Abstracted from Laboratory Operations, Pg. 48, Section 4.5.4. Conductivity
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Conductivity
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Calibration - Reagents and Solutions

i.   DI water, resistivity >18.0 MΩ
ii.   potassium chloride, KCl, pro analysis (p.a.) quality
iii. stock solution A, 0.1M KCl: 7.456 g of pre-dried (2 hour at 105°C) KCl dissolved in DI water and diluted with DI water to 1000 mL at 25°C
iv.   stock solution B, 0.01M KCl: 10 mL of 0.1M KCl (stock solution A) diluted with DI water to 100 mL at 25°C

Keep stock solutions in tightly closed high density polyethylene (HDPE) bottles. Stable for one year.

Calibration - Procedures

1) Calibrate the conductivity meter and cell using more than one standard solution, i.e., perform a multipoint calibration. With each set of precipitation samples, prepare a set of 0.0001M, 0.0005M, and 0.001M KCl standard solutions from the 0.01M KCl stock solution B by diluting with DI water.

2) Measure the conductivity of the DI water used in preparing the standard solutions.

3) Measure the conductivity of the KCl standard solutions and plot them on a graph. If these measurements are outside the limits given in Table 4.10, consult the instrument manufacturer's manual for corrective actions. Repeat the calibration.

4) Read the conductivity of precipitation samples directly from this calibration plot.

Table 4.10: Calibration standards for conductivity (KCl solutions at 25ºC)

Concentration KCl (M)	Theoretical ($\mu S\ cm^{-1}$)	Conductivity ($\mu S\ cm^{-1}$) Upper limit	Conductivity ($\mu S\ cm^{-1}$) Lower limit
0.0001	14.9	16.5	13.5
0.0005	73.9	77.8	70.2
0.0010	147.0	149.0	145.0

Quality Control

Natural precipitation deteriorates with time, even if refrigerated, and should be avoided for use as a QCS for conductivity measurements. Here is a list of recommended QC solutions:

• Certified Reference Material
• pooled inter-comparison samples
• simulated samples made from an alternate standard material

Prepare at least three QC solutions that span the standard range. These solutions should test the low, middle and high range of the calibration curve.

Analytical Procedures

1) Thoroughly rinse the outside of the cell and internal poles with DI water.

2) Rinse the outside of the cell and internal poles with the sample, whether a QCS or precipitation sample. Discard this sample and do not wipe the probe dry.

3) Fill the cell with fresh sample to be measured.

4) Ensure that the poles are covered by the sample and that all air bubbles are eliminated by tapping the outside of the cell.

Note: The conductivity of a solution depends on temperature. When the temperature of a solution rises one degree, the conductivity rises about 2% to 2.5%, (depending on ionic composition) as a result of decreasing ion hydration and decreasing solution viscosity. To ensure consistent laboratory conductivity measurements, the GAW recommends either of the following procedures:

5) a) Measure the conductivity at 25°C using a water bath to equilibrate and stabilize the temperature. Care must be taken to avoid sample contamination from the water bath.

- OR -

b) Measure the conductivity at room temperature so long as the temperature ranges from 18°C to 30°C. Use the built-in temperature sensors and algorithms to correct the readout to 25°C. Check the readout against Table 4.11 to ensure that the result of the internal algorithm is consistent.

- OR -

c) Measure the conductivity at room temperature and then correct the measured value to 25°C using the coefficients given in Table 4.11. Example:

$$\varkappa_{25°C}= \varkappa_{RT} \text{ X Correction Coefficient}$$

where: $\varkappa_{RT}$ = conductivity at room temperature

$$\varkappa_{25°C}= \text{conductivity at 25°C}$$

- OR -

d) Measure a standard solution at the same temperature as the samples to calculate a correction factor which accounts for both cell constant and temperature effects. This method is a one-point calibration method that assumes the calibration curve is linear throughout. Using three calibrators describes the calibration curve more accurately accounting for non-linearity.

6) Enter data into the data set. See Laboratory Operations, pg. 25, section 4.3.13 for manual data verification if the conductivity meter does not have a data export function. Report values to the required decimal places and account for missing samples and contamination by adding comments or codes to the sample result.

7) Follow the manufacturer's directions for operation, maintenance and storage of the measurement cell.

8) Between each sample measurement, rinse the cell thoroughly with DI water; then, rinse the cell 2 or 3 times with the sample to be measured before recording the conductivity. (If it is possible that the cell has become contaminated, see Problem 1 in the section on Troubleshooting for corrective actions.)

9) Store the probe according to the manufacturer's recommendations.

Table 4.11. Correction coefficients to adjust conductivity values to 25ºC

Temperature (°C)	Correction coefficient
18	0.865
19	0.884
20	0.904
21	0.923
22	0.940
23	0.961
24	0.980
25	1.000
26	1.020
27	1.041
28	1.061
29	1.080
30	1.100

Troubleshooting

Problem 1: An accumulation of ionic species or an organic film forms on or near the electrode surface causing polarization and contamination.
Solution 1: Clean the cell often. Carefully remove any accumulation by gently wiping the cell with a cotton swab soaked in a mild detergent. Do not use harsh or abrasive materials for cleaning and never touch the probe with bare hands. Thoroughly rinse the probe and poles with DI water to remove all traces of detergent.

Problem 2: Measurements are frequently biased and it is difficult to get correct results.
Solution 2: Calibrate every 30 to 50 samples. Be aware that the cell constant may change. Make sure that there is adequate sample to completely cover the poles. A two-pole cell must be centered in the measuring vessel. Avoid rubbing the probe; pat it dry to avoid static buildup or damage to the probe.

Problem 3: Measurements are affected by temperature differences between samples and standards.
Solution 3: Ensure that the samples and calibration standards are measured at the same temperature and that stirring is the same for both samples and calibration standards.

Problem 4: The cell surface can be sufficiently porous to adsorb ions from solution leading to a carry-over effect from one sample to the next and resulting in a slower response.
Solution 4: A conductivity sensor with an epoxy body and graphite electrodes is recommended for its durability and superior chemical resistance. Also consider a cell with a steel or titanium body.

Problem 5: Air bubbles in the cell result in unstable readings.
Solution 5: Even a tiny air bubble adhering to the electrode surface increases the resistance, which lowers the conductivity reading. Inspect the cell contents and remove air bubbles before every measurement, whether a precipitation sample, a calibration solution, or a QC sample. Tap the probe lightly to dislodge bubbles.

Problem 6: Calibrating the cell yields inconsistent results.
Solution 6: Conductivity calibration standards are not as robust as pH buffer solutions and are more prone to contamination from dilution and from carbon dioxide entering from atmospheric exposure. Use freshly prepared solutions. Never pour used solutions back into the original containers. Use containers with a tight seal and store solutions at room temperature.