Ion concentration estimation using electrolyte conductivity and temperature

G.R. Langereis, W. Olthuis and P. Bergveld

MESA Research Institute, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

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Abstract

A method for determining separate ion concentrations using a conductivity sensor was developed and tested. While a single electrical conductivity measurement in a solution does not give information on the present ion types, a range of measurements at various electrolyte temperatures does. Since the temperature dependency of the mobility of an ion is unique for that ion, it appeared to be possible to fit ion concentrations from a set of conductivity measurements while heating the electrolyte. For the calculation of the ion concentrations from a conductivity versus temperature sweep, an estimation algorithm is introduced based on the linear minimum mean square of the error. Errors in the measured conductivity will propagate through the algorithm into errors in the fitted ion concentrations. For the validation of the estimation method, this propagation of errors is also evaluated.

Keywords: Electrical conductivity, temperature, ion concentration, parameter estimation

1. Introduction

A single conductivity measurement is not interesting unless the measured value is normalised for temperature. The reason for this is that at a higher temperature, ions become more mobile and will cause an increase in conductivity. So with the same concentration, an increase in temperature results in an increase in conductivity. Therefore, in practical conductivity measurements, the measured conductivity is compensated to 25°C by using a simultaneous temperature measurement.

The total conductivity of an electrolyte expressed in terms of the limiting molar conductivities of the separate ions is given by

$$\Lambda = \sum_{i=1}^{I} |z_i| c_i \lambda_i(T) \tag{1}$$

with z_i the charge of ion i, c_i the concentration, I the number of different types of ions and $\lambda_i(T)$ the limiting molar conductivity of ion i. This last one is dependent on temperature and specific for every single ion. Since a conductivity measurement can not differentiate between ions, it is not possible to eliminate exactly the temperature effect.

Industrial temperature compensation methods use the average temperature dependency of L which is about 2%/°C. This linear fit is the most simple approximation of the temperature dependency and is suitable for most pure water applications over a moderate temperature range [1]. More sophisticated fits compensate by using a third order polynomial, but this method is electrolyte and concentration dependent [2].

An even more complicated temperature compensation can be based on a polynomial fit for the limiting molar conductivities of the separate ions [3]. A third order approximation was proposed by Harned and Owen [4] and tabulated for several ions. The equation is

$$\lambda_i(T) = \lambda_i^0\left[1 + k_{i,1}(T-25) + k_{i,2}(T-25)^2 + k_{i,3}(T-25)^3\right] \tag{2}$$

with λ_i^0 the limiting molar conductivity of ion i at 25°C. This polynomial approach will be used for ion identification.

2. Theory

The generalised polynomial fit of order J with respect to temperature T_0 can be written as

$$\lambda_i(T) = \lambda_i^0 \sum_{j=0}^{J} k_{i,j}\left(T - T_0\right)^j . \tag{3}$$

Together with equation (1) the total conductivity of an electrolyte having I types of ions can now be calculated:

$$\Lambda(T) = \sum_{i=1}^{I}\left[\left|z_i\right| c_i \lambda_i^0 \sum_{j=0}^{J} k_{i,j}\left(T - T_0\right)^j\right]. \tag{4}$$

Manipulation yields:

$$\Lambda(T) = \sum_{i=1}^{I}\sum_{j=0}^{J}\left[\left|z_i\right| c_i \lambda_i^0 k_{i,j}\left(T - T_0\right)^j\right]$$

$$\Lambda(T) = \sum_{j=0}^{J}\sum_{i=0}^{I}\left[\left|z_i\right| c_i \lambda_i^0 k_{i,j}\left(T - T_0\right)^j\right]$$

and

$$\Lambda(T) = \sum_{j=0}^{J}\left[\left(T - T_0\right)^j \sum_{i=0}^{I}\left(\left|z_i\right| c_i \lambda_i^0 k_{i,j}\right)\right]. \tag{5}$$

For conductivity measurements at N different temperatures, I types of ions and a polynomial fit of order J, a matrix equation can be formed using equation (5):

$$\begin{bmatrix} \Lambda_1 \\ \Lambda_2 \\ \cdot \\ \cdot \\ \Lambda_N \end{bmatrix} = \begin{bmatrix} 1 & \left(T_1 - T_0\right) & \left(T_1 - T_0\right)^2 & \cdot & \left(T_1 - T_0\right)^J \\ 1 & \left(T_2 - T_0\right) & \left(T_2 - T_0\right)^2 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 1 & \left(T_N - T_0\right) & \left(T_N - T_0\right)^2 & \cdot & \left(T_N - T_0\right)^J \end{bmatrix} \cdot \begin{bmatrix} k_{1,0} & k_{2,0} & \cdot & k_{I,0} \\ k_{1,1} & k_{2,1} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ k_{1,J} & k_{2,J} & \cdot & k_{I,J} \end{bmatrix} \cdot \begin{bmatrix} \left|z_1\right| c_1 \lambda_1^0 \\ \left|z_2\right| c_2 \lambda_2^0 \\ \cdot \\ \left|z_I\right| c_I \lambda_I^0 \end{bmatrix} \tag{6}$$

or

$$\overline{\Lambda} = \overline{\overline{T}} \cdot \overline{\overline{K}} \cdot \overline{c} .$$

The meaning of the terms is:

$\overline{\Lambda}$	Vector containing measured conductivities at N different temperatures;
$\overline{\overline{T}}$	Matrix with the temperature information;
$\overline{\overline{K}}$	Matrix with the polynomial coefficients $k_{i,j}$;
$\overline{c}$	Vector with the ion concentrations multiplied by the parameters $\lvert z\rvert\cdot l^0$;

The question rises whether it is possible to calculate the vector $\overline{c}$ (containing the concentration information) from a known $\overline{\overline{T}}$ matrix and a measured $\overline{\Lambda}$ vector. It would be interesting to know if the $\overline{\overline{K}}$ matrix can be calculated as well. This would mean that the present ions can be identified by their found $k_{i,j}$ coefficients. However, the calculation of the $\overline{\overline{K}}$ matrix is mathematically not possible since this requires a known vector $\overline{c}$, while the determination of this vector is the desired result. Therefore, equation (6) can only be used for determining ion concentrations after assuming a set of coefficients in the matrix $\overline{\overline{K}}$.

