# *The Application of Good Laboratory Practice in the Selection and Use of Accurate, Traceable Conductivity Standards*

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## Abstract

*All analytical measurements, including conductivity measurements, must be of suitable accuracy and must be proven correct if they are to be fit for purpose. This paper describes how these requirements are achieved through the application of good laboratory practice in the selection and use of calibration and control standards. For high quality analytical measurements, establishing measurement traceability and quantifying the Uncertainty of Measurement are essential. This paper describes how these factors can be established and the critical role that standards play in determining these factors and thus ensuring the quality of conductivity test measurements. As well as giving specific information on conductivity standards, this paper gives details relevant to the selection and use of all analytical standards.*

## 1 Introduction

Analytical measurements, including conductivity measurements, are taken in a wide variety of applications and critical decisions are made based upon these measurements. These decisions can have a serious impact on product integrity, food safety, human health or environmental protection. It is of utmost importance for analysts to have full confidence in the quality of their measurements to ensure that the decisions made based on these measurements are correct. Poor quality analytical measurements will also generate additional demands on analysts' time and budgets through the need to repeat questionable measurements. It is not sufficient for analysts to be able to achieve the correct test result; they must also be able to prove that their test results are correct.

By complying with the principles of good laboratory practice, analysts can demonstrate that their conductivity test results are correct and fit for purpose. This applies equally to laboratory-based measurements, as well as measurements made using portable and on-line conductivity meters. Fulfilling the requirements of good laboratory practice will demonstrate that the conductivity measurements have comparability and so can be accepted regardless of the measurement system used and the time and place of measurement. This paper describes how traceability of conductivity measurements can be achieved to provide this comparability. Comprehensive information is given on how different types of errors affect the accuracy of a conductivity measurement and how they can be quantified by calculating the Uncertainty of Measurement of the test system. By quantifying the Uncertainty of Measurement, the analyst will be able to determine if his analytical results are fit for purpose.

A thorough explanation is given of the types of conductivity standards that are available to the analyst and their critical impact on the traceability and the quality of the analytical conductivity results. Detailed guidance is given on how conductivity standards affect the Uncertainty of Measurement of test measurements and how calibration and control standards should be selected and used to provide high quality analytical results and compliance with good laboratory practice.

## 2 Comparability

A valid comparison of different conductivity measurements can only be made if they are linked to a common reference that is acceptable

to all of the interested parties – usually an internationally recognised standard. If this comparability is achieved then the test result will be universally accepted regardless of the time and place of measurement and the test method and equipment used. Comparability of conductivity test results is essential for the meaningful evaluation of results for such diverse applications as environmental assessment, purified water assessment, in-process solute concentration assessment and food quality testing. Without comparability, a meaningful assessment of a conductivity test measurement cannot be made.

Comparability is achieved through establishing the traceability of the test measurements – this requires the use of conductivity standards that have proven traceability.

# 3 Traceability

Traceability is defined as the *"property of the results of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties"*[(1)].

The common reference points used for comparing analytical chemical measurements are the S.I. Units. Analysts gain access to S.I. units by using standards that are traceable to the S.I Units. The key elements of each step in the chain of comparisons are:

- Documentation of the relationship to stated reference standards
- Calculation of the Uncertainty of Measurement associated with each step
- Competence of the organisations carrying out each step, including evidence that their methods are technically valid – this may be achieved by demonstration of accreditation to a relevant standard - e.g. ISO 17025[(2)].

Only standards that meet all of these criteria should be used for calibration of conductivity instruments and proof of traceability should be provided in the standard manufacturer's Certificate of Analysis.

The use of standards that are not traceable will mean that the analyst will not be able to make valid comparisons of his test measurements with test measurements taken at a different time or in a different place as these measurements are not linked to a common reference.

## 3.1 Traceability of the Units of Conductivity

To facilitate comparability of results, a unique point of reference is required. This internationally agreed unique point of reference is the S.I. Units (*Systeme Internationale*)[(3)]. The S.I. units are the responsibility of the Bureau of International Weights & Measures (BIPM). There are seven base S.I. units - as shown in Table 1.

| Base Unit Property | Name | Symbol |
|---|---|---|
| Length | metre | m |
| Mass | kilogram | kg |
| Time | second | s |
| Electric current | ampere | A |
| Thermodynamic temperature | kelvin | K |
| Amount of substance | mole | mol |
| Luminous intensity | candela | cd |

**Table 1: S.I. Base Units [(3)]**

| Derived Unit Property | Name | Symbol | Relationship to other Derived units |
|---|---|---|---|
| Force | Newton | N | $N = m.kg / s^2$ |
| Energy | Joule | J | J = N.m |
| Power | Watt | W | W = J / s |
| Electrical potential difference | Volt | V | V = W / A |
| Electrical conductance | Siemen | S | S = A / V |

**Table 2: Examples of SI Derived Units [(3)]**

There are a number of derived S.I. units. The derived units can be expressed by multiplication or division of a combination of the base S.I. units. Special names and symbols have been given to certain derived units – the derived units relevant to conductivity measurement are shown in Table 2. Conductivity measurements are expressed using the units µS/cm – these units are based on the derived S.I. unit Siemen, S, and the base S.I. unit metre, m. Hence, the units of conductivity measurement are traceable to base S.I. units.

