

Standard Operating Procedure

Conductivity

SOP # 611S

Revision 3

9/24/98

Prepared By:

PROPRIETARY



Approvals:



Section Manager



Laboratory Manager



Quality Assurance



Laboratory Director

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SOP No.: 611S

Title: Conductivity

Revision No.: 3

Revision Date: 9.24.98

An annual review has been performed on this SOP as required by ARI's Quality Assurance Program. The following staff members have reviewed this SOP and confirm that no modifications are required at this time.

[Signature]
Laboratory Section Supervisor

5-2-01
Date

David R Mitchell
QA Program Manager

5-2-01
Date



SOP No.: 6115

Title: Conductivity

Revision No.: 3

Revision Date: 9-24-98

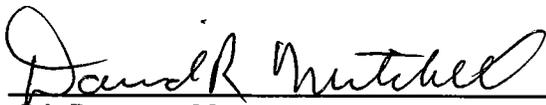
An annual review has been performed on this SOP as required by ARI's Quality Assurance Program. The following staff members have reviewed this SOP and confirm that no modifications are required at this time.


Laboratory Section Supervisor

1-25-00
Date


Laboratory Manager

1/21/00
Date


QA Program Manager

1/24/00
Date



STANDARD OPERATING PROCEDURES CONDUCTIVITY
METHOD: ELECTROCHEMICAL CONDUCTANCE SM 2510 EPA 120.1

HOLDING TIME: 28 days
PRESERVATIVE: None.

1.0 Scope and Application

Conductivity is an expression of the ability of water to conduct electric current. This ability is dependant upon the concentration of inorganic ions (salts or electrolytes) in solution and hence conductivity is also an estimate of the concentration of total dissolved solids (TDS).

TDS by conductivity probe analysis is only a rough approximation. Conductivity measures only ionized constituents. Non-ionized constituents (e.g. non-polar organics, particulates, microbes) are not detected but can contribute to the TDS load. Conductivity in $\mu\text{mhos/cm}$ is multiplied by a conversion factor which may range from 0.55 - 0.80 with a routine standard factor of 0.66. Do not use the probe for routine analysis of TDS, use the gravimetric technique.

Conductivity is measured on aqueous solutions or extracts. The measurement can also be applied to soils and forms a basis for defining soil salinity. Soil conductivity is determined by measurement of an aqueous soil extract. Salinity is defined for the analysis of a "saturation paste" extract but other extraction ratios (1:1, 1:5) are easier to perform and can also provide useful information (Methods of Soil Analysis). We typically use a 1:1 soil water ratio for extraction of aqueous solutions for soil conductivity.

Salt concentration (mg/L) in a soil extract is roughly related to conductivity by multiplying the measured conductivity ($\mu\text{S/cm} \times 0.001 = \text{mS/cm}$ or dS/m) by 640. Other useful relationships are shown in the table below (derived from U.S. Soil Salinity Laboratory Staff, 1954, U.S. Dept Agriculture Handbook No. 956)

Conductivity of Saturation extract (mS/cm)	Total Salt Content (%)	Classification
< 2	< 0.1	Nonsaline
2 - 4	0.1 - 0.15	slightly saline
4 - 8	0.15 - 0.35	moderately saline
8 - 16	0.35 - 0.70	very saline
> 16	> 0.70	extremely saline

The physical measurement is "Specific Conductance" (K) which is the reciprocal of the resistance of a 1 cm cube of water at 25C. Since conductance is the reciprocal of resistance (measured in ohms), the units of conductance are "mhos". In International System (SI) units, the reciprocal of the ohm is siemens (S). The observed conductance depends upon electrode geometry (area and distance between) and for fixed electrodes, these define the cell constant (1.0/cm for our conductivity cell). Conductivity then is the product of the specific conductance times the cell constant which yields the units of mho/cm.