2.1 Calculation of ion concentrations using tabulated coefficients

When the $\overline{\overline{K}}$ matrix is assumed to be known, which implies a chosen set of ions, equation (6) can be written as

$$\begin{bmatrix} \Lambda_1 \\ \Lambda_2 \\ . \\ . \\ \Lambda_N \end{bmatrix} = \begin{bmatrix} \sum\limits_{j=0}^{J} k_{1,j}(T_1 - T_0)^j & \sum\limits_{j=0}^{J} k_{2,j}(T_1 - T_0)^j & . & \sum\limits_{j=0}^{J} k_{I,j}(T_1 - T_0)^j \\ \sum\limits_{j=0}^{J} k_{1,j}(T_2 - T_0)^j & \sum\limits_{j=0}^{J} k_{2,j}(T_2 - T_0)^j & . & . \\ . & . & . & . \\ \sum\limits_{j=0}^{J} k_{1,j}(T_N - T_0)^j & . & . & \sum\limits_{j=0}^{J} k_{I,j}(T_N - T_0)^j \end{bmatrix} \cdot \begin{bmatrix} |z_1|c_1\lambda_1^0 \\ |z_2|c_2\lambda_2^0 \\ . \\ |z_I|c_I\lambda_I^0 \end{bmatrix} \qquad (7)$$

where the $\overline{\overline{T}}\cdot\overline{\overline{K}}$ matrix is written as a single one. The elements in this matrix are polynomials for the n-th temperature (rows) and the i-th ion (columns). If the $\overline{\overline{T}}\cdot\overline{\overline{K}}$ matrix has an inverse, the concentrations will follow from

$$\overline{c} = \left(\overline{\overline{T}}\cdot\overline{\overline{K}}\right)^{-1}\cdot\overline{\Lambda}. \qquad (8)$$

The first condition for having an inverse is that the matrix is square, so the minimal number of necessary experiments is equal to the number of ions to fit ($N = I$). For N larger than I an estimator must be used. The second condition is that the determinant is not equal to zero. This is true when the coefficients are different for every ion and the order of the polynomial is equal or larger than I - 1.

Summarising, it is possible to find the concentrations of individual ions in a solution under the following conditions:

- The measured conductivity scan must be a linear combination of the temperature responses for the individual ions. This means that
    - → Every ion which is significantly present in the electrolyte conductivity must be represented in the calculations;
    - → No two ions may have the same temperature dependency (which will probably never be the case);

    → When I types of ions have to be calculated, the conductivity of the electrolyte must be measured at at least N = I temperatures;
    → The order of the used polynomials is equal to or larger than the number of different ions to fit minus one (J = I - 1);
- The coefficients $k_{i,j}$ of the individual ions must be known. The coefficients for the third order fit are given by Harned and Owen [4] for nine types of ions;

When these conditions are met, the errors in the fitted ion concentrations will be the result of errors in the measured conductivities. The nature of propagation of an error in the measured conductivity to an error in the fitted result depends on the type of the error.

2.2 Error propagation

Three types of errors are considered: errors proportional to the measured conductivity, errors which manifest as a constant offset in the measured conductivity and random noise.

Errors due to systematic errors in conductivity measurements, for example due to an inaccurately assumed sensor slope, representing the sensitivity, can be proportional to the measurand itself. Proportional errors can be written as an undesired multiplication of L by x. For such proportional errors, equation (8) must be expanded to

$$\overline{c}^{\xi} = \left(\overline{\overline{T}} \cdot \overline{\overline{K}}\right)^{-1} \cdot \overline{\Lambda\xi} \tag{9}$$

where $\overline{\Lambda}$ is multiplied per element by the proportional error vector $\overline{\xi}$. When x is equal for every single measurement, this results in

$$\overline{c}^{\xi} = \left(\overline{\overline{T}} \cdot \overline{\overline{K}}\right)^{-1} \cdot \overline{\Lambda} \cdot \xi = \overline{c} \cdot \xi\,. \tag{10}$$

From this equation it can be concluded that an x per cent error in the measured conductivity will result in an x per cent error in the calculated ion concentrations.

Other types of errors might introduce a constant offset in the conductivity measurement. The most likely origin of such an error is the unexpected presence of an ion which is not included in the fitting algorithm. In that case, the observed conductivity versus temperature curve can never be a linear combination of the contributions due to the assumed set of ions. Therefore, this kind of error will be much more severe than a proportional error. Such a systematic error which manifests as an unknown offset in the measurement can be written as a constant addition e of L. In this case equation (8) becomes

$$\overline{c}^{\varepsilon} = \left(\overline{\overline{T}} \cdot \overline{\overline{K}}\right)^{-1} \cdot \left(\overline{\Lambda} + \overline{\varepsilon}\right) \tag{11}$$

and manipulation yields

$$\overline{c}^{\varepsilon} = \left(\overline{\overline{T}} \cdot \overline{\overline{K}}\right)^{-1} \overline{\Lambda} + \left(\overline{\overline{T}} \cdot \overline{\overline{K}}\right)^{-1} \overline{\varepsilon} = \overline{c} + \left(\overline{\overline{T}} \cdot \overline{\overline{K}}\right)^{-1} \overline{\varepsilon} \tag{12}$$

which shows that the faulty fitted vector $\overline{c}^{\varepsilon}$ is equal to the actual vector $\overline{c}$ increased by a constant vector. So the error vector $\overline{\varepsilon}$ will result in unknown additions to all the elements of $\overline{c}$, which are different for every element.

Random noise in the measurement shows up as unknown offsets as well, like described in equation (12). However, the error vector $\overline{c}^{\varepsilon} - \overline{c}$ has another property now: its elements represent random numbers with the average of zero. In other words, when the number of experiments is increased, the average of the elements in $\overline{c}^{\varepsilon} - \overline{c}$ will go to zero. In the next subsection, an estimation algorithm is introduced which allows N > I in order to reduce the error due to random noise in the conductivity measurement.

2.3 A linear minimum mean square estimation

The calculation of ion concentrations using the basic algorithm (8) requires conductivity measurements at as much temperatures as the number of ions to be fitted. It is more accurate to do more measurements (N > I) and use an estimation method. The method introduced here is a matrix based algorithm for minimising the mean square error of the estimation [5]. Consider the generalised system

$$\overline{\Lambda} = \overline{\overline{B}} \cdot \overline{c} + \overline{v} \tag{13}$$

with

$\overline{\Lambda}$ the vector containing the observations,
$\overline{\overline{B}}$ a matrix representing the system (in this context equal to $\overline{\overline{T}} \cdot \overline{\overline{K}}$),
$\overline{c}$ the input vector to be estimated and
$\overline{v}$ the noise or error in the measurement.