## 3.2 Traceability of Standards

### 3.2.1 The Hierarchy of Standards

The hierarchy of the different classes of Standards is shown in Figure 1. Moving down the hierarchy of standards, the accuracy and cost of the standard reduces; but the availability and Uncertainty of Measurement increases. The accuracy of Standards should be the principal factor upon which they are selected – if the accuracy of the Standard results in test measurements of insufficient accuracy then they will not be fit for purpose and an alternative Standard of greater accuracy should be used.

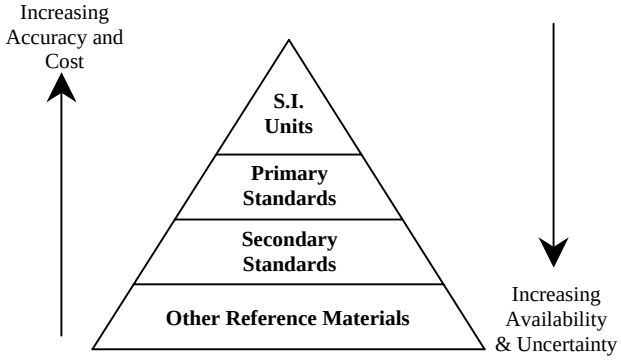


**Figure 1: Hierarchy of Standards**

A **Primary Standard** "is designated or widely acknowledged as having the highest metrological qualities and whose value is accepted without reference to other standards of the same quality" [(4)]. The standard must be pure, stable, have high equivalence and be soluble under the conditions in which it is to be used. In practice, an ideal Primary Standard is difficult to obtain and a compromise between the above ideal requirements is usually necessary. Primary Standards are produced in limited quantities and are expensive, but offer the highest accuracy.

A **Secondary Standard** "has its value assigned by comparison with a primary standard of the same quantity"[(4)] – i.e. a Secondary Standard has its value assigned by a single-step, direct comparison with a Primary Standard. Secondary Standards vary in accuracy, depending on how the comparison with the Primary Standard is performed. For the vast majority of test measurements, Secondary Standards are of sufficient accuracy to generate test measurements that are fit for purpose – a detailed example is given in Section 5.1.

A **Reference Material (RM)** "is a material or substance one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials"[(4)]. 'Reference Material' is a generic term, covering all Standards – Primary and Secondary Standards are high quality sub-sets of Reference Materials. For conductivity measurement, affordable Secondary Standards are widely available and are reasonably priced. This means that lower quality Reference Materials are rarely used for conductivity applications.

A **Certified Reference Material (CRM)** "is a reference material one or more of whose property values are certified by a technically valid procedure, accompanied by a certificate or other documentation that is issued by a certifying body"[(4)]. This certificate will provide detailed information on the analyte values, their associated uncertainties, methods of analysis and traceability. Their production and certification is expensive, therefore they are not used for routine analysis. CRMs are produced by national laboratories as part of their function of providing a practical link to S.I. units for industry.
Producers of CRM's include:

- National Institute of Standards and Technology NIST (USA)*
- Commission of the European Communities BCR (Belgium)
- Laboratory of the Government Chemist LGC (UK)
- National Institute for Environmental Studies NIES (Japan)
- Laboratoire National d'Essais LNE (France).

*CRMs are also referred to as Standard Reference Materials (SRMs) by NIST.

Most CRMs are Secondary Standards, but there are a number of CRMs that are of Primary Standard grade.

