

STANDARD OPERATING PROCEDURES (SOP)
"Total Phosphorus and Nitrogen Persulfate Digestion and Analysis by Lachat Flow-Injection
System"

MED-SOP-CHA032 TNTP-TJ 4-2015

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1.0 SCOPE AND APPLICATION

- 1.1 Modified from Standard Methods 4500-Norg/ 4500-P section 5 APHA 1995. Persulfate digestion oxidizes all nitrogen compounds to nitrate and all phosphorus compounds to orthophosphate. Nitrogen oxidation occurs under alkaline conditions at 100-110°C, while phosphorus oxidizes under acidic conditions at 14-17psi. Both analytes are determined colorimetrically using the respective Lachat QuikChem Methods.
- 1.2 LACHAT QuikChem AE Instrument Manual- stored with the Lachat Instrument (QuikChem Method 10-107-04-1-C) Nitrate+Nitrite in Waters and (QuikChem Method 10-115-01-1-F) Total Phosphorus by persulfate digestion

2.0 SUMMARY OF METHOD

- 2.1 Definitions: deionized water (DIW)
- 2.2 Health and Safety Warnings –Safety glasses, a lab coat and nitrile gloves must be worn at all times.

2.3 Interferences:

Phosphorus: Arsenic and silica compounds react with reagents producing falsely elevated values at the 880nm wavelength. Calcium and magnesium will interfere by forming a white precipitate. High iron or humic concentrations can also form precipitates removing phosphorus which adsorb to it. Bisulfite treatment maybe used if iron interference is suspected.

Nitrate: Chlorine can interfere by oxidizing the Cd column and reducing its efficiency. Adding sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) can reduce this interference.

- 2.4 Clean glassware is extremely important in producing precise data. Care to ensure vials are clean are a must (See 4.3.2)
- 2.5 The brand of persulfate is also an important source of clean technique. At the time of this SOP Amresco LLC ACS grade product# 0363 produced the lowest Nitrogen contamination. This may need to be verified from time to time.

3.0 PERSONNEL QUALIFICATIONS

- 3.1 Proper training in the use, care and troubleshooting techniques is required by the instrument manager before using the Lachat.
- 3.2 Trained personnel are identified in the Lachat logbook.

4.0 MATERIALS AND PROCEDURES

4.1 Materials

- 4.1.1 Acid-washed 20mL scintillation vials with caps and Teflon lined septa
- 4.1.2 Autoclave able to produce 115°C, 14-17psi
- 4.1.3 Various pipettes and appropriate tips
- 4.1.4 Lachat QuikChem 8000 Flow Injection Autoanalyzer
- 4.1.5 Lachat QuikChem (Method 10-115-01-1-B) Orthophosphate manifold with 133 cm sample loop and 100cm back pressure loop.
- 4.1.6 Lachat QuikChem (Method 10-107-04-1-C) Nitrate+Nitrite manifold with 50cm sample loop
- 4.1.7 ASX-520 XYZ autosampler by CETAC Technologies.

4.2 Reagents and Standards

- 4.2.1 All reagents and standards are to be prepared with DIW of 10 megohm or better as indicted by reading on deionized water system meter.
- 4.2.2 Reagent 1: Persulfate/Sodium Hydroxide Digesting Reagent
Dissolve 0.052 g of potassium persulfate ($K_2S_2O_8$) and 0.009 g sodium hydroxide pellets (NaOH) per mL DIW required to complete samples (2.5mls digesting reagent/ sample). Alternately use 0.018 g liquid sodium hydroxide 50/50 w/w. Make fresh **daily**.
- 4.2.3 Nitrate Stock Standard: 100mg/L Nitrate

Dissolve 0.3609g potassium nitrate (KNO_3) dried for one hour at 105°C in DIW to 500mL final volume.

4.2.4 Phosphorus Stock Standard: 100mg/L Phosphate
Dissolve 0.2197g potassium dihydrogen phosphate (KH_2PO_4) dried for one hour at 105°C in DIW to 500mL final volume.

4.2.5 Working Calibration Standards: Prepare standards containing both nitrate and phosphate over the range of analysis from the stock standard.