The aim is to find an estimate $\hat{\overline{c}}$ for the vector $\overline{c}$ satisfying the observed vector $\overline{\Lambda}$. In the ideal case, the estimate is equal to the true value. In practice, however, an error will be present represented by the error vector, defined as

$$\overline{e} = \hat{\overline{c}} - \overline{c} = \hat{\overline{c}} - E\left(\hat{\overline{c}}\right). \tag{14}$$

The aim of the estimation algorithm is to minimise this error vector. Concerning the system of equation (13), consider the assumptions:

→ $\overline{c}$ and $\overline{v}$ are uncorrelated (the moment matrix $\overline{\overline{C}}_{\overline{cv}} \equiv E\left(\overline{c}\,\overline{v}^{T}\right)$ is equal to zero);

→ the elements of $\overline{v}$ are uncorrelated and have equal standard deviations s_v. This also implies that the moment matrix $\overline{\overline{C}}_{\overline{v}} \equiv E\left(\overline{v}\,\overline{v}^{T}\right)$ is finite;

→ the true value of $\overline{c}$ is unknown so its moment matrix satisfies $\overline{\overline{C}}_{\overline{c}} \equiv E\left(\overline{c}\,\overline{c}^{T}\right) \to \infty$ (all variances are very large).

The linear minimum mean square estimate $\hat{\overline{c}}$ of $\overline{c}$ given data $\overline{\Lambda}$ under these conditions is according to Gauss-Markoff theorem equal to [5]

$$\hat{\overline{c}} = \left(\overline{\overline{B}}^{T}\overline{\overline{B}}\right)^{-1}\overline{\overline{B}}^{T} \cdot \overline{\Lambda} \tag{15}$$

which reduces to (8) for a square matrix $\overline{\overline{B}}$.

The propagation of errors was already mentioned in subsection 2.2 for the situation where the number of applied temperatures is equal to the number of ions to be fitted (N = I). However, by using more than N measurements, a decrease in the final error can be expected because of suppression of measurement noise. The Gauss-Markov theorem does also give a method for determining the propagation of errors through the estimation algorithm. Using the assumed equal variances s_v^2 of the vector $\overline{v}$, the moment matrix of the error vector given by equation (14) can be expressed as

$$\overline{\overline{C}}_e = \left(\overline{\overline{B}}^T \overline{\overline{B}}\right)^{-1} \cdot \sigma_v^{\ 2} \qquad (16)$$

which contains all covariances of the fitted vector $\hat{\overline{c}}$ in its entries. So the numbers on the diagonal of this error matrix are the variances of the fitted parameters. Using this knowledge, the standard deviation of the whole fit can be defined as

$$\sigma_c = \sqrt{\mathrm{trace}\left(\overline{\overline{B}}^T \overline{\overline{B}}\right)^{-1}} \cdot \sigma_v \qquad (17)$$

where the trace function is the summing of the elements on the diagonal of a matrix. The standard deviation is determined for the Radiometer CDM210 conductivity meter to be about 0.5 mS/cm in the 400 mS operational range, and 0.05 mS/cm in the 40 mS range, as will be shown in the experimental part.

In figure 1 the normalised calculated standard deviation in the estimated concentration is represented for three different temperature ranges and estimations for N = 2 to 11. For this numerical example, the coefficients $k_{i,j}$ for a 100 mM sodium chloride solution are used. It can be seen that the accuracy of the estimation can be increased, either by increasing the number of measurements or the temperature range. The improvement in accuracy by increasing the temperature range is larger than the improvement obtained by using more measurements.

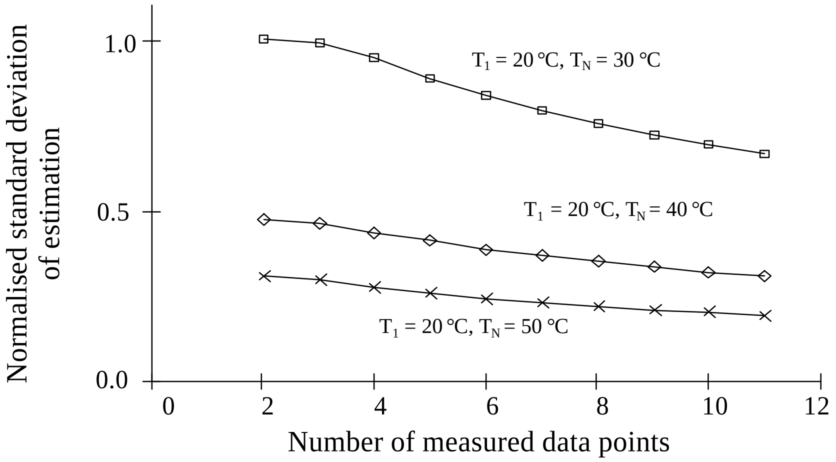


Figure 1: Effect of the temperature range and the number of measurements on the estimation accuracy

2.4 Implementation of the zero charge boundary condition

Because in practical solutions the total charge is equal to zero, the condition

$$\sum_{\text{Cations}} |z_i| c_i = \sum_{\text{Anions}} |z_i| c_i \tag{18}$$

can be implemented in the algorithm in order to increase accuracy and to avoid useless answers like negative concentrations. This equation can be implemented in the model (7) as

$$\begin{bmatrix} \Lambda_1 \\ \Lambda_2 \\ \cdot \\ \cdot \\ \Lambda_N \\ \hline 0 \end{bmatrix} = \left[\begin{array}{cccc} \sum\limits_{j=0}^{J} k_{1,j}(T_1 - T_0)^j & \sum\limits_{j=0}^{J} k_{2,j}(T_1 - T_0)^j & \cdot & \sum\limits_{j=0}^{J} k_{I,j}(T_1 - T_0)^j \\ \sum\limits_{j=0}^{J} k_{1,j}(T_2 - T_0)^j & \sum\limits_{j=0}^{J} k_{2,j}(T_2 - T_0)^j & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \sum\limits_{j=0}^{J} k_{1,j}(T_N - T_0)^j & \cdot & \cdot & \sum\limits_{j=0}^{J} k_{I,j}(T_N - T_0)^j \\ \hline \dfrac{z_1}{|z_1|\lambda_1^0} & \dfrac{z_2}{|z_2|\lambda_2^0} & \cdot & \dfrac{z_I}{|z_I|\lambda_I^0} \end{array} \right] \cdot \begin{bmatrix} |z_1| c_1 \lambda_1^0 \\ |z_2| c_2 \lambda_2^0 \\ \cdot \\ |z_I| c_I \lambda_I^0 \end{bmatrix} \tag{19}$$