### 3.2.2 Traceability of Conductivity Standards

The Organizational Internationale de Metrologie Legale (OIML) and IUPAC specify three Primary Standards for conductivity measurements[5]. These Standards are based on measurements reported by Jones and Bradshaw[6] - the values are outlined in Table 3.

| Demal | κ (µS/cm) | | |
|---|---|---|---|
| | 0 °C | 18 °C | 25 °C |
| 1.0 | 65,140 | 97,810 | 111,310 |
| 0.1 | 7,134 | 11,163 | 12,852 |
| 0.01 | 773.3 | 1,220.1 | 1,408.3 |

**Table 3: Conductivity Values of 0.01 D, 0.1 D, and 1.0 D KCl Solutions [7]**

The unit of concentration, demal scale (D), is defined as an exact mass of potassium chloride in an exact mass of water, and is defined at three concentrations only - see Table 4.

| Demality | g (KCl) / kg (Water) |
|---|---|
| 0.01 | 0.745263 |
| 0.1 | 7.41913 |
| 1.0 | 71.1352 |

**Table 4: Demal Solutions [7]**

To attain accurate and traceable conductivity measurements then accurate and traceable conductivity Standards are required. The highest accuracy is obtained by using Primary Standards. However, the Primary Standards detailed in Table 3 are difficult for the analyst to manufacture. Great care and attention must be taken to produce standards with low levels of uncertainty attached to the standard value. The following materials and equipment must be used for the preparation of a primary conductivity standard:

- Potassium chloride - CRM grade
- Deionised water of known conductivity
- Calibrated and certified analytical balance
- Production equipment and packaging materials must be selected to avoid contamination of the standard.

To fulfil traceability requirements, the analyst must also quantify the Uncertainty of Measurement for the preparation of the Primary Standards.

Due to the difficulty involved in preparation of primary conductivity standards and the expense of the materials and equipment required, the use of Secondary Standards is a common route to providing traceability of analytical results. Primary conductivity standards must be freshly prepared immediately prior to their use – these standards have been selected for their accuracy alone and not for their stability. If the Secondary Standard has fully characterised stability then several aliquots can be used from the same bottle until its expiry date has been reached. Thus, using an appropriate Secondary Standard will save the analyst time and money compared to frequently preparing Primary Standards. It is essential that the Uncertainty of Measurement associated with the stated value of these Secondary Standards is known in order to establish traceability for the test result and to assign an Uncertainty of Measurement to the test result.

## 4 Measurement Accuracy and Uncertainty of Measurement

Analysts must assess if their test measurements have sufficient accuracy for their intended purpose. In order to do this, analysts must be aware of all of the components that have an impact on their measurement accuracy and they must be able to quantify their effect on his measurement accuracy.

**Accuracy** is the closeness of agreement between a test result and the true value of the measurand and is a qualitative term. The Accuracy will be a combination of the Precision and Bias of the test.
**Precision** is "the closeness of agreement between repeated observations"[8] and can be characterised by a standard deviation. Precision quantifies the error caused by random effects. The precision can be quantified by repeated measurements of a standard that is stable and homogeneous.
**Bias** is the difference between the average value of a large set of test results and the true value of the measurand. Bias quantifies the error caused by systematic effects. A large set of test results is required to quantify Bias to ensure that the contribution from random effects is negligible.

These tests must be conducted using a high quality standard.

It is a common mistake to assume that if a set of results shows good precision then they will have good accuracy. This assumption is incorrect, as it does not take any account of the bias of the measurement – good repeatability does not mean that there is good measurement accuracy.

Figure 2 shows four sets of test measurements taken on the same sample.

- Set A has poor precision and bias – these results have a large standard deviation and their mean is far from the true value of the sample.
- Set B has the same poor precision as Set A – the spread of the results is the same; but has improved bias, as the mean is closer to the true value of the sample.
- Set C has the same poor bias as Set A; but has improved precision – the mean is far from the true value of the sample, but the repeatability of the results is good.
- Set D has good precision and bias – these results have good repeatability and their mean is close to the true value of the sample.

The accuracy of the test measurements shown in Figure 2 improves as one moves down and to the right of the figure.

