
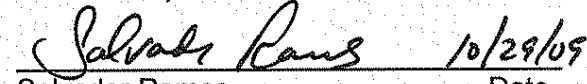
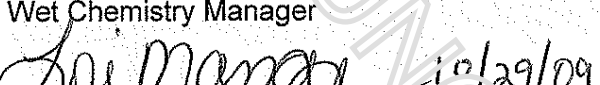

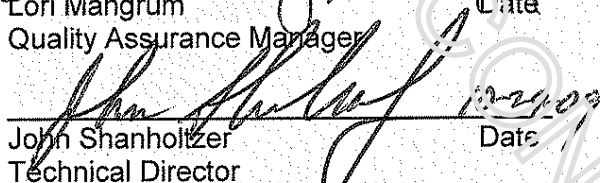


**Title: DETERMINATION OF AMMONIA BY FLOW INJECTION ANALYSIS
(Lachat)**

Method: EPA 350.1

Approvals (Signature/Date):

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1.0 Scope and Application

1.1 Analytes, Matrix(s), and Reporting Limits

This method covers the determination of ammonia in drinking, ground, surface, and saline waters, domestic and industrial wastes. The applicable range for this method is 0.01 – 4.0 mg/L.

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

2.1 The sample is buffered in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is distilled into a solution of sulfuric acid. Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The blue color formed is intensified with sodium nitroprusside and measured colorimetrically at 660nm.

2.2 Reduced volume versions of this method that use the same reagents and molar ratios are acceptable, provided they meet the quality control and performance requirements stated in the method.

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.

4.0 Interferences

- 4.1 Contaminants in solvents, reagents, glassware and other processing apparatus that lead to discrete artifacts may cause Method Interference. All these materials must be routinely demonstrated to be free from interferences in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.
- 4.2 Most interferences are eliminated or reduced using the incorporated distillation procedure.
- 4.3 Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the pH of 9.5 at which distillation is carried out.
- 4.4 Residual chlorine must be removed by pretreatment of the sample with sodium thiosulfate or other reagents before distillation.
- 4.5 Sample turbidity and color may cause interferences. Samples containing particles 0.1µm or greater must be filtered.
- 4.6 Metal ions in high concentrations, which precipitate as hydroxides, may cause poor reproducibility. EDTA introduced into the sample stream usually eliminates precipitation, but in saline waters a sodium potassium tartrate solution may be used.

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 Hydrogen 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 (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Phenol	Corrosive	5 ppm-TWA	Breathing vapor, dust or mist results in digestive disturbances. Will irritate, possibly burn respiratory tract. Rapidly absorbed through the skin with systemic poisoning effects to follow. Discoloration and severe burns may occur, but may be disguised by a loss in pain sensation. Eye burns with redness, pain, blurred vision may occur. May cause severe damage and blindness.
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 Nitroferri-cyanide	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 Poison 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.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit			

6.0 Equipment and Supplies

6.1 Equipment

- Lachat distillation tubes and distilling apparatus
- Balance - Analytical, capable of accurately weighing to the nearest 0.0001g
- Automated continuous flow analysis equipment designed (Lachat Model 8000 FIA) to deliver and react sample and reagents in the required order and ratios.
 - Sampling device (auto-sampler)
 - Multi-channel pump
 - Reaction unit or manifold
 - Colorimetric detector
 - Data recording device, Lachat data system, Omnion

6.2 Supplies

- Volumetric flask, Class A, varying volumes
- Eppendorf pipettes, varying volumes
- Sample cups and reagent wells

7.0 Reagents and Standards

7.1 All reagents 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*. Calibration solutions are prepared from either certified stock solutions, from stock solutions purchased from vendors, or from stock standards prepared from neat materials. Certificates of analysis or purity must be received with all neat compounds and stock solutions and scanned into TALS.

NOTE: All solutions must be made with ammonia-free DI water.

7.2 Sodium phenolate

7.2.1 Using a 1L volumetric flask, dissolve 83g phenol (CASRN 108-95-2) in 500mL of DI water. In small increments, cautiously add with agitation, 32g of NaOH. Periodically cool flask under water faucet. When cool, dilute to 1L with DI water. Stable for at least two weeks or discard when the reagent turns brown.

NOTE: Crystallized phenol is recommended due to its stability, but a phenol solution can also be used. If using an 88% phenol solution, use 94.3mL.

CAUTION: Heat will be evolved as the sodium hydroxide mixes with water. This solution will cause skin burns and destroy unprotected clothing.

