AUTOMATED DETERMINATION OF CONDUCTIVITY USING THE PC-TITRATE INSTRUMENTATION

1. SCOPE AND APPLICATION

1.1. This SOP is applicable for the determination of the specific conductivity in micromhos per centimeter (µmhos/cm) of aqueous samples using an automatic PC-Titrate instrument. The method detection limit (MDL) is 2.0 µmhos/cm and the practical quantitation limit (PQL) is 8.0 µmhos/cm. Samples can be analyzed from the MDL to 199.9 mmhos/cm (depending on the specifications of the conductivity probe used). This method is applicable to drinking, surface, ground, and saline waters as well as aqueous wastes.

1.2. The tests covered by this SOP are W-COND and W-COND-F.

2. SUMMARY OF THE METHOD

2.1. This SOP is based on EPA method 120.1 (Rev. 1982).

2.2. The sample conductivity is measured electrometrically using the PC-Titrate instrument. The results are automatically corrected to 25 °C with a preset temperature coefficient of 1.91%.

2.3. There are no real interferences with conductivity. If readings become erratic or probe response is sluggish, the probe may need re-platinizing. See Section 10 for electrode maintenance.

3. EQUIPMENT AND SUPPLIES

3.1. Instrumentation: See NU-060 for the components of the PC-Titrate instrument.

3.2. Equipment:

Equipment	Manufacturer/Vendor[1]	Model/Catalog Number
Conductivity Electrode	ManTech	PC-96-CT1002
Analytical Balance	Mettler Toledo	MS204TS/0
Volumetric Flask, Class A, Assorted	Fisher (SR)	10-212B; 10-210-5D; 10-212E; 10-212-5L; 10-208M
Graduated Cylinder, Class A, Assorted	Fisher (SR)	08-553A; 08-548D
Glass Beaker, Assorted	Fisher (SR)	02-540E; 02-540G; 02-540K; 02-555-20E
Or Equivalent		
[1]**Note:** (SR) designates equipment is typically ordered through the in-house stockroom		

3.3. Consumables and frequently replaced supplies:

Supplies/Consumables	Vendor[1]	Catalog Number
Lithium Grease	Fisher	NC0484446
Centrifuge Tubes, Polypropylene, 50 mL	Fisher (SR)	05-538-68, 05-53855A
Sample Beakers, Polypropylene, Assorted	Fisher (SR)	08-732-119; 08-732-120; 08-732-122
Weigh Dish, Hexagonal, Assorted	Fisher (SR)	02-202-102; 02-202-100
Weigh Dish, Aluminum, 110 mm	Fisher (SR)	08-732-100

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Pipet, Transfer, Polyethylene, 7mL	Fisher (SR)	13-711-7M
Parafilm	Fisher (SR)	13-374-12
Or Equivalent		
[1]**Note:** (SR) designates supply is typically ordered through the in-house stockroom		

4. REAGENTS AND STANDARDS (SEE DEP SOPS NU-041 and NU-042)

Note: Before preparing reagents or standards, or running samples, please read the safety notes in the safety/hazardous waste section of this SOP and the MSDS for the chemicals used in this analysis.

Note: Standard preparations must be documented in the Laboratory Information Management System (LIMS) 'Standard Preparation Tracker' module. Unique ID numbers for each standard are generated in the module and documented in the reagent and standard logsheet (NU-RGTSTD) submitted with each analysis folder. The reagent and standard logsheet (NU-RGTSTD) template is located at \\floridadep\data\labs\Lab3\Chem_Data\Inorganic\Nutrients\RunData\MetaData\Auto-T\Forms\. Follow preparation and labelling instructions in DEP SOP NU-042. A Certificate of Analysis (CoA) for each purchased reagent and standard is maintained in the CertificatesofAnalysis subfolder within the Auto-T folder on the Nutrients Drive. All containers holding standards or reagents must be labeled with their unique ID and expiration date.

Note: The volumes prepared for the standards may be altered by the analyst as necessary. The final concentrations of the constituents of a standard must not be changed.

4.1. Chemicals:

	Chemical	Alias	Manufacturer[1]	Catalog Number	Purity	Storage
4.1.1.	Potassium Chloride	KCl	Fisher Chemical	P217-500	ACS, ≥99%	Room Temp
4.1.2.	Potassium Chloride Reference Solution, 1408.8 µmhos/cm at 25°C	Conductivity Calibration Standard	Ricca	589532	See CoA	Fridge after opening
4.1.3.	Minerals QC CRM	ALTQC	NSI Lab Solutions	QCI-136	See CoA	Fridge after opening
4.1.4.	DI Water	H_2O	In house	N/A	N/A	N/A
Or Equivalent						
[1]**Note:** (SR) designates chemical is typically ordered through the in-house stockroom						

Deionized water is replaced daily. All other purchased chemicals are give the expiration date from the CoA and/or chemical container. If there is not an expiration date listed, the expiration date is designated by following the protocol in SOPs NU-041 and NU-042.

