## FT 2100 Field Measurement of Nitrate Using Ultraviolet Optical Sensors

##### Use in conjunction with:

###### FT 1000 General Field Testing and Measurement

###### FT 1300 Field Measurement of Salinity

###### FT 1400 Field Measurement of Temperature

* FT 1900 Continuous Monitoring

###### FD 1000 Documentation Procedures

##### Introduction:

##### This SOP describes the required protocols for generating data using optical nitrate probes to measure nitrate concentrations in natural waters under field conditions. This method is a direct spectrophotometric determination of nitrate concentration, where the magnitude of the absorbance at a peak wavelength of 220 nanometers (nm) is proportional to the concentrations of nitrate ions in solution.

##### For more information about probe selection, quality control measures, and data management, including data correction methods, refer to USGS TM1-D5, Optical Techniques for the Determination of Nitrate in Environmental Waters: Guidelines for Instrument Selection, Operation, Deployment, Maintenance, Quality Assurance, and Data Reporting.

##### Data generated by optical nitrate probes will only be used for screening and research purposes. If an alternative methods package has been approved by DEP per 62-160.220, F.A.C., additional uses may be allowed as described in the approval.

##### Equipment and Supplies

##### Field Instrument: Field-deployable ultraviolet nitrate sensor equipped with a spectrometer/photometer with an ultraviolet (UV) lamp that measures wavelengths including 220 nm with pathlengths from 2-10 mm (recommended for fresh and coastal waters). Longer pathlengths are preferred to detect low nitrate concentrations, but interferences can also be greater at longer pathlengths. Instruments must have temperature-salinity correction capabilities if used in predominantly marine waters. Instruments that use the full spectrum or multiple wavelengths within the spectrum (190-400 nm) tend to be more accurate in the presence of interfering substances.

##### Standards: Purchased or laboratory-prepared standard solutions with nitrate values that bracket the expected sample range. Follow instructions in Standard Method 4500-NO3-B to prepare standards. Do not reuse standards for initial calibrations.

##### Interferences

##### The presence of inorganic constituents, such as bromide, hydrogen sulfide, and nitrite, as well as colored dissolved organic matter (indicated by color) and turbidity (particulates), reduces the transmittance of light through a sample and can result in an overestimate of nitrate if not accounted for. Users should conduct tests in the matrix to be sampled to determine effects of these constituents.

##### Estuarine and coastal settings: Typical sea water concentrations of bromide (65 mg/L) at a salinity of 35 PSU can have a strong effect on calculated nitrate concentrations. Bromide is also temperature dependent.

##### Concentrations of bromide, nitrite, sulfide, iron, and iodine in freshwater are typically low enough to minimize any interference on nitrate measurements.

##### Scattering of light by suspended particles in the optical path (indicated by turbidity or TSS) reduces the light reaching the detector and can result in an overestimate of sample absorbance.

##### Quality Control Activities

##### General Concerns

##### **Follow the instrument manufacturer's instructions for the details of operating the instrument.** Conduct maintenance activities per manufacturer’s recommendations.

If corrections for temperature and salinity require the user to input those measurements, temperature and salinity must be calibrated and verified per FT 1400 and FT 1300, respectively.

The quality control measures described in this section provide information regarding potential uses of data generated with UV optical nitrate sensors. Potential uses of sensor data cannot be determined without quality control data.

Initial Calibration: This sonde is factory-calibrated. The user can reset the baseline to zero if blank checks do not meet acceptance criteria. For best results, conduct such resets in a temperature-controlled environment.

##### Initial Method Precision and Detection Limit Evaluations:

##### Before collecting field data, evaluate and document the precision and accuracy of the meter across the range of concentrations that will be measured in the field, and establish a method detection limit (MDL) and practical quantitation limit (PQL). Manufacturer specifications for the sensor may serve as a starting point for these evaluations.

##### To determine precision and accuracy, measure 3-5 standard nitrate solutions across the range of expected concentrations to be measured in the field, including near the expected practical quantitation limit (PQL). Conduct at least seven measurements at each concentration and calculate the accuracy and precision at each concentration. Plot the results to determine if the instrument response is linear.

##### Establish a Method Detection Limit (MDL) following procedures outlined in *Definition and Procedure for the Determination of the Method Detection Limit, Revision 1.11*. This procedure includes measurement of at least seven replicates of blanks and standards, then calculating the MDL based on the results of the blank measurements and the standard deviation of the standard measurements. These measurements can be taken on the same aliquot of standard solution over a period of time. After the initial MDL establishment, ongoing blank and standard measurements are used to evaluate the continue applicability of the MDL.

##### Establish a PQL. The PQL represents the concentration at which the method has been demonstrated to achieve the target range of precision and accuracy for the method. Initial evaluation of standards in subsection 4.3.2 may be used for this purpose. For measurement of nitrate, percent recovery (accuracy of standards measurements) should be 90-110% and relative standard deviation of replicate standard measurements should be ≤20%.

##### Use calibration verifications in subsection 4.4 to track any changes in precision, accuracy, MDL and PQL.

##### Calibration Verifications:

##### Conduct in-air and analyte-free water checks per manufacturer’s instructions. Follow manufacturer’s recommendations to apply a baseline correction if needed, based on diagnostic data from the instrument.

##### Follow the verification activities specified in FT 1000, section 2.2, including requirements for chronological and quantitative bracketing.

##### Analyte-free water shall not be used as a verification standard.

##### Initial calibration verifications must be conducted after any baseline correction.

##### Successful verification of a standard near the PQL will satisfy the requirement for a quantitative bracket for measurements between the MDL and PQL.