were the $\overline{\overline{T}} \cdot \overline{\overline{K}}$ matrix has now become an augmented $\overline{\overline{T}} \cdot \overline{\overline{K}}$ matrix. The elements in the augmented vector $\overline{\Lambda}$ and the augmented matrix $\overline{\overline{T}} \cdot \overline{\overline{K}}$ do not have an equal unity anymore. This does not make any difference for numerical evaluations.

This augmented model can be evaluated like the original model using the same estimation algorithm. However, the condition (18) will have the same priority as every single measurement and so its importance will be suppressed with an increasing number of applied temperatures N. Two options are available for increasing its priority:

- The first option is to give the last row of the augmented $\overline{\overline{T}} \cdot \overline{\overline{K}}$ matrix a weight factor equal to the number of measurements. The weighted least square form of (15) is [5]

  $$\hat{\overline{c}} = \left(\overline{\overline{B}}^T \overline{\overline{W}}^{-1} \overline{\overline{B}} \right)^{-1} \overline{\overline{B}}^T \overline{\overline{W}}^{-1} \cdot \overline{\Lambda} \tag{20}$$

  with $\overline{\overline{W}}$ the weight matrix. This weight matrix is of size (N+1) × (N+1) with on the diagonal the only non-zero entries being the weight factors. Since the matrix $\overline{\overline{B}}$ will be the augmented $\overline{\overline{T}} \cdot \overline{\overline{K}}$ matrix, the element on entry (N+1, N+1) will be the weight factor for the zero charge condition;
- Another possibility is obtained by first reducing the measured information and then implementing the zero charge condition. Concerning equation (6) it can be concluded that the number of measurements is not in the $\overline{\overline{K}} \cdot \overline{c}$ product matrix. The measured information (conductivities at N temperatures) can be reduced to J+1 points by first calculating an estimation for the vector $\overline{\overline{K}} \cdot \overline{c}$ by applying the simple algorithm (15) to equation (6) according to

  $$\overline{\overline{K}} \cdot \overline{c}\,\Big|_{\text{Estimate}} = \left(\overline{\overline{T}}^T \overline{\overline{T}} \right)^{-1} \overline{\overline{T}}^T \cdot \overline{\Lambda}. \tag{21}$$

The result is a vector with length J+1, not dependent on the number of measurements. This estimated vector is equal to the product of the coefficient matrix $\bar{\bar{K}}$ and the concentration vector $\bar{c}$. The zero charge condition can now again be implemented by augmenting a matrix:

$$\left[\begin{array}{c} \bar{\bar{K}}\cdot\bar{c}\big|_{\text{Estimate}} \\ \hdashline 0 \end{array}\right] = \left[\begin{array}{cccc} k_{1,0} & k_{2,0} & \cdot & k_{I,0} \\ k_{1,1} & k_{2,1} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ k_{1,J} & k_{2,J} & \cdot & k_{I,J} \\ \hdashline \frac{z_1}{|z_1|\lambda_1^0} & \frac{z_2}{|z_2|\lambda_2^0} & \cdot & \frac{z_I}{|z_I|\lambda_I^0} \end{array}\right] \cdot \begin{bmatrix} |z_1|c_1\lambda_1^0 \\ |z_2|c_2\lambda_2^0 \\ \cdot \\ |z_I|c_I\lambda_I^0 \end{bmatrix} \tag{22}$$

To solve the concentrations from this equation, a second estimation step is necessary since the augmented $\bar{\bar{K}}$ matrix is not square.

The moment matrix of the error vector (16) has now become meaningless, and so the standard deviation of the fit (17), since these are only valid when having equal variances s_v^2 for all the measurements. The variances are not equal anymore, since the zero charge condition will have another variance than the actual conductivity measurements.

2.5 Summary

Reconsidering the original equation (7), describing the set of conductivity measurements at N temperatures, the ultimate method of determination should be:

- Perform the measurements, by heating a solution while measuring the conductivity. Take more measurements (conductivities at known temperatures) than the number of ions to be fitted (N > I) since this will increase the accuracy of the estimation. Some conductivity meters have an automatic temperature compensation which must be switched off. Also the use of an auto range function will disturb the measurement since the variance in the measurement appeared to be constant per operational range;
- Assume a set of ions and calculate the matrix $\bar{\bar{B}}$ with the elements

  $$\bar{\bar{B}}_{n,i} = \sum_{j=0}^{J} k_{i,j}\left(T_n - T_0\right)^j$$

  with T_0 the reference temperature, T_n the temperature of measurement n, J the order of the polynomial fit and $k_{i,j}$ the polynomial fit coefficients for the temperature dependency of the mobilities (which can be found in literature [4]);
- Create the conductivity vector $\bar{\Lambda}$, which is a column of N conductivity measurements at N different temperatures;
- Use equation (15) for finding the estimation vector $\hat{\bar{c}}$, which is a column of the $|z_i|c_i\cdot l_i^0$ products for the I ions. Because the charge of the ions z_i and the limiting molar conductivity l_i^0 are known, the concentrations of the individual ions can be calculated.

If desired, the boundary condition of the sum of all charge being zero can be implemented as shown in equation (22). However, in that case this condition is mathematically included as a weighted criterion.

3. Experimental verification of the estimation assumptions and a quantitative determination of the fitting errors

Before the actual measurements for fitting are presented, the assumptions which justify the simplification to the estimation algorithm (15) are verified by measurements. The used set-up is the same as will be used later for doing the actual concentration determinations. The data needed for the verification are numerical data on the standard deviations of the conductivity measurements. These results can also be used to evaluate the propagation of errors (as given by equation (17) in terms of standard deviations) quantitatively.