4.2. KCl 1 M stock standard (1M COND) –

KCl (4.1.1.)	74.55 g
DI water (4.1.4.)	up to 1000 mL

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Place 74.55 g dried KCl (two hours at 105 °C) in a 1 L volumetric flask and dilute to the mark with deionized (DI) water.

Store in a refrigerator. Holding time, 180 days.

4.3. KCl 0.01 M stock standard –

KCl (4.1.1.)	0.7455 g
DI water (4.1.4.)	up to 1000 mL

Place 0.7455 g dried KCl (two hours at 105 °C) in a 1 L volumetric flask and dilute to the mark with DI water.

Store in a refrigerator. Holding time, 180 days.

4.4. Working standards:

To a 1 L volumetric flask containing approx. 400 mL DI water add the amount of 0.01 M KCl stock standard (4.3.) indicated in the table. Bring to volume with DI water.

Store in a refrigerator. Holding time, 60 days.

Standard Concentration	QC Standard, Alias	Final Volume (mL)	Vol of 0.01 M KCl standard added (mL)
0.001 M KCl (146.9 µmhos/cm)	LFB_CHCK2, CHCK2	1000	100
0.0005 M KCl (73.5 µmhos/cm)	LFB_CHCK4, CHCK4	1000	50

4.5. Conductivity Calibration Standard (4.1.2.) is used for conductivity electrode calibration at the beginning of every run.

4.6. A certified quality control (QC) sample (ALTQC) (4.1.3.). Prepared following the supplier's instructions, if needed. Standard can be stored at room temp, but is generally stored in the refrigerator. The concentration is provided by the manufacturer. There is not a recommended holding time by the manufacturer, but standard is given a 28-day holding time upon opening.

5. SAMPLE HANDLING AND PRESERVATION

5.1. Samples are stored at ≤ 6°C (not frozen) and must be analyzed within 28 days of collection to avoid qualification.

6. SAMPLE ANALYSIS/QUANTITATION (SEE DEP SOP NU-033)

Note: Allow the samples to come to room temperature prior to measuring the conductivity.

Note: This SOP should be used in conjunction with SOP NU-060 – Automated PC-Titrate Instrument Operating Procedure, which gives a more detailed description of the instrumentation.

6.1. Make sure all sample tubes have their caps removed prior to operation of the instrument or the conductivity probe and sample needles will be damaged.

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6.2. General operation of electrode – The electrode is stored dry automatically and must be conditioned prior to use by running at least one rinse cup prior to the start of analysis. Electrode is fragile; use caution when moving.

6.3. Meter Calibration – Calibrate the meter using the conductivity calibration standard (4.5.). Refer to page 11 of Model 4510 Conductivity Meter Operator Manual for details.

6.4. Start-up of the PC-Titrate Software – Log in to the PC-Titrate software; choose the appropriate method (conductivity alone or in combination with other tests). Set up the run sequence corresponding to the timetable of PC-Titrate software (see DEP SOP NU-060 for details).

6.5. Loading samples – Pour or filter 45 – 47 mL of sample or standard into a 50 mL PP centrifuge tube. If samples will only be run for conductivity, only 35 – 40 mL of sample or standard is needed. Load the sample tubes onto the autosampler in sequence determined in section 6.4. It is recommended to run a DI water sample at the very beginning as a rinse to clean up the system and condition the probe.

Example Run Sequence:

Rinse – Tap water
Conductivity Calibration Standard (4.5.)
Rinse – DI water
MDL (blank – DI water)
CHCK4 (4.4)
ALTQC (4.6, filtered)
1M COND (4.2.)
Conductivity Calibration Standard (COND CAL) (4.5.)
Rinse – DI water
Blank – DI water
MBLK – Method blank – filtered DI water (one per batch)
LFB_CHCK4 or **LFB_CHCK2**
Batched samples: one sample run in duplicate (sample ID_D) for each batch of max. 20 samples.
CHCK2 – alternate with CHCK4 every 20 cups
Blank – DI water

Note: Samples and QC do not need to be filtered if conductivity is the only analyzed test of the run. Samples should be filtered if they are turbid or have obvious particulates AND if alkalinity and/or fluoride are being analyzed as well. The ALQTC must be filtered if any samples in the analytical batch are filtered. The MBLK must be filtered if any samples in the prep batch are filtered. Filtered samples and QC are identified on the backlog and/or bench sheet with an F.