##### Conduct continuing calibration verifications with standards at a frequency determined based on the instrument’s performance or at least once every three months.

##### Acceptance criteria – Expected accuracy varies based upon the meter model and pathlength. Accuracy needed will vary depending on project objectives. For most meters, the following minimum acceptance criteria apply:

##### For sondes with 5 mm path length, analyte-free water check and standards verification results must be within 10% or 0.06 mg/L of the expected value, whichever is greater.

##### For sondes with 10 mm path length, analyte-free water check and standards verification results must be within 10% or 0.03 mg/L of the expected value, whichever is greater.

##### Estimates of Bias: One of the following approaches shall be used to estimate bias due to matrix interference.

##### Comparison Lab Analysis: Conduct side-by-side grab samples to compare the probe results with results generated by a certified lab using accepted lab methods. If the relationship between probe and grab sample results indicates a consistent bias, probe results may be corrected. At least 20 paired measurements are needed for bias correction.

##### Matrix Spikes: Conduct matrix spikes by adding a known amount of reagent-grade standard nitrate solution to a sample of ambient water and compare the matrix spike result with the ambient result plus the spike concentration. Results can indicate whether there is bias in the probe measurements. Matrix spike results can also be used to evaluate precision expected in sample matrix.

##### Measuring Nitrate of Samples:

##### Follow manufacturer’s instructions for sample measurement.

##### If color or turbidity of the ambient water exceed levels expected to interfere with the probe’s optical sensor, either do not conduct measurements or qualify measurements as estimated. Such measurements may be used to evaluate the effects of color or turbidity on nitrate probe measurements. Consult the meter manual for stated tolerances or correction capabilities.

##### Follow FT 1920 for unattended sonde deployment activities.

##### Report results below the MDL or PQL with appropriate qualifier codes.

##### Preventative Maintenance: Refer to FT 1000, section 3.

##### Update reference spectrum per manufacturer’s instructions if sonde performance does not meet acceptance criteria.

##### This update should be done in a controlled environment and not in the field.

##### If the sonde performance still does not meet acceptance criteria after updating the reference spectrum, remove from use. Send it to the manufacturer for repair or factory calibration.

##### Refer to sensor diagnostic tests provided for the meter by the manufacturer to determine when sensor readings might be compromised by instrument or site conditions.

##### Documentation

##### Standard and Reagent Documentation: Document information about standards and reagents used for calibrations, verifications and sample measurements.

##### Note the date of receipt, the expiration date and the date of first use for all standards and reagents.

##### Document acceptable verification of any standard used after its expiration date.

##### Record the concentration or other value for the standard in the appropriate measurement units.

##### Note vendor catalog number and description for preformulated solutions as well as for neat liquids and powdered standards.

##### Retain vendor assay specifications for standards as part of the calibration record.

##### Record the grade of standard or reagent used.

##### When formulated in-house, document all calculations used to formulate calibration standards. Record the date of preparation for all in house formulations.

##### Describe or cite the procedure(s) used to prepare any standards in-house (DEP SOP or internal SOP).

##### Field Instrument Initial Quality Control Documentation

##### Document and retain initial evaluations of precision and accuracy using standards and matrix spikes.

##### Document and retain MDL and PQL determination studies, including any spike concentrations, replicate results, and calculations.

##### Document results of side-by-side grab samples, including laboratory certification, quality control sample results, and any data qualifiers.

##### Field Instrument Calibration Documentation: Document acceptable calibration and calibration verification for each instrument unit and field test or analysis, linking this record with affected sample measurements.

##### Retain vendor certifications of all factory-calibrated instrumentation.

##### Designate the identity of specific instrumentation in the documentation with a unique description or code for each instrument unit used. Record manufacturer name, model number, and identifying number such as a serial number for each instrument unit.

##### Record the time and date of all initial calibrations and all calibration verifications.

##### Record result to the level of resolution stated by the conductivity sensor manufacturer. (value in appropriate measurement units)

##### Record the name of the analyst(s) performing the calibration.

##### Document the specific standards used to calibrate or verify the instrument or field test with the following information:

##### Type of standard or standard name (e.g., conductivity standard)

##### Value of standard, including correct units (e.g., conductivity = 100 µmhos/cm)

##### Link to information recorded according to section 5.1 above

##### Retain manufacturers’ instrument specifications.

##### Document whether successful initial calibration occurred.

##### Document whether each calibration verification passed or failed.

##### Document any corrective actions taken to correct instrument performance according to records requirements of FD 3000.

##### Document date and time of any corrective action.

##### Note any incidence of discontinuation of use of the instrument due to calibration failure.

##### Describe or cite the specific calibration or verification procedure performed (DEP SOP or internal SOP).

##### Follow FT 1920 for documentation of unattended sonde deployment activities.

##### Record all field-testing measurement data, to include the following:

###### Project name

###### Date and time of measurement or test (including time zone, if applicable)

###### Source and location of the measurement or test sample (e.g., monitoring well identification number, outfall number, station number or other description)

* + Latitude and longitude of sampling source location (if required)

###### Analyte or parameter measured

###### Measurement or test sample value result, recorded to the level of resolution stated by the sensor manufacturer (value in appropriate measurement units)

###### Reporting units

* + “J” qualifier code and explanatory comment if the sample measurement is not chronologically or quantitatively bracketed by acceptable calibrations and verifications per requirements in FT 1000, section 2.2
  + Initials or name of analyst performing the measurement

###### Unique identification of the specific instrument(s) used for the test(s)