3.1 Measurement set-up

During some hours, the conductivity meter (Radiometer CDM 210) was used for monitoring temperature and conductivity in stirred potassium chloride solutions. The solution was heated and cooled down several times between room temperature (18 °C) and about 55 °C. In a spreadsheet program, the data was collected and compared to the theoretical conductivities for these temperatures. The results are in table 1.

Table 1: Statistical information on KCl conductivity measurements at temperatures between 18 °C and 55 °C

Concentration KCl [mM]	Measured conductivity (20 °C) [mS/cm]	CDM210 range [mS/cm]	Mean error [mS/cm]	Std. dev. of error [mS/cm]
90	12.6	40	0.0009	0.05
309	38.5	400	0.0053	0.49
413	55.3	400	0.0183	0.50
615	86.2	400	0.0059	0.53

Notice that the conductivity meter had to be switched to the 40 mS range for the first sample which corresponds to a fixed operational frequency of 23.4 kHz, and to the 400 mS range for the other three samples (46.9 kHz). Obviously, the standard deviation is dependent on the chosen operational frequency and not on the electrolyte concentration. However, because the operational frequency is chosen according to the electrolyte concentration, the standard deviation is indirectly dependent on this concentration in practical applications.

All the measured errors of the three samples measured with the 400 mS range were collected into a single error distribution plot as shown in figure 2 which approaches the normal distribution shape.

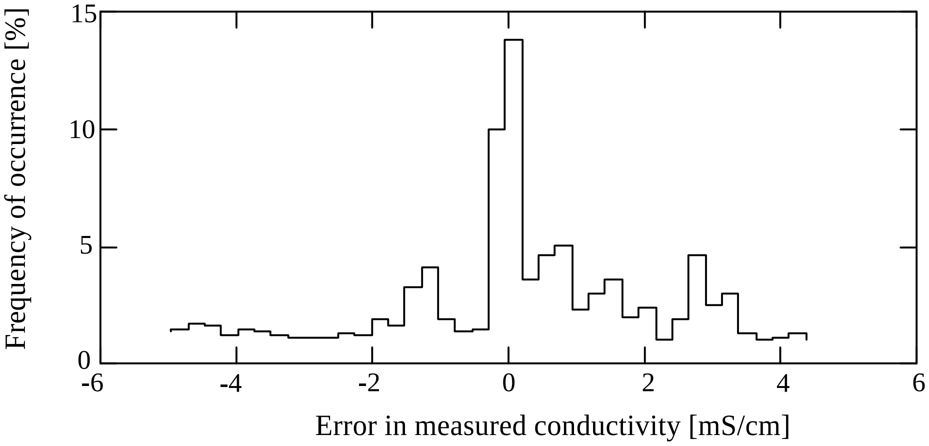


Figure 2: Error distribution in conductivity measurements

3.2 Discussion

Verification of the assumptions

Having this data, the assumptions preceding equation (15) can be verified. Comparing column 4 to column 2 in table 1, it appears that the mean of the error is much lower than the observed conductivities. In other words

$$E(\overline{v}) = 0$$

which implies directly that the covariance with $\overline{c}$ is equal to zero as well:

$$\overline{\overline{C}}_{\overline{c}\overline{v}} \equiv E\left(\overline{c}\overline{v}^T\right) = 0\,.$$

This proves the first assumption of $\overline{c}$ and $\overline{v}$ being uncorrelated.

The other two conditions, being $\overline{\overline{C}}_{\overline{c}} \rightarrow \infty$ and $\overline{\overline{C}}_{\overline{v}}$ is finite, are necessary to ensure that the moment matrix for $\overline{c}$ is much larger than the moment matrix for $\overline{v}$: $\overline{\overline{C}}_{\overline{c}} >> \overline{\overline{C}}_{\overline{v}}$. Since the standard deviations of $\overline{v}$ are finite and known (fifth column of table 1), its moment matrix will be small. More correctly, the moment matrix for $\overline{v}$ will go to zero in relation to the corresponding moment matrix for $\overline{c}$, which will go to infinite because its covariance goes to infinite [5].

The value for the standard deviation appears to be constant at a chosen operational frequency. This means that about 95% of the conductivity measurements is between the real conductivity plus/minus two times this standard deviation for the chosen operational range.

Besides being dependent on the operational frequency of the conductivity meter, the standard deviation might be dependent on temperature. Therefore the data of the three measurements in the 400 mS range, was split into four sets: lower than 30 °C, between 30 °C and 40 °C, between 40 °C and 50 °C and higher than 50 °C. The calculated standard deviations are in table 2.

Table 2: Standard deviations calculated in several temperature ranges

Temperature range [°C]	Standard deviation [mS/cm]
< 30 °C	0.31
30 °C . . 40 °C	0.36
40 °C . . 50 °C	0.40
> 50 °C	0.42

Although there is a small temperature dependency, it might be concluded that no big error is introduced when assuming a temperature independent standard deviation.

The absolute errors in the concentration estimation

Now the variance in the measurement error is experimentally determined, the propagation of this error through the estimation algorithm can be evaluated. The absolute errors in the fitted concentrations due to random noise can be calculated using equation (17). This equation gives the standard deviations in the fitted vector $\hat{\bar{c}}$ which contains the values $|z|c\ l^0$ for all the fitted ions. So, when the error of a certain value is defined by two times its standard deviation (95% probability region), the resulting absolute error in the fitted ion concentration will be

$$e_{c,i} = \frac{2\sigma_v}{|z_i|\lambda_i^0}\sqrt{\left(\overline{\overline{B}}^T\overline{\overline{B}}\right)^{-1}\Big|_{i,i}} \qquad (23)$$

with

$e_{c,i}$	the absolute error in the fitted ion concentration for ion i [10^{-3} mole/litre];
z_i	the ionic charge for ion i [no dimension];
l_i^0	the limiting molar ionic conductivity [m^2 S $mole^{-1}$];
$\overline{\overline{B}}$	the matrix with the temperatures and coefficients $k_{i,j}$;
s_v	the standard deviation in the measured conductivity [S/m];

Evaluation of equation (23) is easier with some numerical examples. When the conductivity meter is used in the 40 mS/cm range, which is equivalent to a maximum of about 300 mM KCl, the standard deviation of the measurement is approximately equal to 0.05 mS/cm as given in table 1. For N = 25 measurements, equidistantly distributed over a temperature range from 20 °C to 55 °C and using a polynomial approximation of J = 3 for the ion conductivities, the absolute errors in the fitted concentrations are calculated. In table 3, the results are summarised for combinations of two, three and four selected ions.