6.6. Click on the START button to start the run.

7. CALCULATIONS

7.1. The specific conductance is reported in micromhos per centimeter (μmhos/cm) at 25 °C. The conductivity meter automatically carries out the temperature

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compensation. The reference temperature is preset to 25 °C. The temperature coefficient is set to 1.91%.

7.2. For general calculations (including relative percent difference (RPD)), refer to the FDEP Quality Manual Section 5.9.

8. QUALITY CONTROL/DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES (SEE DEP SOP NU-038 AND NU-043)

8.1. The conductivity meter is calibrated at the start of every analytical run according to the manufacturer's instructions (see 6.3.). The calibration is acceptable if the initial sequence of check standards, as described in 8.2, show recoveries within the specified acceptance limits.

8.2. A blank, a 111,900 µmhos/cm high calibration check standard (1M COND, 4.2), a 73.9 µmhos/cm continuing calibration verification (CCV) standard (CHCK4, 4.4.), and a QC standard (ALTQC, 4.6.) must be analyzed prior to running samples. Acceptance limits for the recovery of the blank are < 2.0 µmhos/cm and > -2.0 µmhos/cm. Acceptance limits for the recovery of the high check standard and the CCV standard are 85 – 115%. Acceptance limits for the recovery of the QC standard must be within the manufacturer's certified limits but not exceed 85 – 115%.

8.3. Analyze a blank and a CCV (CHCK2 or CHCK4) standard every 20 cups tested and at the end of the analyses. Acceptance limits for the recovery of the blank is < 2.0 µmhos/cm and > -2.0 µmhos/cm, and 85 – 115% for CCVs.

8.4. A method blank (MBLK) and LFB (LFB_CHCK2 or LFB_CHCK4) are also run with every batch (20 samples or less). Acceptance limits for the recovery of the MBLK are < 2.0 µmhos/cm and > -2.0 µmhos/cm, and 90 – 110% for the LFB.

8.5. For every analytical batch of 20 or less samples, a duplicate sample must be analyzed. The RPD must be less than 20%.

8.6. Sample results are compared to the sample's field conductivity shown on the backlog. If the RPD between the lab and field results is not less than 20%, the results must be confirmed.

8.7. For general method performance and acceptance criteria for QC measures and corrective action for out-of-control data and contingencies for handling out-of-control or unacceptable data, refer to DEP SOPs NU-038 and NU-043.

8.8. Calibration – The calibration standard (4.5.) is the Conductivity Calibration Standard (approx. 1409 µmhos/cm at 25 °C) or equivalent. Every day samples are analyzed, a new calibration is performed at the beginning of the analysis.

8.9. The relative error of the calibration is evaluated by analyzing the low check (73.9 µmhos/cm, CHCK4) and the Conductivity Calibration Standard (1408.8 µmhos/cm, COND CAL) following the calibration, prior to samples being analyzed. Acceptance limits for recovery are 85 – 115%.

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8.10. Annual MDL verification is performed using the LIMS statistics tracker module (see DEP SOP NU-043). Method blank (MBLK) data is collected and utilized for the ongoing MDL verification.

9. DATA ARCHIVAL

9.1. All analytical results are automatically saved in the database of the instrument software. Raw data is retrievable with the 'HISTORICAL DATA' function of PC-Titrate software. At the beginning of every month, the raw data is moved to the network drive by the analyst for archiving in the PCT BACKUP SYSTEM 1 (for PC-Titrate 1) or PCT BACKUP SYSTEM 2 (for PC-Titrate 2) folder located at: \\floridadep\data\labs\Lab3\Chem_Data\Inorganic\Nutrients\Archive\PC-TITRATE\.

9.2. A tab delimited text file for each run must be exported to the network drive: \\floridadep\data\labs\Lab3\Chem_Data\Inorganic\Nutrients\RawData\Automatic Titrators\PC-Titrate1\ or \\floridadep\data\labs\Lab3\Chem_Data\Inorganic\Nutrients\RawData\Automatic Titrators\PC-Titrate2\, depending on which instrument is used. The file is stored in the analysis year subfolder for the instrument used. The file name should use the format YYMMDDN-A# where YY is the year, MM is the month, DD is the day, N is the first letter of the test/s conducted, A is auto-titrator, and # is 1 or 2 which indicates what instrument was used (e.g., fluoride and conductivity run = 120206FC-A1). This file is used by QC manager for data processing and uploading into LIMS.

