


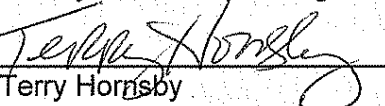
Title: TOTAL KJELDAHL NITROGEN
Automated Colorimetry using Lachat Autoanalyzer

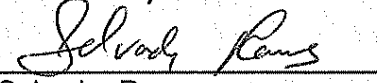
Method: EPA 351.2


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1.0 Scope and Application

1.1 Analytes, Matrix(s), and Reporting Limits

This automated method covers the determination of Total Kjeldahl nitrogen in drinking, surface and saline waters, soils, domestic and industrial wastes. The applicable range for this method is 0.25 – 25.0 mg/L TKN.

The routine target analyte lists, current Reporting Limit (RL), Method Detection Limit (MDL) and precision and accuracy limits associated with this procedure are given in the Method Limit Group (MLGs) in LIMS.

On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 20 in the Quality Assurance Manual.

If for any reason a part of this SOP cannot be followed, seek the guidance of the Department Manager or the Laboratory Technical Director. All abnormalities must be noted on the data or the benchsheet, in the Non-conformance database in LIMS. See the corrective action procedures and Appendix 4 in the QA Manual.

2.0 Summary of Method

The sample is heated in the presence of sulfuric acid, potassium sulfate, and copper sulfate. The residue is cooled, diluted to 20mL with DI water and analyzed for ammonia. The digested sample may also be used for Total Phosphorus determination.

The digested sample goes through an in-line neutralization process that converts the ammonium cation to ammonia. It is then heated with salicylate and hypochlorite to produce a blue color, which is proportional to the ammonia concentration. The color is then intensified by adding sodium nitroprusside. The potassium tartrate prevents precipitation of calcium and magnesium.

3.0 Definitions

- 3.1 Refer to SOP TP-AN-005: Definitions, Terms, and Acronyms and to the current revision of the Tampa's Quality Assurance Manual (TP-QAM) for a complete listing of applicable definitions.
- 3.2 Total Kjeldahl Nitrogen- The sum of free-ammonia and organic nitrogen compounds that are converted to ammonium sulfate, under the conditions of the digestion described.

4.0 Interferences

- 4.1 Samples must not consume more than 10% of the sulfuric acid during the digestion.
- 4.2 High nitrate concentrations (10X or more than the TKN level) result in low TKN values. If interference is suspected, samples should be diluted and reanalyzed.
- 4.3 Digests must be free of turbidity. Some boiling chips have been shown to crumble upon vigorous vortexing.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

Sodium Nitroferricyanide will generate Hyrdogen Cyanide (HCN) gas if combined with strong acids. Inhalation of CN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Sodium Hydroxide	Corrosive	2 Mg/M3 Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sodium Nitroprusside/ Nitroferricyanide	Poison	5 mg/m ³ as HCN gas	This material may cause irritation if it comes into the contact with the skin. The materials will give off HCN gas if combined with strong acids. Inhalation of HCN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death.

Sulfuric Acid	Corrosive Oxidizer Dehydrator Carcinogen	1 Mg/M3 TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Cupric(II) Sulfate Pentahydrate	Irritant	0.1 Mg/M3 Ceiling	Causes irritation to the respiratory tract. Inhalation symptoms include coughing, sore throat, and shortness of breath. Contact with skin causes irritation and itching. Eye contact may cause irritation. If ingested, may cause burning pain in digestive tract, also headaches and cold sweats. Kidney/liver damage. Fatalities have occurred as a result of ingesting gram quantities.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			
2 – Always add acid to water to prevent violent reactions.			