Conductivity is strongly dependent upon temperature and measurements should be made at 25 C or the temperature of measurement is determined and the value is corrected to 25 C. Conductance is read directly in a conductivity meter which yields values of micro- to milli-mhos dependant upon scale (our conductivity meter reads in units of mS or μS). Readings should be taken near room temperature (preferably 25C) and the temperature should be recorded. Standardization of the meter is done by measurement of a potassium chloride solution, 0.0100N, which has a theoretical conductivity of 1413 $\mu\text{mhos/cm}$ (1413 μS) at 25C.

The Conductivity Probes used provide readings which are temperature compensated to 25C and no additional calculation is required.



2.0 Definitions

2.1. International System of Units (SI). In the international system, conductivity is reported as millisiemens/meter (mS/m) where $1\text{mS/m} = 10\mu\text{mho/cm}$. More generally, $1\mu\text{S/cm} = 1\mu\text{mho/cm}$. To report in SI units, divide $\mu\text{mho/cm}$ or $\mu\text{S/cm}$ by 10.

1 mho = 1 Siemen(S)=10 deciSiemens (dS)= 10^3 milliSiemens(mS)= 10^6 microsiemens (μS)

2.2. NIST. National Institute of Standards and Technology

3.0 Supplies and Equipment

3.1 Equipment

Orion Model 115 Conductivity meter (temperature compensated). Range: 0 to 199,900 μS

Corning Checkmate Conductivity Meter (temperature compensated). Range of analysis: 0.01 to 19.99 μS .

3.2 Reagents

3.2.1. Potassium Chloride Calibration Standard (0.0100 N KCl). Dissolve 745.6 mg anhydrous KCl (dried at 105 C) in fresh DI water and dilute to 1,000 mL. This solution has a conductivity of 1413 $\mu\text{mho/cm}$ (1413 $\mu\text{S/cm}$) at 25C and should be used for primary calibration of the conductivity meters. Store in tightly closed container to avoid evaporation. Prepare fresh standard every 6 months. Alternatively, use the primary KCl standard from Orion (1413 $\mu\text{S/cm}$ Conductivity Standard, Orion # 011007).

3.2.2. Calibration Verification Standard (CVS). This standard should be derived from a source other than that used for primary calibration. The standard should be an NIST Traceable Conductivity Standard (Fisher No.09-328-3 or VWR No 23226-625). Conductivity is approximately 1000 $\mu\text{mhos/cm}$ at 25C (varies from Lot to Lot). (These solutions will also contain a value for dissolved solids and hence may be used to verify TDS readings).

3.2.3. De-ionized Water. Type I water is defined as a water having a specific conductance $<0.1\mu\text{mho/cm}$ (or a resistivity >10 megohm, Standard Methods 1080, Page 1-32) which should be satisfied by proper maintenance of our deionized water system. In practice, our DI water quality varies between Type I and Type II. Conductivity will increase upon storage of the water (air contact and dissolution of materials from the container wall) hence, use only freshly delivered water for preparation of conductivity standards and calibration blank analysis.

4.0 Documentation

NA

5.0 In-house Modifications from Referenced Method

NA

6.0 Procedure

6.1. Initial procedures

6.1.1 Aqueous Solutions. Obtain a copy of the ConductivityTemplate file (ARI 6019) from the computer. The file will be opened as *CondTemplateXX*. Note that the current date ("=now()") will be displayed in the "DATE" cell. This is used for comparison to the last date of cell constant adjustment. You must enter the current date to over-ride the value in the date cell, otherwise the current date will be displayed every time the benchsheet is opened. The benchsheet has one set of initial and continuing calibration blanks and standards with space for 10 intervening samples. You may **Copy** and **Insert Paste** the sample blocks and CCB, CCV rows as necessary to fit the needs of the batch run. This benchsheet will be used for handwritten data entry as you proceed through the analysis. Using the **Save As** option, save the file according to our standard benchsheet file format (Parameter MMDDYY Seq., e.g. "Cond031495 1") and Print a copy. You will use the same file later to enter the batch run data from your handwritten benchsheet.



