The sensors for the intelligent micro washing system
Conductivity and temperature

Work report 10, 6-Oct-97
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1. Introduction

Because the mathematics in this report might be quite difficult to follow, this introduction gives a simplified equivalent of the problem. The problem here is to find information on individual terms while only the sum of these terms can be measured.

Consider two parameters y_1 and y_2 which are both a function of the parameter x:

$$y_1 = a_1 x + b_1 , \quad y_2 = a_2 x + b_2 . \tag{1.1}$$

Imagine the situation where only the linear combination of y_1 and y_2 can be observed:

$$y = \alpha_1 y_1 + \alpha_2 y_2 . \tag{1.2}$$

If we are interested in the α coefficients, they can be found from the x-y relation under certain circumstances. The problem is graphically represented by Figure 1.1.

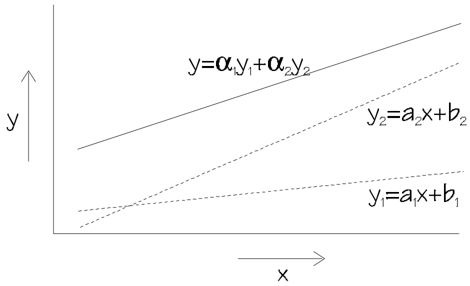


Figure 1.1: Linear combination of two trends

The measured variable y can be written as a slope a’ and an offset b’. From the measured x-y relation this slope and offset can be determined. We have now two equations with two unknown parameters which can be solved:

$$\left.\begin{array}{r} \text{slope}(y) = a' = \alpha_1 a_1 + \alpha_2 a_2 \\ \text{offset}(y) = b' = \alpha_1 b_1 + \alpha_2 b_2 \end{array}\right\} \Rightarrow \begin{bmatrix} \alpha_1 \\ \alpha_2 \end{bmatrix} = \begin{bmatrix} a_1 & a_2 \\ b_1 & b_2 \end{bmatrix}^{-1} \begin{bmatrix} a' \\ b' \end{bmatrix} . \tag{1.3}$$

The conditions are:

- The measured variable y is a linear combination of the curves y_i;
- The coefficients a_i and b_i of the individual curves y_i must be known;
- The measured curve y must be specified by at least two points;
- The functions $y_i(x)$ are not allowed to be parallel;

Under these conditions the coefficients α_i can be solved.

This theory can easily be expanded to the situation of a series of conductivity measurements as a function of temperature. The contributions of the individual ions to the measured conductivity can be compared to equation (1.2) with the factors α_i the ion concentrations. Each ion mobility has a unique response on temperature like equations (1.1). So under the mentioned conditions the individual concentrations of ions can be calculated from a conductivity versus temperature scan.

2. Conductivity and temperature theory

Some parts of this chapter are already presented in a previous work report, for completeness they are repeated here.
First, some theory concerning the influence of temperature on conductivity measurements is shortly described. Next, a mathematical model for the temperature dependency of conductivity is presented. In the third subsection it is proven that it is not possible to identify ions by measuring conductivity at various temperatures. However, it is possible to fit ion concentrations in this way when a set of ions is assumed, which is described in the fourth subsection. Finally, the last subsection deals with the propagation of errors with this method.

2.1 The effect of temperature on conductivity

A single conductivity measurement is not interesting unless the measured value is normalised for temperature. The reason for this is that at 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. In general, the measured conductivity is compensated to 25°C by using a temperature measurement.

The total conductivity of an electrolyte expressed in terms of the limiting molar conductivities of the separate ions can be expressed by:

$$\Lambda = \sum_{i=1}^{I} |z_i| c_i \lambda_i(T) \tag{2.1}$$

with z_i the charge of ion i, c_i the concentration, I the number 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 among ions, it is not possible to eliminate mathematically 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 for a moderate temperature range [1]. More sophisticated fits compensate by using a third order polynomial, but this method is electrolyte and concentration dependent [2].

A more complicated temperature compensation uses 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

$$\lambda_i(T) = \lambda_i^0 \left[1 + k_{i,1}(T-25) + k_{i,2}(T-25)^2 + k_{i,3}(T-25)^3\right] \tag{2.2}$$

with $\lambda_i{}^0$ the limiting molar conductivity of ion i at 25°C. This polynomial approach will be used for ion identification.