6.0 Equipment and Supplies

- 6.1 Analytical balance, capable of accuracy to the nearest 0.001g
- 6.2 Eppendorf Pipettes, varying volumes
- 6.3 Class "A" Volumetric Flasks, varying volumes
- 6.4 Syringes, 10cc
- 6.5 Filters, 45-um
- 6.6 Volumetric flasks: 1000-, 100-, 10-mL
- 6.7 Pipettes: 1.0-, 0.5-, 0.1-, 0.05, 10-mL
- 6.8 Disposable plastic cups or other suitable containers
- 6.9 Block digester and digestion tubes.
- 6.10 Boiling stones or teflon chips
- 6.11 Automated continuous flow analysis equipment designed (Lachat Model 8000 FIA) to deliver and react sample and reagents in the required order and ratios.
 - 6.11.1 Sampling device (auto-sampler)
 - 6.11.2 Multi-channel pump
 - 6.11.3 Reaction unit or manifold
 - 6.11.4 Colorimetric detector
 - 6.11.5 Data recording device, Lachat data system, Omnion.

7.0 Reagents and Standards

- 7.1 All reagents and standards are to be labeled with their unique TALS ID, including name of the material, concentration, date prepared/received, expiration date, and analyst name, according to SOP TP-AN-004, *Standard Material and Reagent Traceability*. Certificates of analysis or purity must be received with all neat compounds and stock solutions and scanned into TALS.
- 7.2 Salicylate Nitroprusside solution
- 7.2.1 Weigh 150g sodium salicylate and 1g sodium nitroprusside and dissolve in about 800mL DI water. Dilute to volume and store in an amber bottle. Store in a dark bottle and **prepare fresh monthly, or when the solution develops a blue to green coloration.**
- 7.3 Sulfuric Acid, concentrated H_2SO_4
- 7.4 Carrier
- 7.4.1 Dilute 1mL Ultrex H_2SO_4 into 500mL. Prepare fresh monthly.
- 7.5 Buffer
- 7.5.1 Dissolve 50g potassium tartrate, 50g sodium hydroxide, and 26.8g sodium phosphate dibasic heptahydrate ($\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$) in approximately 900ml DI water in a 1L flask. Mix until dissolved. Boil for 10 minutes. Cool to room temperature and transfer to a 1 L volumetric flask. Dilute to the mark and invert to mix. **NOTE:** To reduce the possibility of the potassium tartrate being contaminated it is recommended that the tartrate buffer is boiled for 10 minutes.
- CAUTION!!!:** Heat will be evolved as the sodium hydroxide or sulfuric acid mixes with water. These solutions will cause skin burns and destroy unprotected clothing.
- 7.6 Hypochlorite Solution
- 7.6.1 Dilute 15mL 6.0% sodium hypochlorite in a 250mL volumetric flask with DI water. Invert to mix. **Prepare fresh daily.**
- 7.7 Digestion reagent:
- 7.7.1 Dissolve 134g potassium sulfate (K_2SO_4) and 7.3g copper sulfate (CuSO_4) in a 1L volumetric flask with DI water. Carefully add 134mL concentrated sulfuric acid (H_2SO_4). Keep tightly sealed when not in use to decrease the possibility of contamination by ambient ammonia. **Prepare fresh monthly.**
- CAUTION:** Heat will be evolved as the sulfuric acid mixes with water. These solutions will cause skin burns and destroy unprotected clothing.
- 7.8 Diluent Solution for Non-digested Standards and Over-range Samples
- 7.8.1 Dilute 400mL of the digestion solution into a 1L volumetric flask. Bring to volume with DI water. Keep tightly sealed when not in use to decrease the

possibility of contamination by ambient ammonia. **Prepare fresh monthly**

- 7.9 Ammonia stock standard (1000mg/L): commercially purchased
- 7.10 Secondary stock standard can be purchased at a concentration of 1,000mg/L. Secondary stock standard is used for the ICV, LCS, MS and MSD.
- 7.11 Matrix Spike/Matrix Spike Duplicate- MS/MSD (3.0 mg/L)
- 7.11.1 Dilute 60µL of 1000mg/L to 20mL of sample.
- 7.12 Initial Calibration Verification- ICV (2.00mg/L)
- 7.12.1 Dilute 200µL of 1000mg/L to 100mL with DI water.
- 7.13 Laboratory Control Sample- LCS (3.0mg/L)
- 7.13.1 Dilute 300µL of 1000mg/L to 100mL of DI water.
- 7.14 Continuing Calibration Verification- CCV (3.0mg/L)
- 7.14.1 Dilute 300µL of 1000mg/L to 100mL with DI water.
- 7.15 Calibration Standards