Table 3: Absolute errors in fitted concentrations due to random noise,
for N = 25, T = 20 - 55 °C, J = 3, s_v = 0.05 mS/cm

Solution: Fitted ion:	D[Na^+] (mM)	D[H^+] (mM)	D[K^+] (mM)	D[Cl^-] (mM)
K^+ and Cl^-			32	30
H^+ and Cl^-		0.80		3.4
H^+, Na^+, and Cl^-	38	1.3		20
H^+, K^+ and Cl^-		12	253	215
H^+, K^+, Na^+ and Cl^-	90	28	1.2 M	0.9 M

On the average, the fitting of a larger number of ions increases the random noise propagation error. What can also be seen, is that the type of ion does matter. When the combination Cl^- and K^+ is present, the errors are bigger. In addition, the result for H^+ is more accurate, not only in the result for H^+ itself, but also for the other ions in the system. This could be expected since H^+ has a much more characteristic ionic conductivity and therefore ion discrimination is more easy.

Since table 3 is only valid when the meter is switched in the 40 mS/cm range, errors in the concentrations around the one molar limit will certainly exceed the actual concentrations. So the fitting of four ions will probably be much too sensitive to errors.

Remarkable is that the absolute error is not dependent on the concentration, which is the result from the constant standard deviation of the conductivity measurement. So it is important to choose the lowest possible conductivity sensing range on the meter since than the standard deviation is the lowest as can be seen from table 1.

For errors in the measured conductivity which have not a random nature, the noise will not be filtered out by the estimation algorithm. An example which was already mentioned in subsection 2.2 is the presence of a background electrolyte, consisting of one or more ions which are not in the assumed set of ions.

When the error e is assumed to be constant at every temperature, the relative error in the fitted concentration of ion i becomes

$$\frac{\bar{c}^{\varepsilon}{}_{i} - \bar{c}_{i}}{\bar{c}_{i}} = \frac{\left[\left(\bar{\bar{T}} \cdot \bar{\bar{K}}\right)^{-1}\right]_{Row\_i} \cdot \bar{\varepsilon}}{\left[\left(\bar{\bar{T}} \cdot \bar{\bar{K}}\right)^{-1}\right]_{Row\_i} \cdot \bar{\Lambda}} = \frac{\sum_{Row\_i} \left[\left(\bar{\bar{T}} \cdot \bar{\bar{K}}\right)^{-1}\right]}{\left[\left(\bar{\bar{T}} \cdot \bar{\bar{K}}\right)^{-1}\right]_{Row\_i} \cdot \bar{\Lambda}} \cdot \varepsilon \tag{24}$$

where equation (12) is used and for simplicity N = I is taken. When later N > I is needed, the inverse of the $\bar{\bar{T}} \cdot \bar{\bar{K}}$ matrix can simply be substituted by the estimation matrix of equation (15). The elements in the measured conductivity vector $\bar{\Lambda}$ can be normalised to the conductivity at for example 20 °C. The relative error in the fitted concentration becomes equal to

$$\frac{\bar{c}^{\varepsilon}{}_{i} - \bar{c}_{i}}{\bar{c}_{i}} = \frac{\sum_{Row\_i} \left[\left(\bar{\bar{T}} \cdot \bar{\bar{K}}\right)^{-1}\right]}{\left[\left(\bar{\bar{T}} \cdot \bar{\bar{K}}\right)^{-1}\right]_{Row\_i} \cdot \bar{\Lambda}_{20°C}} \cdot \frac{\varepsilon}{\Lambda_{20°C}} \tag{25}$$

which means that the relative error in the fitted ion concentrations is proportional to the relative error due to an offset in the measured conductivity. In table 4 the factors which amplify the relative error in the measurement to relative errors in the fit are given for the same solutions as used in table 3. However, while the concentrations did not matter for the errors due to random noise, now concentrations must be assumed in order to find numerical values.

Table 4: Amplification factor for a relative error due to an offset in the measured conductivity to the relative error in the fitted ion concentrations, for N = 25, T = 20 - 55 °C, J = 3 and L_0 *= 20 °C*

Solution:	Fitted ion:	Na^+	H^+	K^+	Cl^-
10 mM KCl				38	35
10 mM HCl			2.7		7.5
10 mM HCl + 10 mM NaCl		16	4.0		0.6
10 mM HCl + 10 mM KCl			8.7	206	82
10 mM NaCl + 10 mM KCl + 10 mM HCl		21	5.0	3.9	1.5

An entry in this table means that when estimating for example K^+ in a 10 mM KCl solution, a one percent offset in the measured conductivities will result into an 38% error in the fitted concentration.

Some remarks can be made. The error in the fitted H^+ concentration does not escalate excessively, but the error amplification seems to remain lower than ten. A factor ten means that for a 5% error in the fit, a 0.5% error in the measured conductivity is allowed. Roughly speaking, the allowed ”background” normality may therefore not exceed 0.5% of the concentration of interest.

The real problem with this type of error is that it is unpredictable. For example the amplification of errors can range from 0.6 to 206. Without knowing, a small error due to a contamination in the system will be enormously amplified. The maximum amplification which is empirically found here is 206. Although it is not guaranteed that no larger amplifications will be observed in other systems, a rough estimation of the possible detection limit of ions in demi water is possible. Using demi water with a purity of 0.5 mS/cm, for a 5% error in the fitted ion concentrations a conductivity of 2.0 mS/cm is the lower limit. This is equivalent to for example a 15 mM KCl solution. So when trying to fit the ion concentration in solutions with a lower concentration, the impurity of the demi water might already disturb the estimation.

4. Some experimental examples of ion fitting

The fitting theory was tested for electrolytes having only three types of ions. The reason is that in a two ion system the separate concentrations are already determined by a single conductivity measurement, while on the other hand the fitting of four ion types would probably be too sensitive to errors considering the previous subsection.

4.1 Measurement set-up

The presented theory is verified using a Radiometer CDM210 commercial conductivity meter in a computer controlled set-up as shown in figure 3. This meter is capable of measuring conductivity, using a four points electrode (type Radiometer CDC565), and the solution temperature (using a Radiometer temperature probe type T201). For this measurement, the automatic temperature compensation of the CDM210 must be switched off, and the automatic measurement range adaptation as well. Each measurement starts at room temperature. After a heating and stirring step, an equilibrium time of 5 seconds is used before measuring. This sequence is repeated until the temperature exceeds 55ºC.

