPLING**

Sampled By: Juan Rogers  
Received: 05/03/2018  
Received By: David Cassada  
Batch: **W18205**

**Protocol: 02\_03\_01**

Nitrate\_Nitrite Cd-Reduction EPA 353.2

Protocol Reference:

Seal Analytical Nitrate-N + Nitrite-N in  
Drinking and Surface Waters Domestic and  
Industrial Wastes.

\*\*\*\* *Results of Analysis* \*\*\*\*

Lab ID	Sample ID	Collection Date	NO3+NO2-N (mg/L)	Analysis Date
18-1865	D5A	05/02/2018	0.451	05/09/2018
18-1867	D5B	05/02/2018	1.18	05/09/2018
18-1868	D6A	05/02/2018	41.1	05/09/2018
18-1869	D6B	05/02/2018	24.5	05/09/2018
18-1870	D7A	05/02/2018	30.7	05/09/2018
18-1871	D7B	05/02/2018	32.2	05/09/2018
18-1872	D8A	05/02/2018	48.8	05/09/2018
18-1873	D8B	05/02/2018	39.0	05/09/2018
18-1874	D9A	05/02/2018	30.3	05/09/2018
18-1875	D9B	05/02/2018	1.52	05/09/2018
18-1876	D10A	05/02/2018	8.79	05/09/2018
18-1877	D10B	05/02/2018	8.40	05/09/2018
18-1878	D11A	05/02/2018	28.0	05/09/2018
18-1879	D11B	05/02/2018	14.5	05/09/2018
18-1880	E1A	05/02/2018	11.7	05/09/2018
18-1881	E1B	05/02/2018	11.8	05/09/2018
18-1882	E2A	05/02/2018	0.995	05/09/2018
18-1883	E2B	05/02/2018	2.58	05/09/2018
18-1884	E3A	05/02/2018	3.83	05/09/2018
18-1885	E3B	05/02/2018	6.14	05/09/2018
18-1886	E4A	05/02/2018	26.1	05/09/2018
18-1887	E4B	05/02/2018	20.0	05/09/2018
18-1888	E5A	05/02/2018	28.3	05/09/2018
18-1889	E5B	05/02/2018	17.5	05/09/2018
18-1890	E6A	05/02/2018	0.149	05/09/2018
18-1891	E6B	05/02/2018	0.093	05/09/2018
18-1892	E7A	05/02/2018	16.1	05/09/2018
18-1893	E7B	05/02/2018	13.8	05/09/2018

# Water Sciences Laboratory

## Analytical Report



**Nebraska  
Water Center**

Daugherty Water for Food Global Institute

[Nebraska Water Center](http://Nebraska Water Center), a part of the  
[Robert B. Daugherty Water for Food Global Institute at the University of Nebraska](http://Robert B. Daugherty Water for Food Global Institute at the University of Nebraska)  
e: [dsn1@unl.edu](mailto:dsn1@unl.edu) | p: 1 402.472.7539 | f: 1 402.472.9599 | c: 1 402.304.3748

Results Reported To:

Jessica Gray  
Eastern Research Group, Inc.  
14555 Avion Parkway Suite 200  
Chantilly, VA 20151  
(703) 633-1625  
[jessica.gray@erg.com](mailto:jessica.gray@erg.com)

**Project: ERG CSD GROUNDWATER  
SAMPLING**

Sampled By: Cheryl Burdett  
Received: 05/04/2018  
Received By: David Cassada  
Batch: **W18215**

**Protocol: 02\_03\_01**

Nitrate\_Nitrite Cd-Reduction EPA 353.2

Protocol Reference:

Seal Analytical Nitrate-N + Nitrite-N in  
Drinking and Surface Waters Domestic and  
Industrial Wastes.

### \*\*\*\* Results of Analysis \*\*\*\*

Lab ID	Sample ID	Collection Date	NO3+NO2-N (mg/L)	Analysis Date
18-2011	E10A	05/03/2018	0.427	05/09/2018
18-2013	E10B	05/03/2018	0.042	05/09/2018
18-2014	E8A	05/03/2018	28.6	05/09/2018
18-2015	E8B	05/03/2018	21.1	05/09/2018
18-2016	E9A	05/03/2018	20.8	05/09/2018
18-2017	E9B	05/03/2018	20.2	05/09/2018
18-2018	S01	05/03/2018	33.8	05/09/2018
18-2019	S02	05/03/2018	37.4	05/09/2018
18-2020	S04	05/03/2018	47.2	05/09/2018
18-2021	S05	05/03/2018	33.3	05/09/2018
18-2022	S03	05/03/2018	24.3	05/09/2018