Calibrate the conductivity meter and analyze the sample as directed below (6.2 for Orion Model 115 and 6.3 for Corning Checkmate)

6.1.2. Soil Extracts (1:1 Soil:Water Extraction).

Obtain a copy of the Soil pH-ConductivityTemplate file (ARI 6043S) from the computer. The file will be opened as "6043S pH/CondTemplateXX". This benchsheet will be used for handwritten data entry as you proceed through the analysis. Using the **Save As** option, save the file according to our standard benchsheet file format (Parameter MMDDYY Seq., e.g. "SoilCond031495 1") and Print a copy. You will use the same file later to enter the batch run data from your handwritten benchsheet.

6.1.2.1. Weigh out 40 grams of fresh weight soil and transfer to a 50 mL centrifuge cone. Add an equivalent weight / volume of fresh DI water (i.e. if 40 grams soil, add 40 mL DI).

6.1.2.2. Transfer the centrifuge cone to the mechanical shaker and shake for 1 hour.

6.1.2.3. Centrifuge the shaken sample to consolidate the solids and then filter through Whatman 42 filter paper to remove remaining suspended material.

6.1.2.4. Analyze an aliquot of the clarified extract as directed below (6.2 or 6.3, dependent upon meter used). If pH is to be determined on the extract, measure on a separate aliquot or, to avoid possible contamination from the KCl electrolyte on the pH probe, after the conductivity is completed.

Different units are used for expressing soil conductivity, decisiemens / meter (dS/m), millisiemens / centimeter (mS/cm), microsiemens / centimeter (μ S/cm). Our results are expressed in units of μ S/cm hence the conversion would be
$$\mu\text{S/cm} \times 0.001 = \text{dS/m} = \text{mS/cm}$$

Salt concentration (mg/L) in a soil extract is roughly related to conductivity by multiplying the measured conductivity (μ S/cm \times 0.001 = mS/cm or dS/m) by 640.

6.2. Procedures, Orion Model 115

6.2.1 Set-up. verify that the conductivity probe is attached, ATC is active ("ATC" indicator is displayed), the temperature coefficient (set-up S-1) is 2.1% and the reference temperature (set-up S-3) is 25C.

6.2.2. Calibration. Two modes of calibration are possible on the Orion 115, "DirectCal" and "Cell Constant Adjustment". We will use the DirectCal approach for routine calibration and the Cell Constant Adjustment approach for periodic adjustment/verification of the cell constant (90 day frequency) or when calibration difficulties are encountered with the DirectCal approach.

For either procedure, calibration will be conducted using the 1413 Conductivity Standard (prepared 0.01 N KCl or the Orion commercially prepared standard). For most accurate calibration, the standard should be at or near the reference temperature of 25C. Do not try to calibrate with a cold standard.

6.2.2.1. Direct Cal.

1. Press the **CAL** key twice. The "CALIBRATE" indicator should appear in the display
2. Press the **CAL** key until the range displays the 1999 μ S range (this is the range for the 1413 standard)
3. Insert the probe into the standard and gently agitate to remove any air bubbles. The "READY" indicator will be displayed when a stable reading is attained. Note the temperature of measurement and record it on the benchsheet. The "Temperature Corrected Value" (TCV) for the 1413 standard will be calculated on the benchsheet over a temperature range of 13 to 27C. If the temperature is outside this range, determine the value from the Table on page 8 of the operating manual.
4. Enter the TCV into the meter by scrolling with up or down arrows. When the correct value for the TCV is displayed, accept it by pressing the **YES** key. At this point, the display should go blank while the meter calibrates and then returns to the measurement mode.



5. Remove the probe from the 1413 standard and rinse thoroughly with de-ionized water. Verify that the meter is in the measurement mode for conductivity. Determine conductivity values for the de-ionized water blank and the Calibration Verification Standard. Record values onto the benchsheet and verify a blank $< 1 \mu\text{S}$ and verification standard recovery within 10% of the known value. Proceed with samples only if verification is successful.