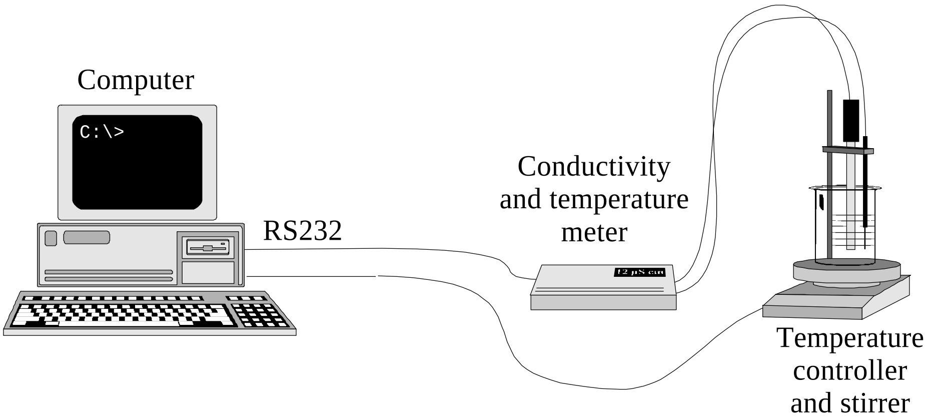


Figure 3: Measurement set-up for recording the conductivity at several temperatures

The protocol is controlled by LabView 3.1 software, providing the user with an interactive interface. First the user is asked to prepare a solution and place it on the heater. The program switches on the heater and measures the conductivity equidistantly over the given range. After the measurement has finished, a dialogue box asks to select the ions which are present in the solution. In a result window, the measured curve, the fitted curve and fitted ion concentrations are presented to the user.
The implementation of the estimation algorithm, both for the normal and the zero charge case, is also done in LabView. The parameters for equation (2) are taken from Harned and Owen [4].

4.2 The measurements

Figure 4 shows a series of conductivity measurements in a solution of 10 mM HCl and 25 mM NaCl while the solution was heated and stirred as described. As an illustration, a fitted third order polynomial is plotted as well. It is this polynomial which is a linear combination of the polynomials for H^+, Na^+ and Cl^-.

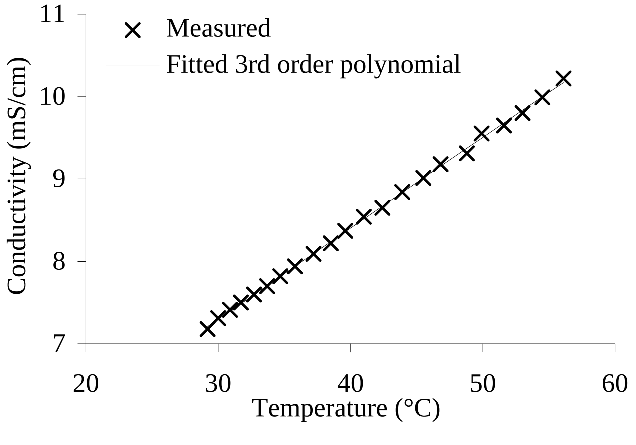


Figure 4: A conductivity versus temperature scan in a solution of 10 mM HCl and 25 mM NaCl

By taking the measured conductivities at 29.2, 37.2 and 53.0°C, equation (7) becomes

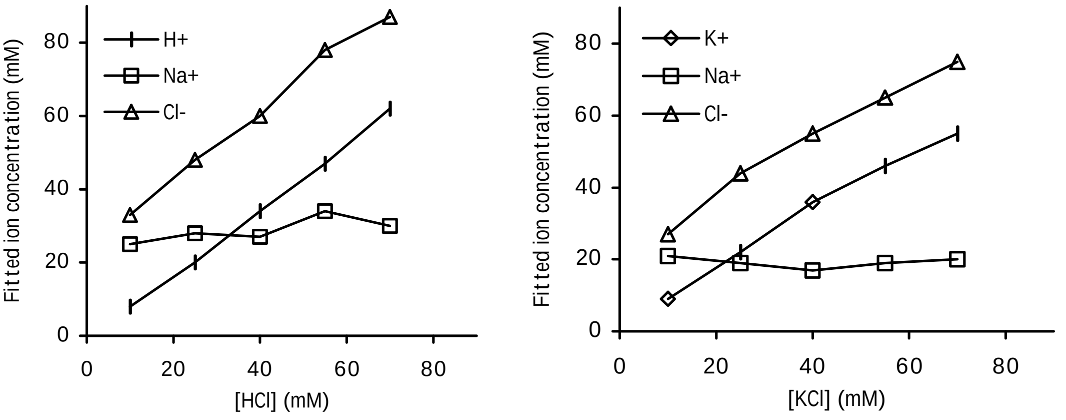
$$\begin{bmatrix} 7.21 \cdot \text{mS/cm} \\ 8.09 \cdot \text{mS/cm} \\ 9.83 \cdot \text{mS/cm} \end{bmatrix} = \begin{bmatrix} 1.057 & 1.093 & 1.086 \\ 1.163 & 1.279 & 1.255 \\ 1.358 & 1.678 & 1.609 \end{bmatrix} \cdot \begin{bmatrix} c_{H^+}\, 349.85 \cdot 10^{-4}\, \text{m}^2\text{S / mol} \\ c_{Na^+}\, 50.15 \cdot 10^{-4}\, \text{m}^2\text{S / mol} \\ c_{Cl^-}\, 76.35 \cdot 10^{-4}\, \text{m}^2\text{S / mol} \end{bmatrix}$$

from which the fitted concentrations are:

$[H^+]$ = 12.9 mM,
$[Na^+]$ = 32.5 mM, and
$[Cl^-]$ = 27.9 mM.

Although errors of 30% are observed with this simple example, it shows the simplicity of the ion estimation method. For further estimations, however, the zero charge condition will be incorporated to increase the accuracy by trimming the ratio between anions and cations.

The were repeated for solutions consisting of 25 mM NaCl and various concentrations (ranging from 10 to 70 mM) of either KCl or HCl. A polynomial approximation of order J = 3 was used, while the number of applied temperatures per electrolyte is N = 25. The results are graphically represented in figure 5. Unlike with the previous small numerical example, now the zero charge boundary condition is used.