Volume (µL) of Stock Std. (1000mg/L)	Final Volume (mL) with DI Water	Conc. Cal Std (mg/L)
1000	100	10
500	100	5.0
200	100	2.0
100	100	1.0
50	100	0.50
20	100	0.20
0	100	0

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time ¹	Reference
Waters	HDPE/GLASS	500mL	Cool $\leq 6^{\circ}\text{C}$	28 Days	40 CFR Part 136.3
Soils	HDPE/GLASS	50g	Cool $\leq 6^{\circ}\text{C}$	28 Days	N/A

¹ Inclusive of digestion and analysis.

9.0 **Quality Control**

Please refer to Appendix 4 of the laboratory QAM for additional information relating to the QC associated with this method.

9.1 **Sample QC**

- 9.1.1 Each analytical batch may contain up to 20 environmental samples. Every 20 or fewer samples, a Method Blank (MB) and a Laboratory Control Standard (LCS) is required. A Matrix Spike (MS) and a Matrix Spike Duplicate (MSD) is required every 10 or fewer samples.

Quality Controls	Frequency	Control Limit
Method Blank (MB)	1 in 20 or fewer samples	< MDL
Laboratory Control Sample (LCS)	1 in 20 or fewer samples	90-110%
Matrix Spike (MS) ¹	1 in 10 or fewer samples	90-110%
MS Duplicate (MSD) ¹	1 in 10 or fewer samples	90-110%

¹ The sample selection for MS/MSD are randomly selected, unless specifically requested by a client.

9.2 **Instrument QC**

- 9.2.1 Before any instrument is used as a measurement device, the instrument response to known reference materials must be determined. The manner in which various instruments are calibrated depends on the particular type of instrument and its intended use. All sample measurements must be made within the calibration range of the instrument.
- 9.2.2 A minimum of two blanks and one mid-range standard should be carried through the digestion when the standards are prepared in the digest mix.
- 9.2.3 A calibration curve is performed daily, followed by an Initial Calibration Verification (ICV) and Initial Calibration Blank (ICB).
- 9.2.4 A Continuing Calibration Verification (CCV) and Calibration Verification Blank (CCB) are analyzed every 10 or fewer samples.

Step	Standards	Type	Control Limit	Frequency
Initial Cal	10ppm, 5.0ppm, 2.0ppm, 1.0ppm, 0.50ppm, 0.20ppm, 0ppm	Linear cal	≥0.995	Daily
ICV	2.0ppm	Linear cal	90-110%	After calibration
ICB	0ppm	Linear cal	<MDL	After ICV
CCV	3.0ppm	Linear cal	90-110%	Every 10 samples
CCB	0ppm	Linear cal	<MDL	After CCV
LCS	3.0ppm	Linear cal	90-110%	Every 20 samples
MS/MSD	3.0ppm	Linear cal	90-110%	Every 10 samples

NOTE: ICV, LCS, and MS/MSD are required to be from a different source standard than the calibration and CCV standards.

- 9.2.5 The accuracy (% Recovery) and precision (% RPD) for the lab spike and matrix spikes should be checked against the limits listed in the method. The lab spikes must meet these accuracy and precision limits. If limits are not met, investigate the cause and either reanalyze or re-extract. The

matrix spike recoveries are used to evaluate the matrix effect on the analysis and are advisory.

9.2.6 Linear Calibration Range

9.2.6.1 After the calibration curve has been analyzed, the low, mid, and high points are analyzed as samples. They are then compared to the actual values, and must agree within 10%. If they are not within the 10%, the calibration curve must be analyzed again, followed by another linear calibration range set. This must be performed initially, and every six months thereafter. Since the initial calibration is performed almost every analytical run, and the initial calibration satisfies the requirements for the LCR, the ICAL will be considered to have fulfilled the LCR requirement.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 Remove the samples from the storage refrigerator and allow the samples to come to room temperature prior to analysis.

