GUAM ENVIRONMENTAL PROTECTION AGENCY
EMAS ANALYTICAL PROGRAM

STANDARD OPERATING PROCEDURE

DETERMINATION OF TOTAL PHOSPHORUS and TOTAL NITROGEN IN WATER BY FLOW INJECTION ANALYSIS COLORIMETRY

Prepared by:	Edelisa S. Yanit, Chemist II	11/07/11 Date
Peer Reviewed by:	Rodolfo B. Paulino, Chemist II	11/07/11 Date
Reviewed by:	Jesse T. Cruz, Administrator EMAS Division	11/10/11 Date
Approved by:	Ivan C. Quinata, Administrator Guam Environmental Protection Agency	11/14/11 Date

Periodic Review:

Signature	Title	Date

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1. SCOPE AND APPLICATION

1.1 This method covers the determination of Total Phosphorus and Total Nitrogen in surface and saline waters, domestic and industrial wastes. This SOP is based on EPA Methods 361.5 and 353.2, QuikChem Methods 31-115-01-3-A and 31-107-04-1-A and USGS method I-2650-03.

1.3 The applicable range is 15 ug/L to 60 ug/L for Total Phosphorus; and 0.30 to 2.0 mg /L for Total Nitrogen. The ranges can be extended for high level samples through dilution.

1.4 The quantitation limit for Total Phosphorus is 15 ug/L.

1.5 The quantitation limit for Total Nitrogen is 0.30 mg/L.

2 METHOD SUMMARY

2.1 A digestion solution (alkaline persulfate reagent) is added to the sample, capped tightly, and digested in an autoclave at 121°C and 15 lb/in^2 for one hour. The alkaline persulfate digestion procedure oxidizes all forms of inorganic and organic nitrogen to nitrate and hydrolyzes all forms of inorganic and organic phosphorus to orthophosphate.

2.2 Calibration standards, blanks and QC samples are treated in the same manner as the routine samples, and the resulting solutions are analyzed using the orthophosphate and nitrate+nitrite methods with the results equaling the total phosphorus and total nitrogen content respectively.

3 INTERFERENCES

3.1 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, sample tubes, digestion tubes and other sample processing apparatus that bias analyte response.

3.2 Alkaline Persulfate Digestion:

1) Chloride concentrations higher than 10,000 mg/L are likely to interfere because of reaction with persulfate to form oxychlorides and chlorine that might deplete persulfate required to oxidize inorganic and organic nitrogen species to nitrate. Resulting active chlorine species also can interfere in colorimetric reactions used to determine nitrate and orthophosphate in digests.

2) Organic carbon concentrations greater than 150 mg/L interfere because of reaction with persulfate to form carbon dioxide, thus depleting persulfate required to oxidize inorganic and organic nitrogen species to nitrate.
3) Over acidification of samples can result in low recovery of inorganic and organic nitrogen.
4) Suspended particle remaining in digests must be removed by sedimentation and decantation or filtration prior to colorimetric analyses.

3.3 Colorimetric Orthophosphate Determination:
Refer to SOP Determination of Orthophosphate in Water by FIA Colorimetry (Number CH-01-02), Section 3.

3.4 Colorimetric Nitrate +Nitrite Determination:
Refer to SOP Determination of Nitrate and/or Nitrite in Water by FIA Colorimetry (Number CH-01-01), Section 3.

4. DEFINITIONS

4.1 Analytical Sample – Any sample in which total phosphorus and total nitrogen is being determined, excluding standards, method blanks, or QC reference samples.

4.2 Calibration Blank (CB) – A volume of reagent water fortified with the same matrix as the calibration standards, but without the analyte.

4.3 Calibration Standard (CAL) – A solution prepared by diluting the primary stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration. In this method for Total Phosphorus and Total Nitrogen, the standards for calibration are derived from organic source of phosphorus and nitrogen. This is compared with the LFB (Section 4.8) which is an inorganic source to determine the efficiency of digestion.

4.4 Field Reagent Blank (FRB) – An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if contamination is occurring in the field environment. Note: Field reagent blanks cannot be used for LD or LFM.

4.5 Field Duplicates (FD) – Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analysis of field duplicates indicate the precision associated with the sample collection and storage as well as the laboratory procedures.

4.6 Instrument Performance Check (IPC) – A standard containing the analyte of interest which is used to verify the accuracy of analysis and monitor instrument drift. It is analyzed periodically through out an analysis sequence.