# Water Sciences Laboratory

## Analytical Report



**Nebraska  
Water Center**

Daugherty Water for Food Global Institute

[Nebraska Water Center](http://Nebraska Water Center), a part of the  
[Robert B. Daugherty Water for Food Global Institute at the University of Nebraska](http://Robert B. Daugherty Water for Food Global Institute at the University of Nebraska)  
e: [dsnow1.unl.edu](mailto:dsnow1.unl.edu) | p: 1 402.472.7539 | f: 1 402.472.9599 | c: 1 402.304.3748

Results Reported To:

Jessica Gray  
Eastern Research Group, Inc.  
14555 Avion Parkway Suite 200  
Chantilly, VA 20151  
(703) 633-1625  
[jessica.gray@erg.com](mailto:jessica.gray@erg.com)

**Project: ERG CSD GROUNDWATER  
SAMPLING**  
Sampled By: Juan Rogers  
Received: 05/01/2018  
Received By: David Cassada  
Batch: **W18197**

**Protocol: 12\_02\_11\_01**

Nitrogen and Oxygen Isotopes using azide reduction and Trace gas Preconcentrator Method

Protocol Reference:

1. Tu, Y.; Fang, Y.; Liu, D.; Pan, Y. (2016) Modifications to the azide method for nitrate isotope analysis.. *Rapid Commun. Mass Sp.*, 30(10), 1213-1222.
2. McIlvin, Matthew R Altabet, Mark A (2005) Chemical conversion of nitrate and nitrite to nitrous oxide for nitrogen and oxygen isotopic analysis in freshwater and seawater. *Anal. Chem.*, 77, 5589-5595.

### \*\*\* Results of Analysis \*\*\*

Lab ID	Sample ID	Collection Date	δ <sup>15</sup> N-NO <sub>3</sub> (‰)	δ <sup>18</sup> O-NO <sub>3</sub> (‰)	Analysis Date
18-1775	A1B	04/30/2018	-4.94	+9.19	05/14/2018
18-1780	A3B	04/30/2018	-4.15	+12.5	05/14/2018
18-1781	A4A	04/30/2018	+4.76	+5.27	05/14/2018
18-1782	A4B	04/30/2018	+3.23	+0.699	05/14/2018
18-1784	B1B	04/30/2018	-3.89	+17.6	05/14/2018
18-1786	B2B	04/30/2018	-7.73	+2.04	05/14/2018
18-1787	B3A	04/30/2018	-4.83	-3.64	05/14/2018
18-1790	B4B	04/30/2018	+1.41	+2.66	05/14/2018
18-1791	C3A	04/30/2018	+3.88	+4.41	05/14/2018
18-1792	C3B	04/30/2018	+0.805	-1.22	05/14/2018
18-1794	C1B	04/30/2018	-11.4	+1.50	05/14/2018
18-1795	C2A	04/30/2018	+0.753	+2.30	05/14/2018
18-1796	C2B	04/30/2018	+3.22	+1.51	05/14/2018

$$\delta (\text{‰}) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000$$

Rstandard: D/H= 0.00015575, 18O/16=0.0020052; Standard Mean Ocean Water; 15N/14N=0.0036765 Atmospheric Nitrogen

# Water Sciences Laboratory

## Analytical Report



**Nebraska  
Water Center**

Daugherty Water for Food Global Institute

Nebraska Water Center, a part of the  
Robert B. Daugherty Water for Food Global Institute at the University of Nebraska  
e: [dsn1@unl.edu](mailto:dsn1@unl.edu) | p: 1 402.472.7539 | f: 1 402.472.9599 | c: 1 402.304.3748

Results Reported To:

Jessica Gray  
Eastern Research Group, Inc.  
14555 Avion Parkway Suite 200  
Chantilly, VA 20151  
(703) 633-1625  
jessica.gray@erg.com

**Project: ERG CSD GROUNDWATER  
SAMPLING**

Sampled By: Cheryl Burdett  
Received: 05/02/2018  
Received By: David Cassada  
Batch: **W18200**

**Protocol: 12\_02\_11\_01**

Nitrogen and Oxygen Isotopes using azide reduction and Trace gas Preconcentrator Method  
Protocol Reference:  
McIlvin, Matthew R Altabet, Mark A (2005)  
Chemical conversion of nitrate and nitrite to nitrous oxide for nitrogen and oxygen isotopic analysis in freshwater and seawater.  
*Anal. Chem.*, 77, 5589-5595.