10.1.2 Allow 15 to 20 minutes for the heating unit to warm up to 180°C.

10.1.3 Prepare the calibration standards and spiking solution while the samples are equilibrating. **Both** standards and samples are carried through the digestion procedure.

10.1.4 Aqueous Samples

10.1.4.1 To a 20mL sample, add 5mL of digestion solution and mix. Alternatively, to 25mL sample, add 10mL of digestion solution, and so on.

10.1.4.2 Add 3-4 boiling chips, or 2-4 Hengar granules, to each tube. **Note:** Too many boiling chips may cause sample to boil over!

10.1.4.3 Place tubes in the preheated block digester for 1hr at 180°C. Add "cold fingers" to the top of the digestion tubes after the water has boiled off.

10.1.4.4 Raise the temperature to 380°C and allow it to come to temperature. When temperature has reached temperature, digest for a minimum of 30 minutes. This time does NOT include the ramp time for the block temperature to come up to 380°C. The typical ramp time is 50 – 60 minutes.

10.1.4.5 380°C **MUST** be maintained for a minimum of 30 minutes.

10.1.5 Solid Samples

10.1.5.1 Thoroughly mix 0.1g of soil and transfer sample into a labeled digestion tube. Record the weight of the samples to the nearest 0.01g. Add 20mL of reagent water to tubes containing soil or sludge samples, rinsing down the sides of the tubes to ensure that all of the sediment is transferred to the bottom of the tube.

10.1.5.2 Prepare a method blank by adding 20mL of reagent water with 0.1g sand to a digestion tube. Add 3-4 boiling stones or teflon chips.

Note: Too many boiling chips may cause sample to boil over!

10.1.5.3 Prepare a LCS by adding 300µL of 1000mg/L standard to 100mL of reagent water in a 100mL volumetric flask. Add 20mL of the LCS just made to 0.1g sand. Add 3-4 boiling stones or teflon chips.

10.1.5.4 Weigh two additional 0.1g aliquots of one of the samples for the MS and MSD. Add 60µL of the 1000mg/L stock and 20mL of sample.

10.1.5.5 Add 5.0mL of digestion solution to each tube giving a final volume of 25mL. Place several boiling chips, or Hengar boiling stones, into each tube.

10.1.5.6 Place tubes in the preheated block digester for 1hr at 180°C. Add "cold fingers" to the top of the digestion tubes after the water has boiled off.

10.1.5.7 Raise the temperature to 380°C and allow it to come to temperature. When temperature has reached temperature, digest for a minimum of 30 minutes. This time does NOT include the ramp time for the block temperature to come up to 380°C. The typical ramp time is 50 – 60 minutes.

10.1.5.8 380°C **MUST** be maintained for a minimum of 30 minutes.

10.1.6 Remove the sample tubes from the block and cool for about three minutes. If sample is not clear at this point, filter using 0.45µm syringe filter. Soil samples always needs filtration.

10.1.7 Dilute to original volume of 20mL (or 25mL, etc) with DI water to each tube and vortex to mix. If additional dilution is required beyond the sample's original volume, use the Diluent Solution for Non-digested Samples Over-range Samples.

10.1.8 Pour the solution in the digestion tube into a labeled container. If samples are not run immediately, they should be covered tightly. The samples are now ready for analysis.

10.1.9 Digestates must be analyzed within 48 hours.

10.2 Calibration

10.2.1 Before any instrument is used as a measurement device, the instrument response to known reference materials must be determined. The manner in which various instruments are calibrated depends on the particular type of instrument and its intended use. All sample measurements must be made within the calibration range of the instrument.

10.2.2 Prepare reagents, standards and matrix spikes.

10.2.3 Make sure that the analysis manifold is set up properly and that the data system parameters are configured correctly.

10.2.4 Secure the pump platens in place and turn on the auto-sampler and the peristaltic pump. Feed wash water through sample lines.