4.7 Calibration Verification (CV) solution: Initial (ICV) and Continuing Calibration Verification (CCV) solutions - A known value standard used to verify instrument performance during analysis. It is analyzed to verify that the initial calibration has not changed significantly during the analysis run. The CV fulfills the requirements of the IPC (4.6).

4.8 Laboratory Fortified Blank (LFB) – An aliquot of reagent water or other blank matrix to which known quantities of method analytes are added in the laboratory. The source of LFB must be independent of the calibration standards. LFB is analyzed like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. The LFB also fulfills the requirements of the QCS (4.14). In this method, the nitrogen and phosphorus is from an inorganic source for the purpose of determining the efficiency of digestion. (See also section 4.3).

4.9 Laboratory Fortified Sample Matrix (LFM) – An aliquot of an analytical sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

4.10 Laboratory Duplicate (LD) – An aliquot of sample prepared and analyzed separately with identical procedures. Analysis of the sample and LD indicates precision associated with the laboratory procedures, but not with sample collection, preservation or storage procedures.

4.11 Laboratory Reagent Blank (LRB) – An aliquot of reagent water or other blank matrix that is treated exactly like a sample. The LRB is used to detect sample contamination resulting from the procedures used to prepare and analyze the samples in the laboratory environment.

4.12 Linear Calibration Range (LCR) – The concentration range over which the instrument response is linear.

4.13 Method Detection Limit (MDL) – The minimum concentration of an

analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

4.14 Quality Control Sample (QCS) – A standard containing nitrate or nitrite which is used to verify the accuracy of the analysis. The method requires that the source of the QCS must be independent of the calibration standards and that the QCS be analyzed quarterly.

4.15 Quantitation Limit (QL) – The concentration at which confidence in the reported value requires no qualifying remarks. The QL, also called as the practical quantitation limit (PQL) is about 5X the MDL and represents a practical and routinely achievable detection limit with a relatively good certainty that any reported value is reliable.

4.16 Stock Standard Solution (SSS) - A concentrated solution containing the method analyte prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

4.17 Sample Delivery Group (SDG) – A group of twenty samples or less from the same case that is sent to the laboratory for analysis.

5 HEALTH AND SAFETY

5.1 The toxicity or carcinogenecity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Safety precautions must be taken when handling solutions and samples. Protective clothing including lab coats, safety glasses and gloves must always be worn. Contact lenses must not be worn. If solutions come into contact with your skin, wash thoroughly with soap and water. Contact your Supervisor or Health and Safety Coordinator to determine if additional treatment is required. Consult the Material Safety Data Sheets (MSDS) for each chemical for specific information regarding the potential hazards and safe handling.

6 EQUIPMENT AND SUPPLIES

6.1 Autoclave (Market Forge Sterilmatic)
6.2 Hot plate stirrer
6.3 Magnetic stirrer bar
6.4 SCHOTT bottles
6.5 Digestion tubes (polycarbonate) 50 ml
6.6 Autoclave-safe tube racks

6.7 Eppendorf pipetters (100-1000 uL; 500-2500 uL)
6.8 pH indicator strips (0-14)
6.9 All of the equipment and supplies listed in the SOP for Determination of Orthophosphate in Water by FIA Analysis (Number CH-01-02), Section 7.
6.10 All of the equipment and supplies listed in the SOP for Determination of Nitrate+Nitrite in Water by FIA Analysis (Number CH-01-01), Section 7.

7 REAGENTS

7.1 Use ASTM Type II reagent water for all solutions.

7.2 Potassium persulfate
7.3 Sodium hydroxide
7.4 Nicotinic acid (organic Nitrogen source)
7.5 (4-Carboxybutyl)triphenyl-phosphonium bromide (organic Phosphorus source)
7.6 All of the reagents listed in the SOP for Determination of Orthophosphate in Water by FIA Analysis (Number CH-01-02)
7.7 All of the reagents listed in the SOP for Determination of Nitrate+Nitrite in Water by FIA Analysis (Number CH-01-01)
7.8 Digestion solution: Transfer 750 ml of reagent water to a 1L SCHOTT bottle containing a magnetic stirrer bar and with stirring dissolve 30.0 $\pm$ 0.1 g potassium persulfate and 4.5 $\pm$ 0.05 g sodium hydroxide (or 6.312 g KOH)
Note: This solution may require warming to dissolve the persulfate (heating should not be greater than 50°C as decomposition of persulfate occurs at 70°C)
7.9 Digested carrier solution: Transfer 125 ml of digestion solution and 375 ml reagent water to a 1L SCHOTT bottle. Cap and autoclave as detailed in step 3 of the digestion procedure.