9.3. The raw data is archived in paper format. A report folder is created for each analytical run. A folder may contain more than one analysis (e.g. Alkalinity, and Conductivity, and/or Fluoride) in it if the analyses are part of the same analytical run. The folder is labeled with the test (ALK, W-COND, and/or W-F), filename/s (YYMMDDN-A#), and initials of the analyst.

9.4. Each report folder should contain the following items – general results report, calibration report(s), running list report (bench sheet), reagent and standard logsheet(s), and a copy of the data and QC assessments uploaded from QC Manager to LIMS at the time of test authorization.

9.5. The report folders are on file with the nutrients and general chemistry supervisory personnel. Periodically, the files are moved to the State Records Center for long time storage according to DEP SOP LB-006.

9.6. The analytical file can be authorized online if necessary by scanning the entire folder into the correct year on the Nutrients drive at \\floridadep\data\labs\Lab3\Chem_Data\Inorganic\Nutrients\RunData\AnalysisFolders\Auto-T\. Once the authorizer has made comments and digitally signed all items of the pdf after reviewal, the QC report from QCM is saved as YYMMDDN-A#_Authorization and digitally signed as well. The signed analytical file and QC report is saved into a folder. The entire contents of this folder is then printed and archived with the original paper format.

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9.7. Method validation data is on file with the supervisor. Digital copy is also stored on the network, under an appropriate sub-folder in \\floridadep\data\labs\Lab5\Chemistry\Inorganic\Nutrient\Validations\PC Titrate.

10. MAINTENANCE OF ELECTRODE

10.1. Clean a dirty electrode with detergent and/or dilute nitric acid (1%) by dipping the cell into cleaning solution and agitating for two to three seconds. Grease, oil, fingerprints and other contaminants on the sensing elements can cause erroneous measurements and erratic responses. Refer to electrode instructions for further information on cleaning and re-platinizing conductivity cells.

10.2. Refer to DEP SOP NU-060 Section 5 for other maintenance procedures.

11. SAFETY AND HAZARDOUS WASTE MANAGEMENT/POLLUTION PREVENTION

11.1. Review the laboratory Health and Safety Plan (accessible at https://floridadep.sharepoint.com/dear/SitePages/Lab%20Health%20and%20Safety.aspx).

11.2. Safety glasses, gloves and lab coats should be worn at all times whilst handling samples and reagents.

11.3. Read the MSDS information for safe reagent and sample handling.

11.4. Dispose of excess samples by flushing them down the sink with plenty of water.

12. REFERENCES/DEFINITIONS

For definitions see section 3 of the FDEP Quality Manual. All abbreviations used throughout the document are defined at least once in the document usually at the first time of use.

12.1. EPA Method 120.1, (Rev. 1982).

12.2. Model 4310 and Model 4510 Conductivity Meters Operating Manual.

12.3. DEP SOP LB-006, Standard Operating Procedure for Records Maintenance and Storage.

12.4. DEP SOP NU-033, Summary of Analysis Procedures for the General Chemistry and Nutrients Workgroups.

12.5. DEP SOP NU-038, Nutrients and General Chemistry: Quality Assurance and Quality Control.

12.6. DEP SOP NU-041, Reagent Preparation Procedure.

12.7. DEP SOP NU-042, Standard Preparation Procedure.

12.8. DEP SOP NU-043, Nutrients and General Chemistry Quality Assurance and Data Authorization Guidelines.

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12.9. DEP SOP NU-060, Automatic PC-Titrate Instrument Operating Procedure.

12.10. Quality Manual, Bureau of Laboratories, FDEP.

12.11. Laboratory Health and Safety Plan.

Appendix of Significant Changes

03/02/2009	Added new high-level check standard to Sections 5.2 and 9.1
02/05/2010	Clarified the Sample Handling and Preservation in Section 6 and the acceptance limits for the ALTQC standard in Section 9.1.
02/03/2015	Data archival information was clarified in Section 9.
02/04/2016	File paths and web addresses were updated.
02/14/2018	Storage location for the Certificates of Analysis of purchased reagents and standards changed to the network drive. Acceptance limits for the LFB and Cal check standard added.
12/10/2019	The run sequence was clarified in Section 6. Acceptance criteria for quality control measures were updated in Section 8.
12/28/2020	In Section 3, the instrumentation, equipment, and supplies were updated and inputted into table format. In Section 4, chemicals were updated and inputted into table format. Preparation procedures for reagents and standards were reformatted.
01/18/2022	Added statement about the evaluation of relative error of the calibration. Made the low check (CHCK4) required to be run first, rather than the option of CHCK4 or CHCK2.
07/14/2023	Updated data drive file path links. Updated the preparation information for the KCl solutions in section 4.2 and 4.3.
10/01/2024	Updated data drive file path links.

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