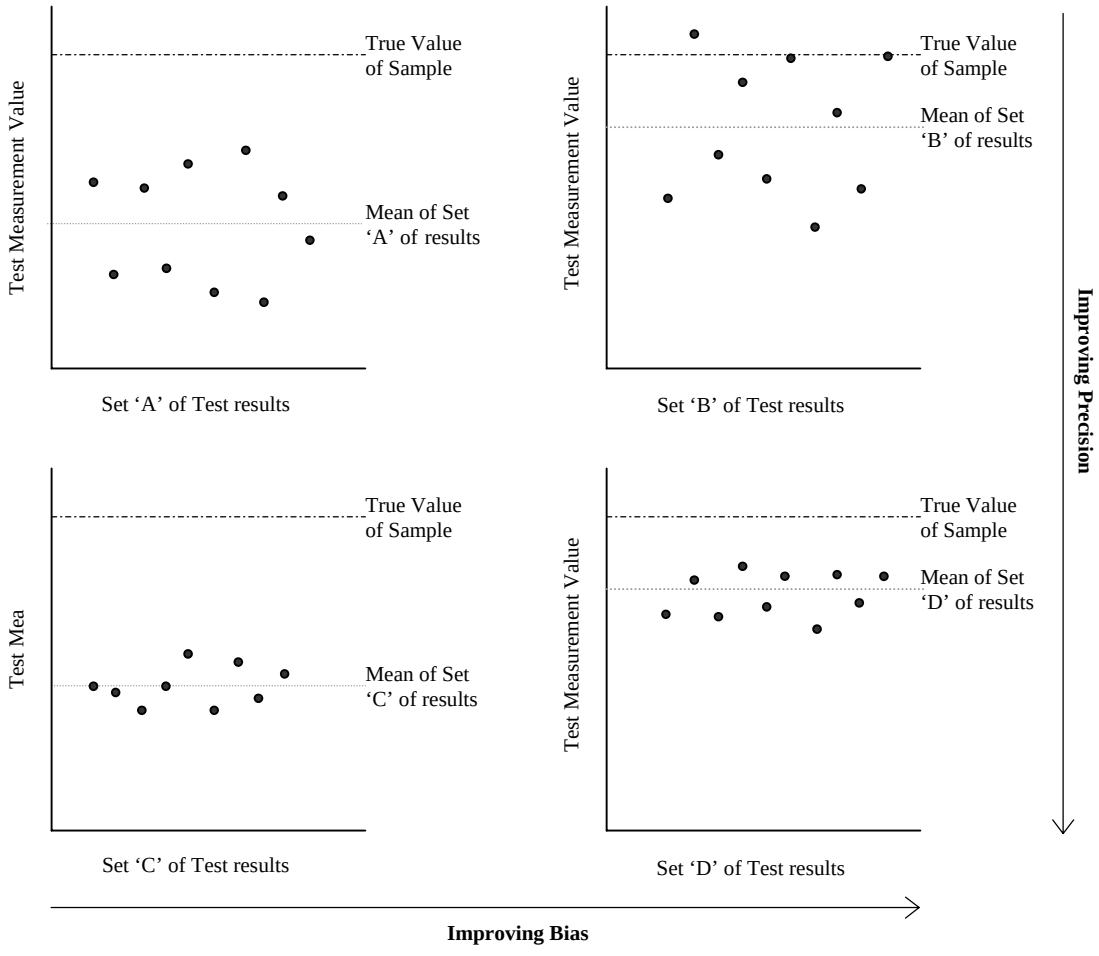


**Figure 2: Precision, Bias and Accuracy of Test Measurements**

Uncertainty of Measurement quantifies the accuracy of the test measurements. Quantifying the Uncertainty of Measurement identifies the contributions from each source of error as well as giving a combined Uncertainty of Measurement for the test system. This will highlight potential modifications to the test method that will improve the measurement accuracy.

## 4.1 Uncertainty of Measurement and Measurement Error

The error associated with a measurement result is defined as "*the difference between the result of the measurement and the true value of the measurand.*"[1].

Uncertainty of Measurement is a measure of the margin of doubt that exists with an analytical result. It is defined as "*A parameter associated with the result of a measurement, that characterises the dispersion of the values that could be reasonably attributed to the measurand*"[1].

All measurements are subjected to error, but it is not possible to quantify the error associated with any single measurement, as the true value of the measurand can never be established. However, quantifying the uncertainty of measurement will give a range of values within which the true value of the measurand can reasonably be assumed to lie. Quantification of the Uncertainty of Measurement also involves assigning a statistical confidence level to the measurement result. By quantifying the Uncertainty of Measurement, the analyst will be able to establish the relationship between a test measurement and the true value of the measurand. Uncertainty of Measurement provides a quantative measure of the accuracy of a test result.

From the definition of traceability (Section 3), it can be seen that quantifying Uncertainty of Measurement is a fundamental requirement to establish the traceability of conductivity standards or a conductivity test measurement.

## 4.2 Sources and Types of Uncertainty

There are many possible sources of uncertainty associated with an analytical result, these include:

- Sampling errors
- Matrix effects
- Temperature fluctuations
- Accuracy of the measuring instrument
- Repeatability of the measuring instrument
- Calibration standards
- The personnel performing the measurement

The possible sources of uncertainty associated with a measurement may be divided into two types[8]:

Type A *(Random Effects)*
Random effects cause errors that vary from measurement to measurement. The Uncertainty of Measurement caused by random effects may be estimated from the standard deviation of a series of measurements taken under the same conditions – i.e. a repeatability study.

Type B *(Systematic Effects)*
Systematic effects result in errors that are constant within the time scale of a repeatability study. As the true value of the measurand can never be established, the exact value of a systematic error cannot be established. However, the Uncertainty of Measurement due to systematic effects can be characterised by the standard deviations of assumed probability distributions, e.g. the resolution of an instrument or data on a calibration certificate.