10.2.5 Click on the Omnicion 3.0 icon to start the data system software.

10.2.6 When the auto-sampler completes its system check, turn on the power to the instrument.

10.2.7 Switch the reagent lines to the reagents for the chemistry being run and allow the system to equilibrate until a stable baseline is present on the software display.

10.2.8 Aliquot the standards for the analysis being run and put them in the proper places in the auto-sampler tray. Place appropriate standards in the sampler in order of decreasing concentration.

10.2.9 Open the appropriate sequence template based on the analyte of interest and quantity of samples.

10.2.10 Calibrate the instrument by injecting the standards. The data system software will produce a calibration curve that correlates the peak area for each standard with its concentration.

10.2.11 Check the correlation coefficient for the curve as soon as the injection of the standards has finished. Calibration curve correlation coefficient (r) must be greater than 0.995, or $r^2 > 0.99$, or re-calibrate. If the value is acceptable, continue with sample analysis.

10.2.12 Immediately, after the calibration has been established, it must be verified by the analysis of a suitable ICV. Following the ICV, run an initial calibration blank (ICB) to verify that there is no system contamination and that the curve is not skewed. If the ICV recovery exceeds $\pm 10\%$ of the true value, the analysis should be terminated and the instrument re-calibrated. The new calibration must be verified before continuing analysis. A continuing calibration verification (CCV, non-distilled) should be analyzed every 10 samples and at the end of the batch. The CCV must be within

10% of the true value or the problem must be identified, corrected, and all affected samples re-analyzed.

10.3 Sample Analysis

- 10.3.1 Enter the sample numbers and required quality control samples into the sequence template (see below for a sequence example). Make sure to properly bracket every 10 samples with a CCV and a CCB. Save the completed sequence template under its own unique filename. The sequence is ready to be started but can be edited if needed.

Sequence Example
10ppm, 5ppm, 2.0ppm, 1.0ppm, 0.5ppm, 0.20ppm, 0ppm
Initial Calibration Verification (ICV)
Initial Calibration Blank (ICB)
MB
LCS
10 samples + MS/MSD
Continuing Calibration Verification (CCV)
Continuing Calibration Blank (CCB)
10 samples + MS/MSD
Continuing Calibration Verification (CCV)
Continuing Calibration Blank (CCB)

- 10.3.2 Aliquot the samples, the check standards, and the matrix spikes, and place them in appropriate positions in the auto-sampler rack.
- 10.3.3 Start the sequence. Monitor the ICV and ICB to insure that they meet acceptable criteria. If either one fails, the instrument must be re-calibrated. If the failure is repeated after re-calibration, check the system for contamination and/or remake the standards from fresh stocks before trying again.
- 10.3.4 Let the sequence run until all the samples have been analyzed.
- 10.3.5 Check the CCV and CCB after each set of ten samples while the run is in progress or at its completion. If either the CCV or CCB does not meet acceptance criteria, the block of ten samples before and after the failing check standards must be reanalyzed.
- 10.3.6 If the concentration of a sample exceeds the value of the highest standard, the sample must be diluted to reduce the value so that it falls within the calibration range (preferably a value in the mid-range of the curve). The dilution must not result in a value that is below the lowest curve standard. The dilution factor is calculated by dividing the final volume of the dilution by the amount of sample actually used.
- 10.3.7 Additional samples or undiluted samples may be added to the run sequence if the run is not complete. Make sure to bracket the additional samples with a CCV and CCB and to save the modified sequence table.

10.3.8 When the data is ready, it may be uploaded electronically or manually entered into TALS at the analyst's discretion.

10.3.9 The software will determine the concentration of each sample from the regression curve. If the concentration of any sample exceeds the highest concentration in the calibration curve, reanalyze a more dilute aliquot of that sample. **Do not dilute digests with DI water, use diluent solution.**

10.3.10 Preventative Maintenance

10.3.10.1 The pump tubes on the manifold and peristaltic pump should be monitored daily for wear and stretching. If tubes show excessive wear due to the frequency of use, they should be replaced immediately. Otherwise, the tubes should be replaced monthly.

10.3.10.2 The valve tubing and flares should be monitored daily for leaks and should be replaced if a leak is detected. Otherwise, replace the tubing and flares annually.