8 STANDARDS

8.1 **Stock Standards:**
Stock standard solutions used to prepare calibration standards are prepared in the laboratory from ACS reagent grade materials and are stable for six months when stored at 4° C.
Second source standards used to prepare Quality Control standards are purchased as certified solutions.

8.2 **Standard 1. Stock Standard 500 mg/L Total Phosphorus:** In a 250 ml volumetric flask dissolve 1.79 g (4-Carboxybutyl)triphenyl-phosphonium bromide in about 150 ml reagent water, dilute to the mark and invert to mix.

8.3 **Standard 2. Stock Standard 500 mg/L Total Nitrogen:** In a 250 ml volumetric flask dissolve 1.0975 g Nicotinic acid in about 150 ml reagent water, dilute to the mark and invert to mix.

8.4 **Standard 1A. Working stock standard for Total P (Substock): 1000 ug/L Total Phosphorus** – In 100 ml volumetric flask , add 0.2 ml stock standard 500 mg/L Total Phosphorus (Standard 1) to about 50 ml reagent water, dilute to mark and shake to mix. Prepare this standard daily.

8.5 **Working Standards for Total P** - Prepare fresh daily. The following calibration standards are prepared using 1000 ug/L Total P (Standard 1A) and diluted with reagent water.

Calibration Standard (TP)	Volume of Standard 1A	Final volume
60 ug/L	12.0 mL	200 mL
30 ug/L , **CV**	6.0 mL	200 mL
15 ug/L	3.0 mL	200 mL
Blank	0	200 mL

QCS (or LFB): 30 ug/L --- prepare as in Section 8.7.1.

8.6 **Working Standards for Total N** – Prepare fresh daily. The following calibration standards are prepared using 500 mg/L Total N (Standard 2) and diluted with reagent water.

Calibration Standard (TN)	Vol. Of Standard 2	Final Volume
2.00 mg/L	800 uL	200 mL
1.00 mg/L , **CV**	400 uL	200 mL
0.50 mg/L	200 uL	200 mL
0.30 mg/L	120 uL	200 mL
Blank	0	200 mL

QCS (or LFB): 1.00 mg/L --- prepare as in Section 8.7.2.

8.7 **Quality Control Standard (QCS):**
Using a second source stock standard 1000 mg/L Phosphate as P (i.e., ERA), prepare a substock 1000 ug/L Phosphate as P. Dilute 0.10 ml or 100 microliter of stock standard to 100 ml with reagent water.

8.7.1 To prepare a **QCS 30 ug/L Phosphate as P,** dilute 3 ml 1000 ug/L phosphate as P to 100 ml with reagent water.

8.7.2 Using a second source stock standard 1000 mg/L Nitrate as N, prepare a **QCS 1.00 mg/L Nitrate as N**. Dilute 0.10 ml or 100 microliter of stock standard to 100 ml with reagent water.

9 SAMPLE HANDLING AND PRESERVATION

9.1 Samples should be collected in plastic or glass bottles. All bottles must be cleaned with detergents and rinsed with 10% HCl. After the bottles have been cleaned, rinse thoroughly with reagent-grade water.

9.2 Volume of samples collected should be sufficient to insure a representative sample, allow for replicate analysis and minimize waste disposal.

9.3 Samples are received in the EMAS Laboratory by a laboratory staff. Sample IDs, dates and times of collection are verified against the chain-of-custody form. Samples are logged in using the Laboratory Information System (LIMS).

9.4 Upon receipt in the laboratory, samples for Total P and Total N must be filtered through a 0.45- um-pore-diameter membrane filter and preserved with 2 mL conc H_2SO_4 per liter of sample to adjust to pH ≤ 2.

9.5 Samples must be received and stored at $4 \pm 2^{o}C$. Any deviations from the $4 \pm 2^{o}C$ temperature requirements must be noted in the report.

9.6 The samples must be digested within 28 days of the sample collection date. Analysis of samples must be completed within two weeks of the digestion date.

10 QUALITY CONTROL PROCEDURES

10.1 Guam EPA operates a formal quality control (QC) program. The QC program consists of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks, QCS samples and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated.