2.2 General description

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

$$\lambda_i(T) = \lambda_i^0 \sum_{j=0}^{J} k_{i,j}\left(T - T_0\right)^j . \qquad (2.3)$$

Together with equation (2.1) the total conductivity of an electrolyte having I ions can now be calculated:

$$\Lambda(T) = \sum_{i=1}^{I}\left[\left|z_i\right|c_i\lambda_i^0 \sum_{j=0}^{J} k_{i,j}\left(T - T_0\right)^j\right] \qquad (2.4)$$

Manipulation yields:

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

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

$$\Lambda(T) = \sum_{j=0}^{J}\left[\left(T - T_0\right)^j \sum_{i=0}^{I}\left(\left|z_i\right|c_i\lambda_i^0 k_{i,j}\right)\right] \qquad (2.5)$$

For N conductivity measurements at different temperatures, I ions and a polynomial fit of order J, a matrix equation can be formed using equations (2.5):

$$\begin{bmatrix}\Lambda_1\\ \Lambda_2\\ .\\ .\\ \Lambda_N\end{bmatrix} = \begin{bmatrix}1 & (T_1-T_0) & (T_1-T_0)^2 & . & (T_1-T_0)^J\\ 1 & (T_2-T_0) & (T_2-T_0)^2 & . & .\\ . & . & . & . & .\\ . & . & . & . & .\\ 1 & (T_N-T_0) & (T_N-T_0)^2 & . & (T_N-T_0)^J\end{bmatrix} \cdot \begin{bmatrix}k_{1,0} & k_{2,0} & . & k_{I,0}\\ k_{1,1} & k_{2,1} & . & .\\ . & . & . & .\\ . & . & . & .\\ k_{1,J} & k_{2,J} & . & k_{I,J}\end{bmatrix} \cdot \begin{bmatrix}|z_1|c_1\lambda_1^0\\ |z_2|c_2\lambda_2^0\\ .\\ |z_I|c_I\lambda_I^0\end{bmatrix} \qquad (2.6)$$

or

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

The meaning of the terms is:

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

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 when 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. The next section, however, shows that this is not possible, unfortunately.

2.3 Identification of ions by solving the coefficient matrix K

If equation (2.6) can be solved completely (both $\overline{\overline{K}}$ and $\overline{c}$ separately), the present ions can be identified by comparing the columns of matrix $\overline{\overline{K}}$ to known coefficients. Afterwards, the corresponding concentrations can be found from the vector $\overline{c}$.

The solution for the $\overline{\overline{K}} \cdot \overline{c}$ product is given by

$$\overline{\overline{K}} \cdot \overline{c} = \overline{\overline{T}}^{-1} \cdot \overline{\Lambda}. \tag{2.7}$$

with:

$$\overline{\overline{K}} \cdot \overline{c} = \begin{bmatrix} k_{1,0} & k_{2,0} & . & k_{I,0} \\ k_{1,1} & k_{2,1} & . & . \\ . & . & . & . \\ . & . & . & . \\ k_{1,J} & k_{2,J} & . & k_{I,J} \end{bmatrix} \cdot \begin{bmatrix} |z_1|c_1\lambda_1^0 \\ |z_2|c_2\lambda_2^0 \\ . \\ |z_I|c_I\lambda_I^0 \end{bmatrix}. \tag{2.8}$$

From this equation it will be clear that the coefficients $k_{i,j}$ can never be calculated without knowing the terms $|z_i|c_i\lambda_i^0$. In other words: for every set of coefficients $k_{i,j}$ another set of concentrations will be found. So the coefficients must be known for solving the concentrations.
Notice that the number of measurements is not visible in equation (2.8) so increasing the number of measurements will not solve the problem of te unsolvable coefficient either.