\*\*\* Results of Analysis \*\*\*

Lab ID	Sample ID	Collection Date	δ <sup>15</sup> N-NO <sub>3</sub> (‰)	δ <sup>18</sup> O-NO <sub>3</sub> (‰)	Analysis Date
18-1813	D2A	05/01/2018	+17.1	+8.63	05/14/2018
18-1814	D2B	05/01/2018	+6.94	+0.877	05/14/2018
18-1815	D3A	05/01/2018	+1.07	+0.470	05/14/2018
18-1816	D3B	05/01/2018	+1.46	+1.57	05/14/2018
18-1817	D4A	05/01/2018	+1.33	-0.252	05/14/2018
18-1818	D4B	05/01/2018	+1.64	-1.72	05/14/2018
18-1819	C5AA	05/01/2018	+2.32	-1.91	05/14/2018
18-1820	C5AB	05/01/2018	+3.42	-0.803	05/14/2018
18-1821	C6A	05/01/2018	+2.40	-0.950	05/14/2018
18-1822	C6B	05/01/2018	+1.19	+0.788	06/06/2018
18-1823	C7A	05/01/2018	+0.446	-0.847	05/14/2018
18-1824	C7B	05/01/2018	+0.780	+2.17	05/14/2018
18-1825	C8A	05/01/2018	+1.99	+10.4	05/14/2018
18-1826	C8B	05/01/2018	+6.53	+1.34	05/14/2018
18-1827	C9A	05/01/2018	+1.81	+3.76	05/14/2018
18-1828	C9B	05/01/2018	-6.33	+4.59	05/14/2018
18-1829	C10A	05/01/2018	-1.46	+5.69	05/14/2018
18-1830	C10B	05/01/2018	+3.03	+5.99	05/14/2018
18-1832	C11B	05/01/2018	+6.10	+12.3	05/14/2018

$$\delta (\text{‰}) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000$$

Rstandard: D/H= 0.00015575, 18O/16=0.0020052; Standard Mean Ocean Water; 15N/14N=0.0036765 Atmospheric Nitrogen

# Water Sciences Laboratory

## Analytical Report



**Nebraska  
Water Center**

Daugherty Water for Food Global Institute

Nebraska Water Center, a part of the  
Robert B. Daugherty Water for Food Global Institute at the University of Nebraska  
e: [dsn1@unl.edu](mailto:dsn1@unl.edu) | p: 1 402.472.7539 | f: 1 402.472.9599 | c: 1 402.304.3748

Results Reported To:

Jessica Gray  
Eastern Research Group, Inc.  
14555 Avion Parkway Suite 200  
Chantilly, VA 20151  
(703) 633-1625  
jessica.gray@erg.com

**Project: ERG CSD GROUNDWATER  
SAMPLING**

Sampled By: Juan Rogers  
Received: 05/03/2018  
Received By: David Cassada  
Batch: **W18206**

**Protocol: 12\_02\_11\_01**

Nitrogen and Oxygen Isotopes using azide reduction and Trace gas Preconcentrator Method  
Protocol Reference:  
McIlvin, Matthew R Altabet, Mark A (2005)  
Chemical conversion of nitrate and nitrite to nitrous oxide for nitrogen and oxygen isotopic analysis in freshwater and seawater.  
*Anal. Chem.*, 77, 5589-5595.