7.3 Sodium hypochlorite solution

7.3.1 Dilute 250mL of a bleach solution containing 6.0% NaOCl (CASRN 7681-52-9) to 500mL with DI water. Available chlorine level should approximate 2% to 3%. The analyst must remain alert to detecting any variation in this product significant to its use in this procedure. Due to the instability of this product, **prepare fresh daily**.

7.4 Sodium nitroprusside (0.05%)

7.4.1 Dissolve 3.5g of sodium nitroprusside (CASRN 14402-89-2) in 1L of DI water. Prepare fresh every 1 to 2 weeks.

7.5 Disodium ethylenediamine-tetraacetate (EDTA) (5% buffer)

7.5.1 Dissolve 50g of EDTA (disodium salt) (CASRN 6381-92-6) in 1L of DI water.

7.6 Calibration Diluent Solution: Acidified Water

7.6.1 Water containing 2mL concentrated ultra pure sulfuric acid (H_2SO_4) per liter DI water.

7.7 Sodium hydroxide Solution, 1M

7.7.1 While cooling under tap water or in an ice batch, slowly add 40g of sodium hydroxide in about 800mL DI water while swirling. Cool to room temperature, then dilute to 1L. Commercial source acceptable. Dilute to mark.

CAUTION Heat will be evolved as the sodium hydroxide mixes with water. These

solutions will cause skin burns and destroy unprotected clothing.

7.8 Distilled Ammonia Borate buffer

7.8.1 Dissolve 9.5g sodium tetraborate*10 H₂O in 750mL reagent water, add 0.8mL of 10N NaOH, shake, dilute to 1 liter with reagent water.

7.9 De-chlorinating reagent, Sodium thiosulfate

7.10 Primary stock standard can be purchased at a concentration of 1,000mg/L or made from Ammonium Chloride. Primary stock standards are used for calibrants and the CCV.

7.10.1 Dissolve 0.3819g of anhydrous ammonium chloride, NH₄Cl (CASRN 12125-02-9), dried at 105°C, in reagent water, and dilute to 100mL. 1.0mL = 1.0mg NH₃-N. Commercial source at 1000ppm is acceptable. Store at 4°C.

7.11 Preparation of Working Standard Solutions:

Concentration mg N/L	0.0	0.020	0.050	0.200	0.500	1.00	2.00	4.00
Volume (mL) Top standard diluted to final volume with Calibration Diluent	0	10mL of 0.200 std	10mL of 0.500 std	10mL of 2.00 std	50	100	200	400
Final Volume (mL)	100	100	100	100	100	100	100	100

7.12 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.

7.13 Blank: Calibration diluent solution

7.14 Initial Calibration Verification- ICV (1.00mg/L)

7.14.1 Add 100mL of the secondary stock standard to 100mL flask and bring to volume with calibration diluent.

7.15 Laboratory Control Sample- LCS (0.500mg/L)

7.15.1 Add 50mL of the secondary stock standard to 100mL flask and bring it to volume with calibration diluent.

7.16 Matrix Spike/Matrix Spike Duplicate- MS/MSD (1.00mg/L)

7.16.1 Add 10mL of the secondary stock standard to a 100mL flask and bring to volume with DI water. Add 100uL of the solution to 10mL sample.

7.17 Continuing Calibration Verification- CCV (2.00mg/L)

7.17.1 Add 200mL of the primary stock standard into a 100mL volumetric flask

and bring to volume with calibration diluent.

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	250mL	pH \leq 2 H ₂ SO ₄ , Cool \leq 4°C	28 Days	40 CFR Part 136.3
Soils	HDPE	25g	Cool \leq 4°C	28 Days	N/A

¹Inclusive of digestion and analysis.

8.1 Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis (if required), and minimize waste disposal.

8.2 All samples should be verified for proper preservation and residual chlorine in custody. If chlorine and/or pH are not appropriate, the samples will be marked for the deficiency. Appropriate steps must be taken by the analyst to adjust the pH and chlorine if samples are not properly preserved. Acid or sodium hydroxide can be added to samples to adjust the pH and sodium thiosulfate is added for residual chlorine.

8.3 Aqueous Samples

8.3.1 Samples are collected in 250mL plastic containers and are preserved with H₂SO₄ to a pH $<$ 2. They are stored at 4°C (less than 6°C with no frozen samples) until time of analysis. Samples should be analyzed as soon as possible after collection. Holding time is 28 days from the date of collection.