10.2.1 Initial Demonstration Proficiency – Each analyst must complete an initial demonstration of proficiency prior to analyzing samples following this method.

10.2.2 MDL – A method detection limit must be confirmed annually and must be <1/2 the QL or corrective action must be initiated.

10.2.3 QCS – a QCS must be prepared and analyzed when beginning the use of this method, on a quarterly basis or as required, to meet data-quality needs. The source of the QCS must be independent of the calibration standards. The QCS verifies the calibration standards. Guam EPA Laboratory fulfills the requirements of the QCS with analysis of the LFB.

10.3 Routine Analytical Quality Control

10.3.1 The instrument must be calibrated with a blank and at least three standards. The correlation coefficient of the calibration curve must be ≥ 0.995 or the instrument must be recalibrated.

10.3.2 CV – The accuracy and stability of the calibration shall be verified by the periodic analysis of a CV standard. It must be analyzed at the beginning of an analytical run (the ICV), after every 10 analytical samples (the CCV), and at the end of an analytical run (the closing CCV). The CV solution should be prepared from the same standard stock solutions used to prepare the calibration standards.

The recovery of Total P or Total N in the CV is calculated as follows:

$$\%\,R = \frac{M}{T} \times 100$$

Where

%R = percent recovery of the standard
M = measured concentration of Total P or Total N, ug/L or mg/L
T = true concentration of Total P or Total N in the IPC or CV,ug/L or mg/L

If the CV recovery exceeds the limits of 90 – 110%, the analysis shall be terminated. The cause of the poor recovery must be determined and the problem corrected. The instrument must be re-calibrated and all samples not bracketed by acceptable CV results must be reanalyzed.

10.3.3 CB (ICB/CCB) – The stability of the baseline must be monitored by analyzing a CB immediately after every CV standard. If the absolute value of the CB result equals or exceeds the QL, the analysis must be terminated. The cause of high CB result must be determined and the problem corrected. The instrument must be re-calibrated and all samples not bracketed by acceptable CB results must be reanalyzed.

10.3.4 QL – The accuracy of the calibration at the reporting limit may be verified by the analysis of a QL standard. The QL should be analyzed at the beginning of analytical run, prior to the analysis of environmental samples.

10.3.5 LRB – The laboratory must analyze at least one LRB daily or with each batch of 20 or fewer samples of the same matrix, whichever is more frequent. LRB data are used to assess contamination in the laboratory environment. LRB values that exceed the MDL indicate potential laboratory contamination. If the potential contamination significantly impacts the analytical results, the LRB must be re-prepared along with affected samples, and reanalyzed.

10.3.6 LFB – An LFB must be prepared and analyzed with each batch of 20 or fewer samples. The LFB assures that the calibration standards used to calibrate are accurate. The LFB is the QCS. The recovery of analyte in the LFB is calculated as follows:

$$\%R = \frac{LFB}{s} X100$$

Where

%R = percent recovery
LFB = measured concentration of analyte in the LFB, ug/L or mg/L
s = analyte concentration in the LFB, ug/L or mg/L

The recovery of analyte in the LFB must be within the 90 – 110% limits. If the recovery exceeds the limits, the analysis system is judged to be out-of-control, and the source of the problem must be identified and resolved before continuing analyses.

10.3.7 LD – Sample homogeneity can affect the quality and interpretation of the data. LD results can be used to assess sample homogeneity.

One LD must be prepared for every 10 routine samples of the same matrix in a sample batch (e.g., 1 LD for a batch containing 1-10 routine samples, 2 LDs for a batch containing 20 routine samples, etc.). Shake the sample selected as the LD, obtain a representative aliquot, and proceed with the sample preparation and analysis, treating the LD sample as a routine sample.

Calculate the relative percent difference (RPD) using the following equation:

$$RPD = \frac{(C_{ld} - C)}{(C_{ld} + C) / 2} X\ 100$$

Where

RPD = relative percent difference
C_{ld} = measured analyte in the LD ,ug/L or mg/L
C = measured analyte in the routine sample, ug/l or mg/L

The relative percent difference (RPD) must be ≤20% for samples with analyte levels greater than or equal to 5X the QL. For other samples, the absolute difference between duplicate results must be less than the QL. If the control limits are exceeded, flag all associated analyte results.