2.4 Calculation of ion concentrations by assuming coefficients

When the $\overline{\overline{K}}$ matrix is assumed to be known, equation (2.6) can be written as

$$\begin{bmatrix} \Lambda_1 \\ \Lambda_2 \\ . \\ . \\ \Lambda_N \end{bmatrix} = \begin{bmatrix} \sum_{j=0}^{J} k_{1,j}(T_1 - T_0)^j & \sum_{j=0}^{J} k_{2,j}(T_1 - T_0)^j & . & \sum_{j=0}^{J} k_{I,j}(T_1 - T_0)^j \\ \sum_{j=0}^{J} k_{1,j}(T_2 - T_0)^j & \sum_{j=0}^{J} k_{2,j}(T_2 - T_0)^j & . & . \\ . & . & . & . \\ \sum_{j=0}^{J} k_{1,j}(T_N - T_0)^j & . & . & \sum_{j=0}^{J} k_{I,j}(T_N - T_0)^j \end{bmatrix} \cdot \begin{bmatrix} |z_1|c_1\lambda_1^0 \\ |z_2|c_2\lambda_2^0 \\ . \\ |z_I|c_I\lambda_I^0 \end{bmatrix} \tag{2.9}$$

where the $\overline{\overline{T}} \cdot \overline{\overline{K}}$ matrix is written as a single one. The terms 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

$$\overline{c} = \left(\overline{\overline{T}} \cdot \overline{\overline{K}}\right)^{-1} \cdot \overline{\Lambda} \,. \qquad (2.10)$$

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>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.

So 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 must be represented in the calculations;
  - → No two ions may have the same temperature dependency (which will probably never be the case);
  - → When I ions have to be calculated, at least I measurements should be performed;
  - → The order of the used polynomials is larger than the number of 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 9 ions;

As could be expected, these conditions resemble the ones as empirically stated in the introduction.

2.5 Error propagation

Two kinds of errors can be expected during measurement:

- Inaccuracy in the measurement which causes proportional errors;
- Systematic errors which result in an unintended offset in the measured conductivity. This can be the result of the conductivity due to an ion which is not implemented in the calculation algorithm;

Proportional errors

Errors due to the inaccuracy of the conductivity measurement are proportional to the measurement itself. This can be written as an undesired multiplication of L by x. For proportional errors equation (2.10) can be written as:

$$\overline{c}^{\xi} = \left(\overline{\overline{T}} \cdot \overline{\overline{K}}\right)^{-1} \cdot \overline{\Lambda\xi} \,. \qquad (2.11)$$

When x is equal for every single measurement, this results in

$$\overline{c}^{\xi} = \left(\overline{\overline{T}} \cdot \overline{\overline{K}}\right)^{-1} \cdot \overline{\Lambda} \cdot \xi = \overline{c} \cdot \xi \qquad (2.12)$$

so an x percent error in the measured conductivity will result in an x percent error in the calculated ion concentrations.

Systematic errors

A systematic error manifests as an unknown offset in the measurement. This can be written as a constant addition e of L. For systematic errors equation (2.10) becomes:

$$\overline{c}^{\varepsilon} = \left(\overline{\overline{T}} \cdot \overline{\overline{K}}\right)^{-1} \cdot \left(\overline{\Lambda} + \overline{\varepsilon}\right). \qquad (2.13)$$

Manipulation yields:

$$\overline{c}^{\varepsilon} = \left(\overline{\overline{T}} \cdot \overline{\overline{K}}\right)^{-1} \overline{\Lambda} + \left(\overline{\overline{T}} \cdot \overline{\overline{K}}\right)^{-1} \overline{\varepsilon} = \overline{c} + \left(\overline{\overline{T}} \cdot \overline{\overline{K}}\right)^{-1} \overline{\varepsilon}\,. \qquad (2.14)$$

It will be clear that this kind of error can have a lot more influence on the fitted $\overline{c}$ vector than proportional error. The reason is that the error vector $\overline{\varepsilon}$ is unpredictable and will be amplified by the algorithm.

3. Estimation method

The previous method is not very accurate because the number of parameters to be solved is equal to the number of experiments. It is better to do more measurements ($N > I$*) and use an estimation method. In order to find the best fit from the measurements, some theory concerning parameter estimation is necessary. This is done in the first subsection. In the next subsection, the estimation algorithm is reduced to a more convenient form. The implementation of the condition that the sum of charge in a solution will be equal to zero is implemented in the third subsection.*

3.1 Parameter estimation theory

The method introduced here is a matrix based algorithm for minimising the mean square error of the estimation [5]. Consider the generalised system:

$$\overline{\Lambda} = \overline{\overline{B}} \cdot \overline{c} + \overline{v} \tag{3.15}$$

with

$\overline{\Lambda}$ the vector containing the observations,
$\overline{\overline{B}}$ a matrix representing the system (in our case 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 $\overline{\Lambda}$. When the average of the estimate is the true value:

$$E\left(\hat{\overline{c}}\right) = \overline{c} \tag{3.16}$$

then the estimate is called unbiased. 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:

$$\overline{e} = \hat{\overline{c}} - \overline{c} = \hat{\overline{c}} - E\left(\hat{\overline{c}}\right). \tag{3.17}$$