## 4.3 Quantifying Uncertainty of Measurement

To quantify the Uncertainty of Measurement associated with an analytical process, the analyst is required to examine the full analytical process, from sampling through to reporting of the analytical result, and identify all possible sources of uncertainty. The process of quantifying measurement uncertainty is a four-step process[8].

*Step 1 Define The Measurand.*
The measurand is clearly identified. For conductivity measurement, the sampling process may contribute significant sources of Uncertainty of Measurement – these contributions can only be quantified if the measurand is fully defined.

*Step 2 Identify The Uncertainty Sources.*
A full list of all possible sources of uncertainty must be compiled.

*Step 3 Quantify The Uncertainty Components .* The magnitude of each uncertainty component, $u_i$, is measured or estimated and expressed as a standard deviation.

*Step 4 Calculate The Combined Uncertainty .* All of the sources of uncertainties, quantified in step 3, are combined and expressed in terms of one standard deviation, $u_c$. An Expanded Uncertainty, U, is calculated by multiplying the combined uncertainty by a coverage factor, k. The coverage factor will determine the confidence level associated with the analytical result. The standard coverage factor used for analytical chemistry is k=2 - see Table 5.

| Coverage Factor | Confidence Level |
|---|---|
| 1 | 68% |
| 2 | 95% |
| 3 | 99.7% |

**Table 5: Coverage Factor and Associated Confidence**

## 4.4 Reporting of Test Results and Associated Uncertainty of Measurement

The result, x, should be stated together with the expanded uncertainty, U, and the coverage factor used. The recommended form is:[8]

"Result = x ± U units
The reported uncertainty is calculated using a coverage factor of 2, which gives a level of confidence of approximately 95%"

The expanded uncertainty, U, is reported to two significant digits. As this is an estimate of the range within which the true value of the measurand lies, then quoting more significant digits would imply a greater certainty of the true value of the measurand than can be claimed.

## 4.5 Uncertainty of Measurement for Conductivity Measurements

In order to estimate the uncertainty associated to a conductivity measurement, the sources of uncertainty must be identified. Conductivity measurement may be broken down into two stages - cell constant determination and measurement on the sample. An example of the sources of uncertainty for a conductivity application in which all the measurements are taken with samples placed in a water bath is shown in Figure 3. Analysts must use their experience and knowledge of their own measurement process to identifying sources of uncertainty – factors such as sampling[9] and temperature compensation[10] may also contribute to the Uncertainty of Measurement.

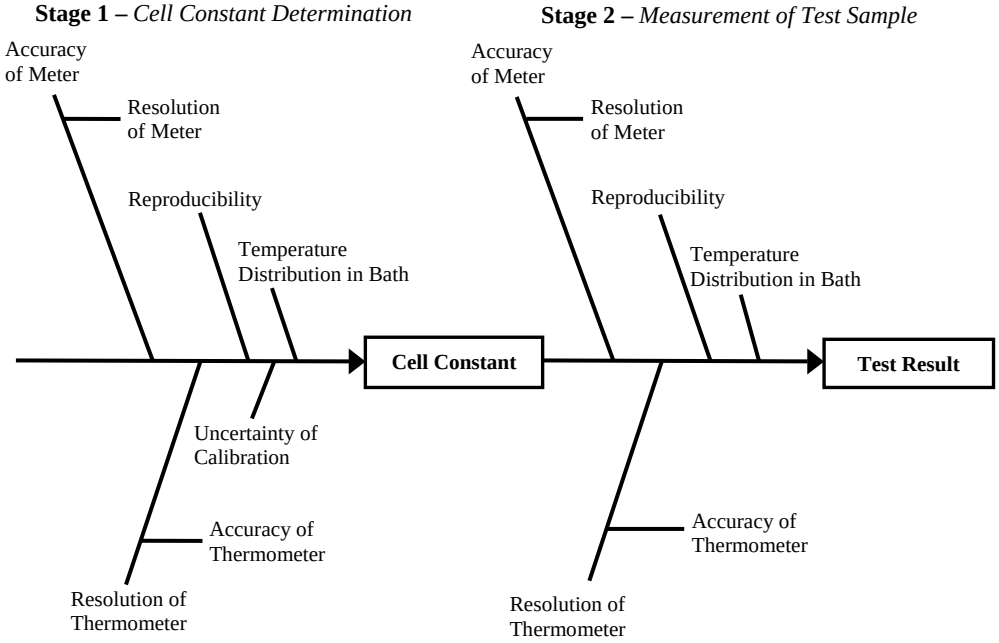


**Figure 3: Cause & Effect Diagram of Sources of Uncertainty**

| Information | |
|---|---|
| Meter | Knick 913 Conductivity Meter |
| Calibration Standard | Reagecon 1413 µS/cm |
| Temperature Coefficient of Variation | 2% / °C |
| Nominal Cell Constant | 0.475 $cm^{-1}$ |
| Resolution of Thermometer | 0.1 °C |
| Reproducibility | 10 Results |
| Nominal Conductivity of Sample | 150 µS/cm |