Nitrate (ug/L)	5000	2500	1000	500	250	100	50	25	0
Phosphate (ug/L)	1000	500	200	100	50	25	10	2	0

4.2.6 Nitrite Stock Standard: 100mg/L Nitrite
Dissolve 0.3044g potassium nitrite (KNO_2) dried for one hour at 105°C in DIW to 500mL final volume.

4.2.7 Nitrite Column Check Standard: 250 ug/L Nitrite
Dilute 4mL of stock standard to 200mL final volume.

4.2.8 Quality Control Standard: A second source standard should be prepared within the expected sample concentration range.

4.2.9 Bisulfite treatment
Acidic: 5.2mL H_2SO_4 + 5.2g Sodium Bisulfite in 95ml DIW
Neutral: 5.2g Sodium Bisulfite in 100ml DIW

4.3 Procedure

4.3.1 Unfiltered water samples are stored frozen until analysis within 6 months of collection.

4.3.2 20mL digestion vials should be cleaned with the following procedure:

- A. Clean vials in lab grade phosphorus free detergent with bottle brush.
- B. DIW rinse 2-3 times
- C. Soak overnight in 1:3 H_2SO_4 : DIW acid bath
- D. DIW rinse 2-3 times to remove all acid.
- E. DIW soak overnight.
- F. Dry in the fume hood overnight

- 4.3.3 Pipette 10mL of standard or sample into cleaned/dry scintillation vial
- 4.3.4 Pipette 2.5mL of digesting reagent
- 4.3.5 Tightly cap scintillation vial with teflon-lined clean/dry caps
- 4.3.6 Autoclave for 45 minutes at 115°C, 14-17psi. Follow operating directions on the autoclave.
- 4.3.7 Let samples cool before storing in refrigerator.
- 4.3.8 Bisulfite treatment (only if iron interference is suspected)
Add 1ml neutral bisulfite treatment, autoclave 95°C 40 minutes
- 4.4 Lachat setup and analysis
 - 4.4.1 Nitrogen and Phosphorus are ran simultaneously using the TNTP_YYYY_method.omn. Reagents and procedures can be found in MED SOP CHA-033 "Simultaneous Nitrate-Nitrite and Orthophosphate Analysis Using the Lachat Flow-injection System"
- 4.5 Data calculations
 - 4.5.1 Lachat software yields results directly as mg/L N and P. Occasionally it is appropriate to split a curve for greater sensitivity. If this is required the data can be exported to an excel spreadsheet where the analyst can recalculate the standard curve equations by regression and recalculate the sample concentrations using the peak areas based on the new curve equation.
- 5.0 QUALITY CONTROL AND QUALITY ASSURANCE
 - 5.1 Laboratory replicates and spiked samples should be prepared for at least 5% of samples to be analyzed.
 - 5.2 Duplicate field samples and blanks should be collected for at least 5% of the total number collected.

- 5.3 Check standards and/or QC samples should be analyzed at least 5% of the total number of samples analyzed.
- 5.4 Method blanks and lab fortified blanks should be analyzed two per batch.
- 5.5 Standard curve is automatically calculated by the software when the set of working Calibration Standards are ran as sample type "Calibration" in the sample table. A standard curve should be ran daily or at a minimum with each batch for fresh reagents. A set of Working Calibration Standards should be run at the end of each run as "unknown" samples to verify calibration. Should instrument drift occur this set of standards could be recalculate the standard curve equations by regression and recalculate the sample concentrations using the peak areas based on the new curve equation.

6.0 REFERENCES

- 6.1 Lachat Instruments Quik Chem Method No. 10-115-01-1-F Total Phosphorus in Persulfate Digestions. August 1992
- 6.2 Lachat Instruments Quik Chem Method No.10-107-04-1-C Nitrate+Nitrite in waters. August 1992.
- 6.3 Lachat QuikChem 8000 Operating Manual
- 6.4 APHA. 1995. Standard Methods for the examination of water and wastewater. Method 4500-P E and 4500-Norg. EPA Method 365.2.