The aim of the estimation algorithm is to minimise this error vector. In general a function of $\overline{e}$ is chosen for optimisation, which can be the average mean square error of the components of $\overline{e}$:

$$\overline{\overline{C}}_{\overline{e}} \equiv E\left(\overline{e}\,\overline{e}^T\right) = E\left[\left(\hat{\overline{c}} - E\left(\hat{\overline{c}}\right)\right)\left(\hat{\overline{c}} - E\left(\hat{\overline{c}}\right)\right)^T\right] \tag{3.18}$$

known as the covariance matrix of the estimate. The diagonal terms of this matrix are the variances of the estimate's components. The best estimate can now be defined as the one having the smallest variances: the minimum variance unbiased estimator.

If $\overline{c}$ and $\overline{\Lambda}$ are random variables with moment matrices

$$\begin{aligned}
&\overline{\overline{C}}_{\overline{c}} \equiv E\left(\overline{c}\,\overline{c}^{T}\right)\\
&\overline{\overline{C}}_{\overline{c}\overline{\Lambda}} \equiv E\left(\overline{c}\,\overline{\Lambda}^{T}\right)\\
&\overline{\overline{C}}_{\overline{\Lambda}} \equiv E\left(\overline{\Lambda}\,\overline{\Lambda}^{T}\right)
\end{aligned} \tag{3.19}$$

where $\overline{\overline{C}}_{\overline{\Lambda}}$ is non-singular, then the linear minimum mean square estimate $\hat{\overline{c}}$ of $\overline{c}$ given data $\overline{\Lambda}$ is according to the Gauss-Markoff theorem [5] equal to

$$\boxed{\hat{\overline{c}} = \overline{\overline{C}}_{\overline{c}\overline{\Lambda}}\,\overline{\overline{C}}_{\overline{\Lambda}}^{-1} \cdot \overline{\Lambda}}\,. \tag{3.20a}$$

The associated error matrix of the estimate is

$$\boxed{\overline{\overline{C}}_{\overline{e}} = \overline{\overline{C}}_{\overline{c}} - \overline{\overline{C}}_{\overline{c}\overline{\Lambda}}\,\overline{\overline{C}}_{\overline{\Lambda}}^{-1}\,\overline{\overline{C}}_{\overline{c}\overline{\Lambda}}^{T}}\,. \tag{3.20b}$$

Now the theorem will be written in terms of the covariance matrices $\overline{\overline{C}}_{\overline{c}}$ and $\overline{\overline{C}}_{\overline{cv}}$ because these are the closest to physical interpretation. The first one is the auto covariance of the concentration vector and the second one represents the correlation between concentration and noise. Substituting (3.15) in (3.19) yields:

$$\overline{\overline{C}}_{\overline{c}\overline{\Lambda}} = \overline{\overline{C}}_{\overline{c}}\,\overline{\overline{B}}^{T} + \overline{\overline{C}}_{\overline{cv}}\,. \tag{3.21}$$

And for $\overline{\overline{C}}_{\overline{\Lambda}}$:

$$\overline{\overline{C}}_{\overline{\Lambda}} = \overline{\overline{B}}\,\overline{\overline{C}}_{\overline{c}}\,\overline{\overline{B}}^{T} + \overline{\overline{C}}_{\overline{cv}}^{\;T}\,\overline{\overline{B}}^{T} + \overline{\overline{B}}\,\overline{\overline{C}}_{\overline{cv}} + \overline{\overline{C}}_{\overline{v}}\,. \tag{3.22}$$