10.3.10.3 Negative peaks in the blanks or low-level standards are indicative of carrier contamination. If these dips in the baseline are seen in the chromatograms, replace the contaminated carrier with fresh (make sure to thoroughly clean and rinse the container before refilling it with fresh carrier).

11.0 Calculations / Data Reduction

11.1 Accuracy

$$\text{ICV / CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

$$\text{MS \% Recovery} = \frac{(\text{spiked sample}) - (\text{unspiked sample})}{\text{spiked concentration}} \times 100$$

11.2 Precision (RPD)

$$\text{Matrix Duplicate (MD)} = \frac{|\text{orig. sample value} - \text{dup. sample value}|}{[(\text{orig. sample value} + \text{dup. sample value})/2]} \times 100$$

$$11.3 \quad \text{Concentration} = \text{mg/kg or L} = \frac{C \times V \times D}{W}$$

Where:

C = sample concentration in extract (ppm)

V = Volume of extract (mL)

D = Dilution Factor

W = Weight/Volume of sample aliquot extracted (grams or mLs)

NOTE: All dry weight corrections are made in LIMS at the time the final report is prepared.

12.0 Method Performance

- 12.1 Method Detection Limit Study (MDL) - The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined accordance with 40 CFR, Chapter 1, Part 136, Appendix B and with reference to the laboratory's MDL procedure in Section 20 of the Quality Assurance Manual. An MDL reflects a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.
- 12.2 Demonstration of Capabilities - Each analyst must perform an Initial Demonstration of Capability (IDOC) in accordance with the procedure outlined in Section 20 of the Quality Assurance Manual. The evaluation of the IDOC data should be completed prior to the analysis of samples. A Continuing Demonstration of Capability (CDOC) must be performed annually or whenever there is a significant change in the instrument parameters or the associated method.
- 12.3 Training Requirements - Each analyst's required employee training (such as orientation to the laboratory's policies and procedures and in-house method training) are outlined in Section 15 of the Quality Assurance Manual.

13.0 Data Assessment And Acceptance Criteria For Quality Control Measures

- 13.1 The following represent data assessment for samples and acceptance criteria for QC measures. Corrective actions for any failure in QC measures are shown in Section 13.
- 13.2 QC sample acceptance criteria
 - 13.2.1 **Method Blank.** No target analytes may be present in the method blank above the reporting limit. RL > 0.2 mg/L
 - 13.2.2 **Laboratory Control Sample (LCS).** 90 - 110% The analyte must be within established control limits for accuracy (%Recovery) and precision (RPD). Exceptions are allowed only with QA and project management approval.
 - 13.2.3 **Matrix Spike/Matrix Spike Duplicate (MS/MSD).** 90 - 110% The analyte should be within established control limits for accuracy (%Recovery) and precision (%RPD). Deviations from this may be the results of matrix effects, which are confirmed by passing LCS/LCSD. No specific corrective actions are required in the evaluation of the MS/MSD results provided that the batch LCS is in control. Analysts should use sound judgment in accepting MS/MSD results that are not within control limits, especially if the LCS results are borderline. Check with supervisor, Lab Manager and or Project Manager on reporting out of control limits QC.

13.3 Sample result evaluation

13.3.1 Dilutions: If the response for any compound exceeds the working range of the analytical system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit in the upper half of the calibration range. The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

14.0 Corrective Actions For Out Of Control Data

14.1 Method Blank. The samples in the batch associated to the defective method blank are evaluated. If the analyte found in the method blank is confirmed to not be present in one or more of the associated samples at any level, the contamination did not affect those samples. This represents a non-impact situation and no specific corrective action is taken. A nonconformance memo is written to notify project management of the situation for evaluation against project requirements. If the analyte found in the method blank is confirmed to be present in one or more of the associated samples, the concentrations are compared. If the concentration in the method blank exceeded 10% of concentration found in one or more samples, the prescribed corrective action is to re-analyze all affected samples. If the concentration in the method blank was less than 10% of the concentration found in one or more samples, the sample can be reported by qualifying the affected analytes. A nonconformance memo (NCM) is written and discussed with the laboratory supervisor and Project Management for evaluation against project requirements.