### \*\*\* Results of Analysis \*\*\*

Lab ID	Sample ID	Collection Date	$\delta^{15}\text{N-NO}_3$ (‰)	$\delta^{18}\text{O-NO}_3$ (‰)	Analysis Date
18-1865	D5A	05/02/2018	-0.684	+1.22	05/23/2018
18-1867	D5B	05/02/2018	-8.93	-4.10	06/06/2018
18-1868	D6A	05/02/2018	-0.828	-2.95	05/23/2018
18-1869	D6B	05/02/2018	-2.70	-0.508	05/23/2018
18-1870	D7A	05/02/2018	-2.62	+1.53	05/23/2018
18-1871	D7B	05/02/2018	-4.99	-3.17	05/23/2018
18-1872	D8A	05/02/2018	+8.24	+4.86	06/06/2018
18-1873	D8B	05/02/2018	+0.232	+2.27	05/23/2018
18-1874	D9A	05/02/2018	-1.65	+1.23	05/23/2018
18-1875	D9B	05/02/2018	+2.72	+1.35	05/23/2018
18-1876	D10A	05/02/2018	-6.75	-3.01	06/06/2018
18-1877	D10B	05/02/2018	-1.72	+0.082	05/23/2018
18-1878	D11A	05/02/2018	+1.96	+5.26	05/23/2018
18-1879	D11B	05/02/2018	+5.06	+2.47	05/24/2018
18-1880	E1A	05/02/2018	+3.35	+6.17	05/24/2018
18-1881	E1B	05/02/2018	+6.84	+5.39	05/24/2018
18-1882	E2A	05/02/2018	+2.63	+6.36	05/24/2018
18-1883	E2B	05/02/2018	+1.89	-0.204	05/24/2018
18-1884	E3A	05/02/2018	-0.027	+1.74	05/24/2018
18-1885	E3B	05/02/2018	+0.684	+1.59	05/24/2018
18-1886	E4A	05/02/2018	+3.69	+5.12	05/24/2018
18-1887	E4B	05/02/2018	-0.840	+4.71	05/24/2018
18-1888	E5A	05/02/2018	+1.29	+4.91	05/24/2018
18-1889	E5B	05/02/2018	+2.59	+5.44	05/24/2018
18-1890	E6A	05/02/2018	-6.39	+3.20	05/24/2018
18-1891	E6B	05/02/2018	-2.48	+4.47	05/24/2018
18-1892	E7A	05/02/2018	+3.76	+7.91	05/24/2018
18-1893	E7B	05/02/2018	-4.23	-2.39	05/24/2018

$$\delta (\text{‰}) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000$$

Rstandard: D/H= 0.00015575, 18O/16=0.0020052; Standard Mean Ocean Water; 15N/14N=0.0036765 Atmospheric Nitrogen

# Water Sciences Laboratory

## Analytical Report



**Nebraska  
Water Center**

Daugherty Water for Food Global Institute

[Nebraska Water Center](http://Nebraska Water Center), a part of the  
[Robert B. Daugherty Water for Food Global Institute at the University of Nebraska](http://Robert B. Daugherty Water for Food Global Institute at the University of Nebraska)  
e: [dsn1@unl.edu](mailto:dsn1@unl.edu) | p: 1 402.472.7539 | f: 1 402.472.9599 | c: 1 402.304.3748

Results Reported To:

Jessica Gray  
Eastern Research Group, Inc.  
14555 Avion Parkway Suite 200  
Chantilly, VA 20151  
(703) 633-1625  
[jessica.gray@erg.com](mailto:jessica.gray@erg.com)

**Project: ERG CSD GROUNDWATER  
SAMPLING**

Sampled By: Cheryl Burdett  
Received: 05/04/2018  
Received By: David Cassada  
Batch: **W18216**

**Protocol: 12\_02\_11\_01**

Nitrogen and Oxygen Isotopes using azide reduction and Trace gas Preconcentrator Method  
Protocol Reference:  
McIlvin, Matthew R Altabet, Mark A (2005)  
Chemical conversion of nitrate and nitrite to nitrous oxide for nitrogen and oxygen isotopic analysis in freshwater and seawater.  
*Anal. Chem.*, 77, 5589-5595.

### \*\*\* Results of Analysis \*\*\*

Lab ID	Sample ID	Collection Date	δ <sup>15</sup> N-NO <sub>3</sub> (‰)	δ <sup>18</sup> O-NO <sub>3</sub> (‰)	Analysis Date
18-2011	E10A	05/03/2018	-4.15	+2.91	06/07/2018
18-2013	E10B	05/03/2018	+12.6	+35.9	05/30/2018
18-2014	E8A	05/03/2018	+11.5	+16.0	05/30/2018
18-2015	E8B	05/03/2018	+6.01	+9.17	05/30/2018
18-2016	E9A	05/03/2018	+29.6	+22.8	05/30/2018
18-2017	E9B	05/03/2018	+9.39	+13.2	05/30/2018
18-2018	S01	05/03/2018	+7.33	+9.15	05/30/2018
18-2019	S02	05/03/2018	+4.76	+8.57	05/30/2018
18-2020	S04	05/03/2018	+3.70	+5.16	05/30/2018
18-2021	S05	05/03/2018	+4.90	+9.20	05/30/2018
18-2022	S03	05/03/2018	+4.14	+6.25	05/30/2018

$$\delta (\text{‰}) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000$$

Rstandard: D/H= 0.00015575, 18O/16=0.0020052; Standard Mean Ocean Water; 15N/14N=0.0036765 Atmospheric Nitrogen