| Source of Uncertainty | Value | Unit | Probability Distribution | Divisor | $u_i$ (%) | $u_i^2$ |
|---|---|---|---|---|---|---|
| **a. Cell Constant** | | | | | | |
| Accuracy of Meter[11] | 0.5 | % | Rectangular | 1.732 | 0.288683 | 0.08334 |
| Uncertainty of Standard | 1 | % | Normal | 2 | 0.500 | 0.25000 |
| Resolution of Thermometer * | 0.1 | °C | Rectangular | 1.732 | 0.1154734 | 0.01333 |
| Accuracy of Thermometer * | 0.16 | °C | Normal | 1 | 0.1600 | 0.02560 |
| Temperature Distribution in Water Bath * | 0.1 | °C | Triangle | 2.45 | 0.08163 | 0.00666 |
| Resolution of Cell Constant display | 0.001 | $cm^{-1}$ | Rectangular | 1.732 | 0.060503 | 0.00366 |
| Repeatability of Cell Constant | | | | | 0.07921 | 0.00628 |
| | | | | | | |
| **b. Measurement of Sample** | | | | | | |
| Accuracy of Meter | 0.5 | % | Rectangular | 1.732 | 0.288683 | 0.08334 |
| Resolution of Meter | 0.1 | µS/cm | Rectangular | 1.732 | 0.057737 | 0.00333 |
| Resolution of Thermometer * | 0.1 | °C | Rectangular | 1.732 | 0.1154734 | 0.01333 |
| Accuracy of Thermometer * | 0.16 | °C | Normal | 2 | 0.16 | 0.02560 |
| Temperature Distribution in Water Bath * | 0.1 | °C | Triangular | 2.45 | 0.08163 | 0.00666 |
| Repeatability of Measured Value | | | | | 0.03311 | 0.00110 |
| | | | | | | |
| | | | **Sum of the Squares** | | | 0.49929 |
| * A temperature coefficient of variation of 2% per °C was used in these uncertainty calculations | | | **Combined Uncertainty (Square root of the sum of the squares)** | | | **0.707 %** |

**Table 6: Sample Budget of Uncertainty**

Having identified the sources of uncertainty, they must be quantified and a combined uncertainty calculated. This requires a Budget of Uncertainty to be compiled. An example using commercially available conductivity meters and Secondary Standards for the measurement of samples of nominal conductivity 150µS/cm at 25°C is shown in Table 6.

The above budget of uncertainty shows a calculated Combined Uncertainty, $u_c$, of 0.71%. Applying a coverage factor of 2 gives an Expanded Uncertainty of 1.42%.
Therefore, the analyst can report the result as:

**150.0 ± 2.2 µS/cm at 25°C**
*The reported uncertainty is calculated using a coverage factor of 2, which gives a level of confidence of approximately 95%.*

## 4.6 Accuracy of Conductivity Measurements

The Budget of Uncertainty example shown in Table 6 gives an overall expanded Uncertainty of Measurement of 1.42%; whereas the conductivity meter's accuracy, taken from the manufacturer's specification[11], is < 0.5%. Conductivity meter manufacturers assign this figure by replacing the conductivity cell with a traceable, certified Standard Resistor. The meter accuracy quoted in the manufacturer's specification relates solely to the accuracy of processing this input signal. The meter accuracy should not be taken as an indication of the combined Uncertainty of Measurement that may be obtained for measurements taken using the meter in question.

Most Budgets of Uncertainty highlight that there are 3 or 4 sources that account for the majority of the overall Uncertainty of Measurement; whereas the other sources of uncertainty only provide a minor contribution. As well as establishing the traceability and accuracy provided by a conductivity measurement system, compiling the Budget of Uncertainty will also identify these major sources of uncertainty. If the accuracy of the measurement needs to be improved, the analyst will then be aware of the factors that should first be addressed to improve the overall Uncertainty of Measurement.

For full confidence in the results obtained from a conductivity meter and cell, it is essential to verify that they are being used correctly and that their performance complies with that detailed in the manufacturer's specification. These requirements form part of Method Validation and Equipment Qualification, full details of which are given in further Reagecon conductivity measurement papers[12,13].