The Gauss-Markoff theorem (3.20) can now be written as:

$$\boxed{\hat{\overline{c}} = \left(\overline{\overline{C}}_{\overline{c}}\,\overline{\overline{B}}^{T} + \overline{\overline{C}}_{\overline{cv}}\right)\left(\overline{\overline{B}}\,\overline{\overline{C}}_{\overline{c}}\,\overline{\overline{B}}^{T} + \overline{\overline{C}}_{\overline{cv}}^{\;T}\,\overline{\overline{B}}^{T} + \overline{\overline{B}}\,\overline{\overline{C}}_{\overline{cv}} + \overline{\overline{C}}_{\overline{v}}\right)^{-1} \cdot \overline{\Lambda}} \tag{3.23a}$$

and

$$\boxed{\overline{\overline{C}}_{\overline{e}} = \overline{\overline{C}}_{\overline{c}} - \left(\overline{\overline{C}}_{\overline{c}}\,\overline{\overline{B}}^{T} + \overline{\overline{C}}_{\overline{cv}}\right)\left(\overline{\overline{B}}\,\overline{\overline{C}}_{\overline{c}}\,\overline{\overline{B}}^{T} + \overline{\overline{C}}_{\overline{cv}}^{\;T}\,\overline{\overline{B}}^{T} + \overline{\overline{B}}\,\overline{\overline{C}}_{\overline{cv}} + \overline{\overline{C}}_{\overline{v}}\right)^{-1}\left(\overline{\overline{C}}_{\overline{c}}\,\overline{\overline{B}}^{T} + \overline{\overline{C}}_{\overline{cv}}\right)^{T}} \tag{3.23b}$$

3.2 Simplified estimation algorithm

In order to eliminate the covariance matrices $\overline{\overline{C}}_{\overline{c}}$ and $\overline{\overline{C}}_{\overline{cv}}$ some assumptions can be made [5]:

→ the elements of $\overline{v}$ are uncorrelated and have equal standard deviations s_v;

→ $\overline{c}$ and $\overline{v}$ are uncorrelated ($\overline{\overline{C}}_{\overline{cv}} = 0$);

→ the true state of $\overline{c}$ is unknown so its moment matrix satisfies $\overline{\overline{C}}_{\overline{c}} \to \infty$ (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:

$$\boxed{\hat{\overline{c}} = \left(\overline{\overline{B}}^{T}\,\overline{\overline{B}}\right)^{-1}\overline{\overline{B}}^{T} \cdot \overline{\Lambda}} \tag{3.24a}$$

which reduces to (2.10) for a square matrix $\overline{\overline{B}}$. The associated error matrix of the estimate is

$$\boxed{\overline{\overline{C}}_e = \left(\overline{\overline{B}}^T\overline{\overline{B}}\right)^{-1} \cdot \sigma_v{}^2} \tag{3.24b}$$

The numbers on the diagonal of this error matrix are the covariance coefficients of the fitted parameters, so the standard deviation of the fit is given by:

$$\sigma_c = \sqrt{\mathrm{trace}\left(\overline{\overline{B}}^T\overline{\overline{B}}\right)^{-1}} \cdot \sigma_v \tag{3.25}$$

where the trace function is the summing of the elements on the diagonal of a matrix.

Summary

Applying this theory to equation (2.9), the method becomes:

- Calculate the matrix $\overline{\overline{B}}$ with the elements:

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

  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 (from table);
- Create the conductivity vector $\overline{\Lambda}$, which is a column of N conductivity measurements at N different temperatures;
- Use equation (3.24a) for finding the vector $\hat{\overline{c}}$, which is a column of the $|z_i|c_i\lambda_i^0$ products of the I ions. Because z_i and λ_i^0 are known, the concentrations of the individual ions can be calculated;
- The propagation of errors through this estimation method is represented by equation (3.24b).

By examining equation (3.25) it can be seen that the accuracy of the estimation can be increased either by increasing the number of measurements or the temperature range.

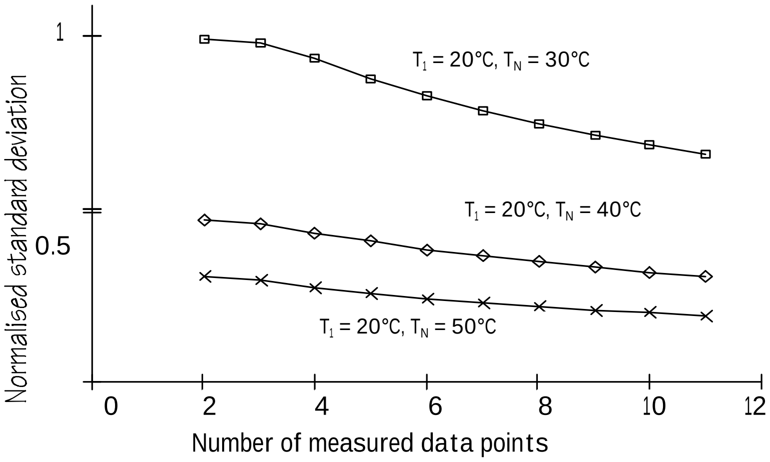


Figure 3.1: Effect of the temperature range and the number of measurements on the estimation accuracy.