10.3.8 LFM – The LFM is designed to provide information about the effect of sample matrix on the measurement system. One LFM must be prepared for every ten routine samples of the same matrix in a sample batch. The sample chosen as the LD should be used as the sample LFM. Samples identified as field blanks cannot be used for LFM sample analysis. The analyte concentration must be high enough to be detected above the original sample and should not be less than 4X the MDL. Percent recovery may be calculated using the following equation:

$$\%R = \frac{C_{lfm} - C}{s} \times 100$$

Where %R = percent recovery
C_{lfm} = measured concentration of analyte in the LFM, corrected for any dilutions, ug/L or mg/L
C = measured concentration of analyte in the routine sample, corrected for any dilutions, ug/L or mg/L
s = expected analyte concentration of the added spike in the LFM, corrected for any dilutions, ug/L or mg/L

If the value of **C** is less than 4X the value of s, the acceptance window for %R is 75 – 125%. If the recovery falls outside the acceptance window other QC data must be examined to determine if a matrix problem exists. If the laboratory performance for that analyte is in control (i.e., the CV, QL, and the LFB results are acceptable, the poor LFM recovery is most likely matrix related. Lab duplicate results should also be examined to gain additional insight as to whether the matrix components or matrix heterogeneity are the cause of the unacceptable recovery. In either case, the problem should be discussed in the report and the data user informed that the result for that analyte in the unfortified sample is suspect due either to heterogenous nature of the sample or a matrix effect. Flag any out-of-control analytes.

11 ANALYTICAL PROCEDURES

11.1 Digestion Procedure

1) To a 50 ml polycarbonate tube, add 20 ml of sample and 8.57 ml digestion solution.
2) Screw the tube cap on "fingertight" and invert to mix.
3) Digest in an autoclave for 1 hour at 121°C and 15 psi.
4) At the end of the autoclave period, remove the tubes, ensure the caps are tight and allow them to return to room temperature.
5) Mix thoroughly either by manual inversion (3 times) or with a vortex mixer (3, 5-second cycles).
6) Check the pH of one of the blanks by transferring a couple of drops to a pH 1-14 indicator strip. It should indicate a value of 2-3. (If not, do not proceed to analyze the samples, as there is either a problem with the autoclave step or the oxidizing reagent has been made incorrectly).
7) Analyze using the orthophosphate or nitrate chemistry using the "digested solution Carrier" as the carrier reagent.

Note: All calibration standards, blanks and QCS samples are to be treated in the same manner.

11.2 Calibration and Standardization

Total Phosphorus and Total Nitrogen are determined colorimetrically using the Lachat Automated Ion Analyzer. The analyst is advised to follow the recommended operating conditions provided by the manufacturer. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions satisfy the analytical requirements, to maintain quality control data verifying instrument performance.

11.3 Instrument Set-up

Refer to SOP Determination of Orthophosphate in Water by FIA (Number CH-01-02), Section 10.1.1 and SOP Determination of Nitrate and/or Nitrite in Water by FIA (CH-01-01), 10.1.1.

11.4 Calibration and Sample Analysis

1) Pour the calibration standards and the blank into standard tubes and position them in decreasing order in the standards rack at the rear of the autosampler.

2) Load the analytical and QC samples into the samples rack using the sample tubes.
3) The usual sample loading sequence is listed in the following table:

Row	Sample ID	Cup #	Sample Type	Level
1	Cal Std 1	1	Cal Std	1
2	Cal Std 2	2	Cal Std	2
3	Cal Std 3	3	Cal Std	3
4	Cal Std 4	4	Cal Std	4
5	Blank	5	Cal Std	5
6	ICV	1	Unknown	0
7	ICB	2	Unknown	0
8	LFB (QCS)	3	Unknown	0
9	LRB	4	Unknown	0
10	Sample 1	5	Unknown	0
11	Sample 1 – LD	6	Unknown	0
12	Sample 1 – LFM	7	Unknown	0
13	Sample 2	8	Unknown	0
14	Sample 3	9	Unknown	0
15	Sample 4	10	Unknown	0
16	Sample 5	11	Unknown	0
17	Sample 6	12	Unknown	0
18	CCV	13	Unknown	0
19	CCB	14	Unknown	0
20	Sample 7	15	Unknown	0
21	Sample 8	16	Unknown	0
22	Sample 9	17	Unknown	0
23	Sample 10	18	Unknown	0
24	Sample 11	19	Unknown	0
25	Sample 11 – LD	20	Unknown	0
26	Sample 11 –LFM	21	Unknown	0
27	Sample 12	22	Unknown	0
28	Sample 13	23	Unknown	0
29	Sample 14	24	Unknown	0
30	CCV	25	Unknown	0
31	CB (CCB)	26	Unknown	0
32	Sample 15	27	Unknown	0
33	Sample 16	28	Unknown	0
34	Sample 17	29	Unknown	0
35	Sample 18	30	Unknown	0
36	Sample 19	31	Unknown	0
37	Sample 20	32	Unknown	0
38	CCV	33	Unknown	0