(a) (b)

Figure 5: Result of fitting ions in 25 mM NaCl with various (a) HCl or (b) KCl concentrations, using the zero charge condition

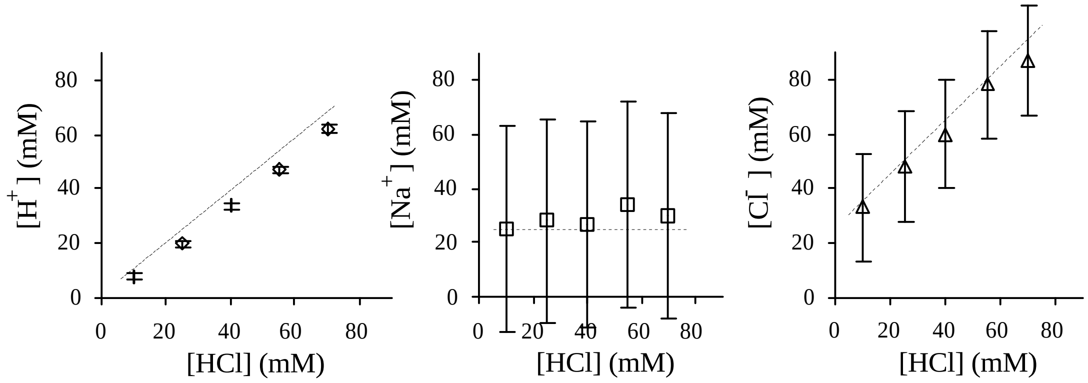
4.3 Discussion

A proportional relationship between the fitted ion concentrations for H^+, K^+ and Cl^- and the actual concentration is certainly observed, while the fitted Na^+ concentration remains constant. However, the ratio between the imposed ion concentration and the calculated concentration is not equal to one. In figure 5a the fitted concentrations are only 80% of the real concentrations, while this is even lower in figure 5b. Such proportional errors where already mentioned in subsection 2.2.

Other types of errors discussed in this subsection, are errors due to random noise and errors due to offsets in the measurements. While the effect of the error due to random noise in the observed conductivity is minimised by taking a large number of measurements, the size of the error due to offsets in the measured conductivity is unknown up to now. In subsection 4.4 the propagation of errors of this type will be discussed.

4.4 Error propagation

With the knowledge of the absolute errors introduced in subsection 3.2, error bars can be drawn in previously measured concentration plots. For example, figure 6 is repeated from figure 5a, but now with error bars and plotted in three separate graphs. Since there is no formula derived for the absolute errors when using the zero charge condition, the error bars for the non-zero charge method are placed in the graph with concentrations fitted using the zero charge condition. This will result into a worst case guess of the error. The dotted lines in the graphs are the imposed ion concentrations.



(a) (b) (c)

Figure 6: Fitted ion concentrations with error bars in solutions with 25 mM NaCl and several HCl concentrations. (a) H^+, (b) Na^+ and (c) Cl^-

The error bars are obviously a bit too pessimistic for Na^+ and Cl^- since the correlation between fitted concentration and the real concentration is much larger than may be assumed according to these error bars.

When implementing the zero charge condition, the matching between anions and cations will be improved. Although no algorithm is given here for calculating the absolute errors in the fitted results when this condition is included, it may be assumed that the errors will decrease.

Although this decrease is not known, it is probably meaningless to fit four ions, since table 3 shows that then the worst case error will exceed the one molar limit. Because the given values are only valid in the 40 mS/cm range, the errors are far more than the present ion concentrations.

5. Conclusions

From a non-selective conductivity measurement, it is possible to find specific ion concentrations by recording the conductivity at different temperatures. The key to this is that every ion has its own specific limiting molar conductivity which depends uniquely on temperature. This method needs an assumed set of ions: the electrolyte conductivity is a linear combination of the specific ionic conductivities of these ions.

The first condition needed for making the system solvable is that in order to fit I ions, at least N = I measurements at different temperatures are needed. However, to increase the accuracy, more measurements are preferred and subsequently an estimation algorithm is used to find the best fit. The second condition is that the characteristic polynomial used for the temperature dependencies of the limiting molar ionic conductivities is at least of order J = I - 1. Next, the coefficients $k_{i,j}$ in this polynomial must be unique for every single ion because the whole recognition is based on the difference in these coefficients. This is true since every single ion has a different size and mass and will therefore have another temperature dependency in its ionic conductivity. Finally, every ion which is significantly present in the solution must be included in the calculation, since the method is based on the conductivity being a linear combination of all the separate ionic conductivities.

In order to increase the accuracy of the calculated ion concentrations, either the temperature sweep or the number of points N can be increased. Increasing the temperature sweep, however, has a much more positive effective result on the accuracy.
For N = I, one unique solution for the ion concentrations is possible. For N > I, an estimation algorithm must be chosen. A linear estimation algorithm based on the minimum mean square error was introduced.
Actually, there is a third method for increasing the accuracy. The knowledge that the sum of all charges is zero in equilibrium can be included in the estimation algorithm as a boundary condition. Especially for “difficult” ion pairs (like chloride and potassium for example) the use of this condition appeared to be essential.
However, the use of an estimation algorithm can only decrease the errors due to random noise. An error in the observed conductivities due to the presence of an ion which is not in the assumed set, will propagate to an error in the fitted ion concentrations which can not be decreased by taking more measurements.

For only two ions in the solution, the introduced method is not necessary because then a single conductivity measurement already determines both ion concentrations. For four ions, the method is probably too sensitive to errors because a small error in the measured conductivity might result into an enormous error in the fitted ion concentration. A worst case analysis shows that the absolute error in the fitted concentration becomes sometimes more than one molar when the conductivity meter is switched in the 40 mS/cm range. So, in conclusion, the method will show the best results in systems having three different types of ions.

Summarising, it can be said that the advantage of this method is that it introduces selectivity by smart data interpretation, and not by the sensor itself. In general, when a sensor is made selective, fragile and complex selective membranes are introduced. This results into transducers with a whole sandwich of membranes on top of it. Electrolyte conductivity sensing, on the other hand, is easy, chemically inert and mechanically stable since it uses a solid metal structure. It is a reproducible technique since the cell constant which determines the sensitivity shows no drift in principle.

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