Figure 3.1 shows that the improvement in accuracy by increasing the temperature range is larger than the improvement obtained by using more measurements.

3.3 Implementing the zero charge condition

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

$$\sum_{\text{Cations}} |z_i| c_i = \sum_{\text{Anions}} |z_i| c_i \tag{3.26}$$

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 (2.9) as

$$\begin{bmatrix} \Lambda_1 \\ \Lambda_2 \\ \cdot \\ \cdot \\ \Lambda_N \\ \hline 0 \end{bmatrix} = \left[\begin{array}{cccc} \sum\limits_{j=0}^{J} k_{1,j}(T_1 - T_0)^j & \sum\limits_{j=0}^{J} k_{2,j}(T_1 - T_0)^j & \cdot & \sum\limits_{j=0}^{J} k_{I,j}(T_1 - T_0)^j \\ \sum\limits_{j=0}^{J} k_{1,j}(T_2 - T_0)^j & \sum\limits_{j=0}^{J} k_{2,j}(T_2 - T_0)^j & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \sum\limits_{j=0}^{J} k_{1,j}(T_N - T_0)^j & \cdot & \cdot & \sum\limits_{j=0}^{J} k_{I,j}(T_N - T_0)^j \\ \hline \dfrac{z_1}{|z_1|\lambda_1^0} & \dfrac{z_2}{|z_2|\lambda_2^0} & \cdot & \dfrac{z_I}{|z_I|\lambda_I^0} \end{array} \right] \cdot \begin{bmatrix} |z_1| c_1 \lambda_1^0 \\ |z_2| c_2 \lambda_2^0 \\ \cdot \\ |z_I| c_I \lambda_I^0 \end{bmatrix} \tag{3.27}$$

were the augmented $\overline{\overline{T}} \cdot \overline{\overline{K}}$ matrix is now referred to as $\left[\overline{\overline{T}} \cdot \overline{\overline{K}}\right]_{\text{Augm}}$.

This augmented model can be evaluated like the original model using the same estimation algorithm. However, the condition (3.26) will have the same priority as every single measurement and so its importance will be suppressed. Two options are available for increasing this 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 (3.24) is [5]:

  $$\hat{\overline{c}} = \left(\overline{\overline{B}}^T \overline{\overline{W}}^{-1} \overline{\overline{B}}\right)^{-1} \overline{\overline{B}}^T \overline{\overline{W}}^{-1} \cdot \overline{\Lambda} \tag{3.28a}$$

  $$\overline{\overline{C}}_e = \left(\overline{\overline{B}}^T \overline{\overline{W}}^{-1} \overline{\overline{B}}\right)^{-1} \cdot \sigma_v^{\,2} \tag{3.28b}$$

  with $\overline{\overline{W}}$ the weight matrix (an I×I square matrix with on the diagonal the only non-zero entries being the weight factors).

- Another possibility is obtained by first reducing the measured information and then implementing the zero charge condition.
  Concerning equation (2.8) it was concluded that the number of measurements is not in the $\overline{\overline{K}} \cdot \overline{c}$ matrix. The measured information (conductivities at N temperatures) can be reduced to J+1 points by first calculating the vector $\overline{\overline{T}}^{-1} \cdot \overline{\Lambda}$ using the simple estimation algorithm. This vector represents the coefficients of an J-th order fit of the measured conductivity versus temperature sweep.