39	CCB	34	Unknown	0

4) Input the information required by the data system such as concentrations, replicates and quality control scheme.
5) Calibrate the instrument by injecting the working standards. The system will analyze the calibration standards and calculate a calibration curve prior to analyzing any of the samples. A correlation coefficient of ≥0.995 is the requirement for the calibration to pass. The system will now automatically analyze the samples loaded in the sample tray.

11.5 **Post-analysis Review**

1) QC Sample Results – Review the results for all QC samples for compliance with the criteria specified in Section 10. If results are not acceptable, take appropriate corrective action.

2) Off-scale Results – Review results for samples that exceed the calibration range. Samples having analyte concentrations larger than the highest calibration standard must be diluted and reanalyzed.

11.6 Instrument Shutdown

Refer to SOP Determination of Orthophosphate in Water by FIA (Number CH-01-02), Section 10.1.4 and SOP Determination of Nitrate and/or Nitrite in Water by FIA (CH-01-01), Section 10.1.4.

11.7 **Data Reduction and Reporting** – After manual set-up and calibration the software reports the results for the analyzed solution in units of ug/L or mg/L. No further calculations are necessary and values may be reported directly from the data system. All results should be reported using no more than three significant figures; however, no values of less significance than the MDL may be reported. Results less than the MDL should be reported as <MDL values. Values between the MDL and the QL will be flagged as estimated (J flag).

11.8 Sample results are entered into the Laboratory Information Management System (LIMS) and analytical results are reported.

11.9 Before releasing the results, the laboratory conducts data verification and validation. This is done through peer review of the data and validation by another analyst. The QA Manager makes the final audit and validation prior to the release of the results.

12 DOCUMENTATION

Refer to SOP Determination of Orthophosphate in Water by FIA (Number CH-01-02), Section 11 and SOP Determination of Nitrate and/or Nitrite in Water by FIA (CH-01-01), Section 11.

13 REFERENCES

13.1 USGS Method I-2650-03, U. S. Geological Survey National Water Quality Laboratory, Denver, CO.

13.2 Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory – Evaluation of Alkaline Persulfate Digestion as an Alternative to Kjeldahl Digestion for Determination of Total and Dissolved Nitrogen and Phosphorus in Water -- Water –Resources Investigations Report 03-4174.

13.3 EPA Method 365.1, Phosphorus, All Forms (Colorimetric, Automated, Ascorbic Acid) Methods for Chemical Analysis of Water and Wastes, USEPA, Cincinnati, Ohio, USA.

13.4 QuikChem Method 31-115-01-3-A, Determination of Phosphorus by Flow Injection Analysis Colorimetry.

13.5 Method 4500-P-F, Standard Methods for Examination of Water and Wastewater, 20th Edition, 1998.

13.6 EPA Method 353.2, Determination of Nitrate-Nitrite Nitrogen By Automated Colorimetry, Environmental Monitoring Systems Laboratory, Revision 2.0, August 1993.

13.7 QuikChem Method 31-107-04-1-A, Determination of Nitrate And/Or Nitrite By Flow Injection Analysis Colorimetry

13.8 Method 4500-NO_3, Standard Methods For Examination of Water and Wastewater, 20th Edition, 1998.

13.9 USEPA Region Lab. SOP 594, Analysis of Nitrite and Nitrate in Water, November 15, 1999.

Attachment A

Deviations from Reference Method

A.1 Samples for Total P and Total N are filtered and preserved upon arrival in the laboratory with conc. H_2SO_4 instead of at the time of collection.

A.2 Samples are digested in an autoclave at 121 – 122° C and 15 psi for 1 hour.

A.3 Stock standard solutions used to prepare calibration standards for Total P and Total N are prepared in the laboratory from ACS reagent grade (4-Carboxybutyl)-triphenyl-phosphonium bromide and Nicotinic acid respectively. Stock standards used to prepare Quality Control standards are purchased as certified solutions.