14.2 Laboratory control sample. If the analyte is out of control for accuracy (90 - 110%), the associated samples are evaluated. If the recovery is biased high and the associated samples have no positive results for that analyte, a non-impact situation ensues. A nonconformance memo (NCM) is written to notify project management of the situation for evaluation against project requirements. If the recovery is biased high and the associated samples have positive results for that analyte, the prescribed corrective action is reanalysis of the affected sample(s). If the recovery is biased low and the samples have no positive results for that analyte, the prescribed corrective action is reanalysis of the affected sample(s). If the analyte is out of control for precision (RPD), the associated samples are evaluated. All decisions about corrective action(s) are made in consultation with the project manager. If there are no positive results in one or more samples, a non-impact situation ensues for those samples. A nonconformance memo is written to notify project management of the situation for evaluation against project requirements.

14.2.1 If there are positive results for one or more analytes, the likelihood of poor reproducibility increases and corrective action must be evaluated. A nonconformance memo is written and discussed with the laboratory supervisor and Project Management of the situation for a project decision on whether the affected sample(s) should be reanalyzed.

15.0 Contingencies For Handling Out-Of-Control Or Unacceptable Data

- 15.1 **Method blanks.** If there is insufficient sample to perform re-analysis; the analyst must notify the project manager for consultation with the client. In this situation, all associated samples are flagged with a "I" qualifier and appropriate comments in the narrative.
- 15.2 **LCS/LCSD.** If the batch is not reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. Acceptable matrix spike recoveries are not sufficient justification to preclude re-extraction of the batch. If reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation. An NCM will have to be filled out stating this problem and or a solution.
- 15.3 **Insufficient sample.** If there is insufficient sample to repeat the analysis, the situation is discussed with the project manager for consultation with the client and documentation is provided in an NCM.
- 15.4 **Procedural Variation** One time procedural variations are allowed only if deemed necessary in the professional judgment of the analyst to accommodate variation in sample matrix, radioactivity chemistry, sample size, or other parameters. Any variation shall be completely documented using a Nonconformance Memo and approved by the Supervisor and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

16.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

17.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Tampa's current revision of SOP TP-HAZ-001 *Waste Management*). The following waste streams are produced when this method is carried out.

18.0 References / Cross-References

- 18.1 *Standard Methods for the Examination of Water and Wastewater*, 21st Edition; American Public Health Association: Washington, DC, 2005

- 18.2 Methods for Chemical Analysis of Water and Wastes; U.S. EPA Office of Research and Development, Cincinnati, OH, March, 1983.
- 18.3 EPA Method 351.2 Revision 2.0, August 1993. US EPA, Cincinnati, Ohio.
- 18.4 Lachat QuikChem Method 10-107-06-2-M "Determination of Total Kjeldahl Nitrogen by Flow Injection Analysis Colorimetry-Copper Catalyst/Block Digestor Method", Revision dated 27 March 2006, Lachat Instruments, Loveland, Co.
- 18.5 TestAmerica's *Environmental Health & Safety Manual* CW-E-M-001, Most current revision.
- 18.6 Tampa's *Quality Assurance Manual* (TP-QAM), most current revision
- 18.7 TestAmerica Tampa SOP's:
 - 18.7.1 TP-HAZ-001 *Waste Management*
 - 18.7.2 TP-AN-004: Standard Materials and Reagent Traceability
 - 18.7.3 TP-AN-005: Definitions, Terms, and Acronym
 - 18.7.4 TP-AN-016 Glassware Cleaning Procedures

19.0 Method Modifications:

Item	Method 351.2	Modification
1.1	1.0	This method has been modified to include the digestion and analysis of solid samples.

20.0 Attachments

None.

21.0 Revision History

- Revision 5, dated 15 February 2010
 - Minor format changes
- Revision 4, dated 15 November 2009
 - Minor changes: temperatures, clarification LCS preparation for solids