  According to equation (2.6) this vector is equal to $\overline{\overline{K}} \cdot \overline{c}$. The zero charge condition can now again be implemented by augmenting a matrix:

$$\left[\begin{array}{c} \bar{\bar{T}}^{-1}\cdot\bar{\Lambda} \\ \hdashline 0 \end{array}\right] = \left[\begin{array}{cccc} k_{1,0} & k_{2,0} & . & k_{I,0} \\ k_{1,1} & k_{2,1} & . & . \\ . & . & . & . \\ k_{1,J} & k_{2,J} & . & k_{I,J} \\ \hdashline \frac{z_1}{|z_1|\lambda_1^0} & \frac{z_2}{|z_2|\lambda_2^0} & . & \frac{z_I}{|z_I|\lambda_I^0} \end{array}\right] \cdot \left[\begin{array}{c} |z_1|c_1\lambda_1^0 \\ |z_2|c_2\lambda_2^0 \\ . \\ |z_I|c_I\lambda_I^0 \end{array}\right] \tag{3.29}$$

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

4. Measurements

The first section of this chapter describes shortly the automated measurement set-up which was used to verify the developed theory. Some measurements using this set-up were carried out in solutions having only one cation and one anion. These are reported in the second section. The third section reports measurements in solutions having three types of ions. Finally, a more practical application is described in the last section: the measurement of pH by fitting the hydrogen concentration.

4.1 Method

Using a Radiometer CDM210 commercial conductivity meter in a computer controlled set-up as shown in Figure 4.1, the theory was verified.

First, the temperature compensation of the CDM210 was switched off. Each measurement started at room temperature. After a heating and stirring step, an equilibrium time of 5 seconds was used before measuring. This sequence was repeated until the temperature was about 55ºC.

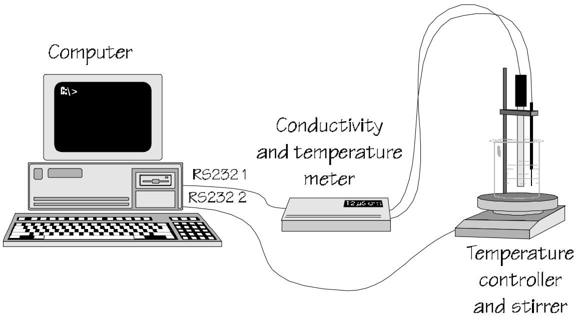


Figure 4.1: Measurement set-up

The protocol was controlled by LabView 3.1 software. For fitting, the parameters given by Harned and Owen [4] were used. These were converted to use with equation (2.2) and can be found in Table 4.1.

Table 4.1: Coefficients to use with equation (2.2) [4]

Ion	Limiting molar conductivity λ^0 [10^{-4} m^2 S mol^{-1}]	k_1	k_2	k_3
H^+	349.85	1.376576×10^{-2}	-2.947692×10^{-5}	-2.192368×10^{-7}
Li^+	38.64	2.302950×10^{-2}	1.140657×10^{-4}	-5.284679×10^{-7}
Na^+	50.15	2.176670×10^{-2}	9.401795×10^{-5}	-2.293121×10^{-7}
K^+	73.50	1.949143×10^{-2}	5.518776×10^{-5}	-4.330612×10^{-7}
Rb^+	77.81	1.901465×10^{-2}	4.935098×10^{-5}	-5.825729×10^{-7}
Cs^+	77.26	1.874062×10^{-2}	4.950815×10^{-5}	-2.653378×10^{-7}
Cl^-	76.35	2.017511×10^{-2}	6.090373×10^{-5}	-1.683039×10^{-7}
Br^-	78.17	1.974799×10^{-2}	5.718306×10^{-5}	-2.942305×10^{-7}
I^-	76.90	1.963498×10^{-2}	5.689207×10^{-5}	-2.821847×10^{-7}

T_{Ref} = 25.0°C

The implementation of the estimation algorithm (3.24), both for the normal and zero charge case, was also done in LabView. Figure 4.2 shows some screenshots of the used program. In the menu shown in the left part, the selection of the ions to fit can be done. The right part shows the result window with the measured curve, the fitted curve and the fitted parameters.