6.2.2.2. Cell Constant Adjustment. This procedure should be run every 3 months (90 days) and/or whenever problems are encountered with the DirectCal approach. Whenever the benchsheet is opened, the current date will appear in the "DATE" cell. This will be evaluated with respect to the date of the last cell constant adjustment. If 90 or more days have elapsed since the last adjustment date, flags will appear which warn the operator to adjust the cell constant. Otherwise, the "Status" box will say "Constant OK!".

1. Press the CAL key once to begin calibration. The "CALIBRATE" indicator and the "last cell constant" should appear in the display. Record the "last cell constant" into the "Current Value" cell of the benchsheet
2. Insert the probe into the standard and gently agitate to remove any air bubbles. Accept the current value for the cell constant by pressing the YES key until the meter automatically returns to the measurement mode (repeated pressing of the YES key cycles through decimal placement and digit scrolling). The "READY" indicator will be displayed when a stable reading is attained. Note the temperature of measurement and record it on the benchsheet. The temperature corrected value for the 1413 standard will be calculated on the benchsheet over a temperature range of 13 to 27C and automatically entered into the "Expected" cell of the benchsheet. If the temperature is outside this range, determine the value from the Table on page 8 of the operating manual and then manually enter the "Expected" value. Enter the displayed value into the "Displayed" cell of the benchsheet.
3. The benchsheet will automatically calculate the percent error associated with the conductivity values and an adjusted value for the cell constant (the value appearing in the "Adjust to" cell of the benchsheet).
4. If the error is greater than 1%, enter the "Adjust to" value as the new cell constant. Do this by repeating step 1 using the up and down arrows for decimal placement and scrolling of the digits. Accept the final value by pressing the YES key and the meter will return to the measurement mode.
5. Remove the probe from the 1413 standard and rinse thoroughly with de-ionized water. Verify that the meter is in the measurement mode for conductivity. Determine conductivity values for the de-ionized water blank and the Calibration Verification Standard. Record values onto the benchsheet and verify a blank $< 1 \mu\text{S}$ and verification standard recovery within 10% of the known value. Proceed with samples only if verification is successful.

6.3 Procedure, Corning Checkmate Meter

6.3.1. Make sure the conductivity sensor is in place and that the probe and plastic shield are clean. Rinse probe and shield with DI water and then dry with a Kimwipe.

6.3.2. Use 2-point calibration for each use. Hold clean dry probe in free air and press CAL. "CAL 1" should be displayed and the reading should be 0.00 μS . Place the sensor in the 0.0100 N KCl solution such that there are no bubbles in the measuring chamber and electrode surfaces are totally immersed. Allow approximately 1 minute for temperature equilibration. Press CAL and "CAL 2" should be displayed followed by a reading 1413 μS . Record both calibration readings on the benchsheet. If the recorded values differ from 0.00 or 1413 $\pm 1\%$, the calibration has failed and a "Recalibrate" message will appear.

6.3.3. Begin the analysis by measuring the concentration of a fresh DI water blank solution and then the CVS. The blank reading should be $< 1.0 \mu\text{S}$ and the CVS should agree within $\pm 10\%$ of its certified value. Recalibrate the instrument if these conditions are not satisfied.

6.3.4. Rinse the probe and shield with DI water. Insert probe into sample to be measured making sure there are no air bubbles and that the electrodes are covered by solution. Press READ and then allow the instrument to come to a stable reading. Note the units for the reading (should be either μS , mS or S) and record on the bench sheet along with the temperature of measurement.



If the reading is offscale or greater than 20 mS, dilute the sample with fresh DI water and repeat the measurement. Record the dilution factor as:

$$DF = \text{mL sample} / (\text{mL DI} + \text{mL sample})$$

6.3.5. Press MODE and the display should change to TDS. Record the mg/L value (This takes only a few seconds and may prove to be useful in further data analysis)

7.0 Review

7.1. The supervisor reviews Service Request, enters information into the Conventionals database and assigns samples to the analyst.

7.2. The analyst verifies Service Request, reviews the SOP and proceeds with the analysis.

7.3. The final computer generated result is placed into the method folder in chronological sequence and a copy is placed into the job folder.