# 5 Selection and Use of Standards for Conductivity Measurement

As can be seen from the worked example given in Table 6, the uncertainty associated with the value of the Secondary Standard used for cell constant determination has an effect on the overall Uncertainty of Measurement of the conductivity test result. The following factors will affect the choice of standards for conductivity measurements

- Use of Primary or Secondary Standards
- Stability of Standards
- Accreditation of Standard Manufacturer
- Use of Control Standards
- Information provided on Secondary Standards' Certificates of Analysis

## 5.1 Implications of Using Primary or Secondary Standards

Conductivity Primary Standards can be prepared from CRM grade Potassium Chloride, using deionised water of known conductivity and a calibrated and certified balance. The Uncertainty of Measurement for the production of the Primary Standard can be calculated by taking into account the following contributory factors:

- Purity of the potassium chloride CRM
- The Uncertainty assigned to the Primary Standard by the CRM manufacturer
- The Accuracy of the balance used.
- The Resolution of the balance used.

If the 0.01D KCl Primary Standard (see section 3.2.2) is manufactured using a balance with a readability of 0.01mg then this Primary Standard can be manufactured with an associated Uncertainty of Measurement of 0.107%. If this Primary Standard is used for the cell constant determination in the example given in Table 6 then this will lead to an Expanded Uncertainty of Measurement of 1.01%, i.e. a test result that can be reported as:

**150.0 ± 1.5 µS/cm at 25°C**
*The reported uncertainty is calculated using a coverage factor of 2, which gives a level of confidence of approximately 95%.*

Table 6 shows that, when a Secondary Standard was used for the cell constant determination, the Expanded Uncertainty of Measurement associated with the test results was ± 2.2 µS/cm, or 1.42% (see Section 4.5). The use of Primary Standards instead of Secondary Standards for calibration only gives a marginal improvement of the accuracy of the sample measurement.

Very few measurements applications require a level of Uncertainty of Measurement that can only be achieved by the use of Primary Standards. For these applications, a research-grade conductivity instrument, specially designed conductivity cells and tight control of temperature are required to produce a low Uncertainty of Measurement. For all other applications, high quality Secondary Standards can be used instead of Primary standards without having a significant impact on the overall Uncertainty of Measurement. Secondary Standards offer the benefit of being supplied ready for use and are considerably cheaper than Primary Standards.

## 5.2 Stability of Standards

The instructions for use of conductivity Primary Standards requires that they are used and discarded immediately after preparation, as their stability cannot be guaranteed. Manufacturers of conductivity Secondary Standards should provide an expiry date by which the Secondary Standard should be used or discarded. These

expiry dates typically run from 3 – 24 months from the date of manufacture, depending on the manufacturer and the conductivity value of the standard.

The main causes of instability of conductivity standards are absorption of atmospheric carbon dioxide and absorption of platicizers from the packaging bottle[14]. These factors are of particular concern for low-level conductivity standards. It is essential that the analyst has full confidence in the stability of the conductivity standards for their entire working life and so the standards' manufacturer must be able to provide detailed stability data for these standards[14].

## 5.3 Accreditation of the Standards' Manufacturer

As confidence in conductivity test measurements requires confidence in the standard used for assigning the cell constant, then it is essential that such standards be sourced from reputable manufacturers. The most transparent means of fulfilling this requirement is to use standards' manufacturers who have been accredited to meet the requirements of ISO 17025 - "General Requirements for Calibration and Testing Laboratories" [2].

Accreditation to ISO 17025 requires a fully documented Quality Management System, verification of traceability of measurement and Uncertainty of Measurement claims as well as demonstrating the technical validity of the calibration and test procedures and the technical competence of the personnel performing the tests.

It is important to note that national manufacturers of CRMs, e.g. NIST are not responsible for monitoring claims of traceability to their CRMs and cannot make any guarantees regarding any third party's claim of traceability. Any manufacturer can claim 'traceable to NIST' for their standards; but only those who are accredited to ISO 17025 are required to provide proof of such claims. Analysts can therefore have increased confidence in their own analytical results by using conductivity standards from ISO 17025 accredited manufacturers.

## 5.4 Use of Control Standards

Quantifying the Uncertainty of Measurement of a conductivity measurement system is a valuable step to determine the possible spread of errors associated with the measurement. However, compiling a Budget of Uncertainty is not sufficient to give confidence in individual conductivity measurement results. In order to comply with the requirements of good laboratory practice and to improve confidence in test results then a Control should be tested with each batch of samples.