8.4 Solid Samples

8.4.1 Solid samples are routinely collected in wide-mouthed plastic jars. They are stored at 4°C (less than 6°C with no frozen samples) until time of analysis. Samples should be analyzed as soon as possible after collection. Holding time is 28 days from the date of collection.

8.4.2 Solid samples are extracted with deionized water, filtered, and the extract is analyzed in the same manner as aqueous samples.

8.5 Distillation

NOTE: All NPDES samples must be distilled before analysis. TALS will have the prep of DISTILL_ Ammonia logged in for samples requiring distillation prior to analysis.

8.5.1 The distillation can be carried out in any distillation apparatus. Sodium hydroxide is added to the sample in the distillation apparatus to bring the sample pH above 10 to convert the ammonium ions to ammonia. The

distillate must be collected under 0.02N sulfuric acid; that is, the tip of the condenser must be under the surface of the acid solution to trap the ammonia. The volume of distillate collected should be 60-80% of the original sample volume. The distillate is diluted to the original volume with 0.02N sulfuric acid. The pH of the distillate must be <2 or the distillation must be repeated with a smaller aliquot of sample.

8.5.2 In Lachat distillation tubes, add trapping solution and bring back to 6mL volume.

NOTE: A distillation study has to be performed. Samples that are tested against a compliance limit must be distilled or a comparison of distilled and undistilled aliquots must be on file to demonstrate that the sample is free from interference and that the analysis of the undistilled sample yields comparable results. Comparable results means the result for the distilled and undistilled agree within 10% (percent difference less than 10%) using the distilled aliquot result as the reference.

9.0 Quality Control

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

Instrument conditions must be the same for all standards, samples and QC samples

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 needed 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 is 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 calibration curve is performed daily, followed by an Initial Calibration Verification (ICV) and Initial Calibration Blank (ICB).

9.2.3 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	4ppm, 2ppm, 1ppm, 0.5ppm, 0.2ppm, 0.05ppm, 0.02ppm, 0ppm	Linear cal	>0.995%	Daily
ICV	1.0ppm	Linear cal	90-110%	After calibration
ICB	0ppm	Linear cal	<MDL	After ICV
CCV	1.0ppm	Linear cal	90-110%	Every 10 samples
CCB	0ppm	Linear cal	<MDL	After CCV

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

9.2.4 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.

9.2.5 Linear Calibration Range

9.2.5.1 After the calibration curve has run, the low, mid, and high points are run 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.

10.0 Procedure

10.1 Sample preparation

10.1.1 Mix all aqueous samples thoroughly before analysis and allow samples to come to room temperature.

10.1.2 Soils for this analysis are to be leached with DI water.

10.1.2.1 Homogenize the sample and weigh out 5.0g of sample into a 50mL plastic container. Record the weight to the nearest 0.1g. A percent solid analysis must be done on any soil samples that are leached by this procedure.

10.1.2.2 Add 500mL of reagent water to the plastic bottle containing the sample.

10.1.2.3 Shake or rotate the sample for 2 hours.

10.1.2.4 Allow the sediment to settle and filter 25mL of the sample through a 0.45um syringe filter.

10.1.2.5 The sample can now be treated as an aqueous sample and must be run within 48 hours.

10.1.3 Prepare a series of seven standards, covering the desired range, and a blank by diluting suitable volumes of standard solutions per Section 9.4.3.

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 as described in Section 7.
- 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 Omnion 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. Allow the Lachat system to warm up as required (about 30 minutes).
- 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.

10.3 Sample Analysis

- 10.3.1 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.
- 10.3.2 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	
4ppm, 2ppm, 1ppm, 0.5ppm, 0.2ppm, 0.05ppm, 0.02ppm, 0ppm	
Initial Calibration Verification (ICV)	
Initial Calibration Blank (ICB)	
MB	
LCS	
10 samples (including MS/MSD)	
Continuing Calibration Verification (CCV)	
Continuing Calibration Blank (CCB)	
10 samples (including MS/MSD)	
Continuing Calibration Verification (CCV)	
Continuing Calibration Blank (CCB)	

- 10.3.3 Aliquot the samples, the check standards, and the matrix spikes, and place them in appropriate positions in the auto-sampler rack.
- 10.3.4 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.
- 10.3.5 Let the sequence run until all the samples have been analyzed.
- 10.3.6 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.
- 10.3.7 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.
- 10.3.8 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.
- 10.3.9 When the data is ready, it may be uploaded electronically or manually entered into TALS at the analyst's discretion.

10.4 Preventative Maintenance

- 10.4.1 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.