7.4. The supervisor reviews the job folder for completeness of analysis (all requested parameters have been run) and sufficiency of Quality Control.

7.5. Completed analysis is given to the Data Section for QC evaluation and entry of data into LIMS (initial creation of worklist files).

7.6. The completed analysis package and worklist files are then reviewed by the Conventionals QA Reviewer. All Conductivity QC data (calibration blanks and verification standards) are entered onto control charts for plotting chronological sequence of analysis. Control limits are set at ± 2 and ± 3 standard deviations of the historical average for "warning" and "control" limits, respectively. Worklists are then distributed and the final report printed.

7.7. The final report is then again reviewed for accuracy and completeness, signed by the Conventionals QA reviewer and delivered to the Project Manager for final disposition to the client.

8.0 QC Limits

8.1. The conductivity of the calibration blank solution should be less than 1.0 μS . The calibration blank will be run immediately after calibration and then again after every 10 samples analyzed for continuing verification.

8.2. The value for the NIST traceable calibration verification standard (CVS) should be within $\pm 10\%$ of its certified value. The CVS will be run immediately after calibration and then again after every 10 samples analyzed for continuing verification.

8.3. Duplicate analyses are run with each job number or batched client jobs. Duplicate RPD's should be within $\pm 20\%$.

9.0 Corrective Actions

9.1 If holding times (28 days, or 24 hours if unfiltered) have been exceeded or if there is insufficient sample to run the analysis, the supervisor will be immediately notified. The supervisor will inform the project manager for resolution with the client.

9.2. If any calibration blank value is $> 1.0 \mu\text{S}$, the probe has become contaminated or the quality of the DI water is suspect. Thoroughly rinse the probe and shield with fresh DI water and repeat the blank measurement with fresh DI water. If the blank reading is still $> 1 \mu\text{S}$, stop the analysis and determine the source of problem. All samples must be bracketed by in-control blanks hence, re-run all samples between the last in-control blank and the out-of-control blank. Notify the supervisor of any conductivity blank problems as these may indicate problems with the DI source water.

9.3 The instrument is calibrated against a 0.01 N KCl solution. Calibration verification is conducted by measuring an NIST traceable CVS prior to any sample analysis. If the reading for the initial



CVS is not within $\pm 10\%$ of its certified value, the calibration is suspect and the meter will be re-calibrated. If the recalibration yields a CVS reading still outside the prescribed limits, the 0.01N KCl standard is suspect and a fresh KCl calibration standard should be prepared and the instrument re-calibrated and verified. Do not proceed with the analysis unless the calibration has been verified.

If any continuing CVS is not within the prescribed limits, thoroughly rinse the probe with DI water and repeat the CVS determination. If the reading is in-control, proceed with the analysis. If the reading is still out-of-control, recalibrate and verify the meter. All samples must be bracketed by an in-control CVS hence, re-run all samples between the last in-control CVS and the out-of-control CVS.

- 9.4 If duplicate RPD's are outside the prescribed limits, this would indicate possible contamination problems. Thoroughly rinse the probe and shield and repeat the analysis for a triplicate determination. If the triplicate agrees with either the original or duplicate ($\pm 20\%$), reject the outlying analysis and report the two agreeing readings as duplicates along with the associated relative percent difference (RPD). If the triplicate does not agree with either the original or duplicate, report all three determinations along with the associated relative standard deviation (RSD).

10.0 Miscellaneous Notes and Precautions

NA

11.0 Method References

Standard Methods for the Examination of Water and Wastewater. 18th ed. 1992. Method Number 2510. Conductivity

Methods for Chemical Analysis of Water and Wastes. EPA 600/4-79-020 (Rev March 1983). Method 120.1

Methods of Soil Analysis, Agronomy Part 2 No. 9, 2nd ed.. Chapter 10, Soluble Salts (10-2.3.2, 10-3.3).

Models 105 and 115 Conductivity Meters. Instruction Manual. Orion 1996.