If an Out Of Specification (OOS) reading is obtained for the control, this will immediately highlight an error and prevent incorrect results being recorded and incorrect actions being taken based upon these readings. Possible causes of OOS results include:

- Contamination of the calibration standard
- A change in cell constant over time
- Incorrect temperature reading
- Analyst error
- Measurements being taken outside the linear range of the conductivity cell

The Control should have a similar conductivity value to the samples being tested and should match the matrix of the samples. The Control's matrix is of particular significance for low conductivity measurement – few manufacturers of conductivity standards provide low conductivity standards of aqueous matrix, the sample matrix most commonly encountered for low conductivity measurements[14].

The same criteria of verifiable traceability, stability and Uncertainty of Measurement for Calibration Standards should be used when selecting suitable Control Standards.

## 5.5 Information Required on Secondary Standards' Certificates of Analysis

In order to establish traceability, the following information regarding Secondary Standards must be included on the Secondary Standard's Certificate of Analysis (CoA):

- Manufacturer's Product Number
- Manufacturer's Lot Number
- Expiry Date
- Date of Test
- The Mean Assay Value assigned to the Secondary Standard
- Uncertainty of Measurement associated with this value

- Test method utilised
- Full details of the Primary Standard that the Secondary Standard is traceable to – e.g. NIST SRM 918a (Potassium Chloride)
- Details of any relevant accreditation that the manufacturer has attained.

The CoA must be retained for future reference so that the traceability of past readings can be verified.

### 5.6 Correct Use of Conductivity Standards

The correct use of conductivity standards is essential to ensure the accuracy of the cell constant assignment and the test sample readings. The following guidelines apply equally to calibration standards, control standards and test samples:

- Always use a fresh aliquot of standard for each measurement – failure to do so will result in errors due to contamination of the standard.
- Thoroughly rinse the measurement container or beaker, the conductivity cell and the temperature sensor at least 3 times with the solution being measured. This must be performed to prevent carry-over from the previous measured solution.
- Ensure that the conductivity cell and the measurement samples or standards are at the same temperature before taking readings. Temperature has a significant influence on conductivity - accurate temperature measurement is required for accurate conductivity measurement[10].
- Ensure that the cell's electrodes are fully immersed in the measurement sample or standard.
- Ensure that there are no air bubbles lodged on the electrode surfaces – these can be dislodged by gently tapping the cell.
- Rinse the cell with purified water after each measurement.

The above guidelines should be included in the Test Procedure. Failure to follow these guidelines will result in significant errors that will not have been accounted for in the assessment of the Uncertainty of Measurement, leading to false claims of accuracy of analysis.

## 6 Conclusion

Analysts can demonstrate that their conductivity test results are fit for purpose if they quantify their Uncertainty of Measurement and show that their measurements are traceable to S.I. Units. Establishing traceability is essential if meaningful comparisons are to be made of conductivity measurements. Quantifying the Uncertainty of Measurement and proving traceability of conductivity measurements can only be made through the correct use of appropriate, traceable conductivity standards.

For all but the most exacting conductivity measurement applications, suitable measurement accuracy can be obtained by using Secondary Standards. However, care must be exercised when selecting and using secondary conductivity standards – these should only be used from manufacturers who can demonstrate that their conductivity standards have fully characterised Uncertainty of Measurement, have been manufactured and tested in a competent fashion and are traceable. These criteria must be fulfilled if the manufacturer is accredited to ISO 17025 – such accreditation provides the analyst with an easy means of assessing that a conductivity standards' manufacturer meets these criteria. The conductivity standards should also be matched to the samples' matrix (usually aqueous) and evidence of their stability should be available – this is of particular relevance to low conductivity standards.

In addition to calibration standards, it is essential to use suitable control standards for compliance with the requirements of good laboratory practice and to provide maximum confidence in conductivity test measurements. Control standards should be of similar value to the samples' conductivity and should be selected using the same criteria that apply to calibration standards.

## 7 References


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* These papers form part of a comprehensive series of papers that the authors have written covering all of the practical requirements for accurate conductivity measurement. These papers and the authors' book, "A Practical Guide to Accurate Conductivity Measurement" are available via Reagecon's website at www.reagecon.com.

### Biographical Notes:

John J Barron is Managing and Technical Director of Reagecon Diagnostics Limited. The company, which was founded in 1986, is the largest producer worldwide of Conductivity Standards and is also a major producer of other chemical standards. Mr. Barron is an expert in several areas of analytical chemistry, including electro-chemical analysis, good laboratory practice (GLP) and chemical metrology. He has written and lectured extensively and is credited with several scientific discoveries including stable low level conductivity standards.

Colin Ashton has worked in the Reagecon group since 1994 and is currently Head of the Chemical Metrology Department. A graduate of the University of Southampton, he has developed particular expertise in the development, stabilisation, manufacture and validation of cation, anion and electro-chemical standards. He has particular scientific interest in all aspects of on line chemical analysis and has lectured and published on several areas of this field.


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