10.4.2 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.

10.4.3 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 Prepare a calibration curve by plotting instrument response against standard concentration. Compute sample concentration by comparing sample response with the standard curve. Multiply answer by appropriate dilution factor.

11.2 Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed

11.3 Accuracy

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

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

11.4 Precision (RPD)

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

$$11.5 \text{ Concentration = mg/kg or L} = \frac{C \times V \times D}{W}$$

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 The laboratory operates a formal quality control (QC) program. The minimum requirements of this program are an initial demonstration of laboratory capability and

the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory maintains performance records that define the quality of the data that are generated.

12.2 Method Detection Limit Study (MDL)

- 12.2.1 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.

12.3 Initial Demonstration of Capabilities

- 12.3.1 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.
- 12.3.2 The analyst is required to perform a Continuing Demonstration of Capability (CDOC) annually or whenever there is a significant change in the instrument parameters or the associated method. The IDOC includes the preparation of standards, demonstration of instrument linearity, and the analysis of a mid-point laboratory standard within 90-110% recovery. The IDOC must be from a source other than the source used for the calibration standards

12.4 Linear Calibration Range

- 12.4.1 The LCR must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. The verification data exceeds the initial values by $\pm 10\%$ of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial demonstration of MDL's or continuing with on-going analyses.

- 12.5 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 18 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 Laboratory Method Blank (MB) -- The laboratory must analyze at least one MB with each batch of samples. Data produced are used to assess contamination from the laboratory environment. Values that exceed the method detection limit indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis. If the sample concentration is greater than 10 times the blank, the result may be reported.

13.2.2 Laboratory Control Sample (LCS/ICV) 90-110% The laboratory must analyze at least one LCS with each batch of samples. Calculate accuracy as percent recovery (Section 9.4.2). If the second-source recovery of any analyte falls outside the required control limits of 90-110%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

13.2.3 Calibration Verification (CCV) -- For all determinations the laboratory must analyze the CCV (a mid-range check standard) and a calibration blank immediately following daily calibration, after every tenth sample, and at the end of the sample run. Analysis of the CCV must verify that the instrument is within $\pm 10\%$ of calibration. Subsequent analyses of the CCV solution must verify the calibration is still within $\pm 10\%$. If the calibration cannot be verified within the specified limits, reanalyze the CCV solution. If the second analysis of the CCV solution confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift, the instrument re-calibrated. All samples following the last acceptable CCV solution must be reanalyzed. The analysis data of the calibration blank and CCV solution must be kept on file with the sample analyses data.

13.2.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD) 90-110% The laboratory must add a known amount of analyte to a minimum of 10% of the routine samples (one MS for each 10 samples). In each case the MS aliquot must be a duplicate of the aliquot used for sample analysis. The analyte concentration must be high enough to be detected above the original sample and should not be less than four times the MDL. If the recovery of any analyte falls outside the designated MS recovery range and the laboratory control sample (LCS) for that analyte is shown to be in control, the recovery problem encountered with the MS is judged to be either matrix or solution related, not system related.

13.2.5 Where reference materials are available, they should be analyzed to provide additional performance data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably.

13.3 Procedural Variations

13.3.1 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.

13.4 Non-Conformance Memo and Corrective Action

13.4.1 Any deviations from QC procedures must be documented as a non-conformance memo (NCM), with applicable cause and corrective action approved by the facility QA Manager.

13.4.2 When data is out-of-control or does not meet the acceptance criteria, the laboratory supervisor and Project Management must be notified immediately and a NCM must be written as documentation for the PM to include in the project folder.

13.4.3 Data that does not meet acceptance criteria may be conditionally reported with the use of data flags on the final report or through the use of a case narrative attached to the final report.

13.5 Sample result evaluation

13.5.1 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 an "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.

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

17.1 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:

17.1.1 Aqueous acidic/alkaline material from the auto-analyzer. All waste is to be segregated and put into the waste container to be disposed of by the hazardous waste coordinator.

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

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 350.1 Revision 2.0, August 1993. US EPA, Cincinnati, Ohio.

18.4 Lachat QuikChem Method 10-107-03-1-J "Determination of Ammonia by Flow Injection Analysis (Low Flow Method)", Revision dated 29 November 2007, 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-005: Definitions, Terms, and Acronym

18.7.3 TP-AN-016 Glassware Cleaning Procedures

19.0 Method Modifications:

Item	Method 350.1	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 0, dated 01 November 2009
 - Initial Release

UNCONTROLLED