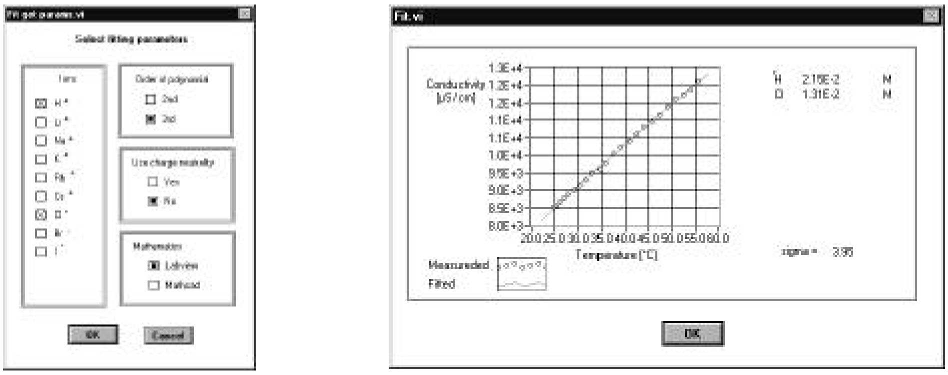
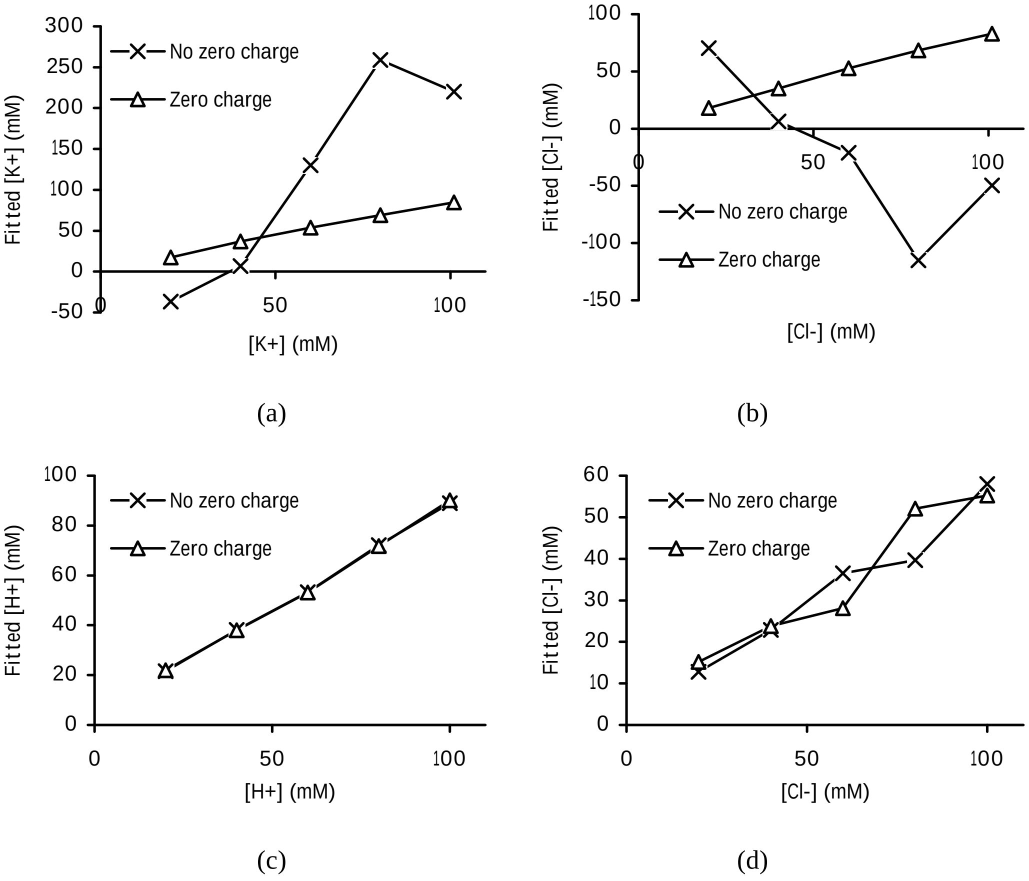


Figure 4.2: Some screenshots of the user interface based on the Labview 3.1 program

4.2 Two ions

First, the theory was tested for electrolytes having only one type of anion and one type of cation, both with and without using the zero charge condition (3.29).



(a) (b)

(c) (d)

Figure 4.3: Fitted ion concentrations for KCl (a) and (b), and HCl (c) and (d)

It is not very surprising that the fitting of hydrogen chloride is much more accurate then potassium chloride because the mobility (and the temperature dependency of this mobility) of potassium and chloride ions is almost equal (a property used in chloride based reference electrodes) which is not the case with hydrogen and chloride. The result is that for fitting KCl the usage of the zero charge condition is essential, while for HCl this is not strictly required.

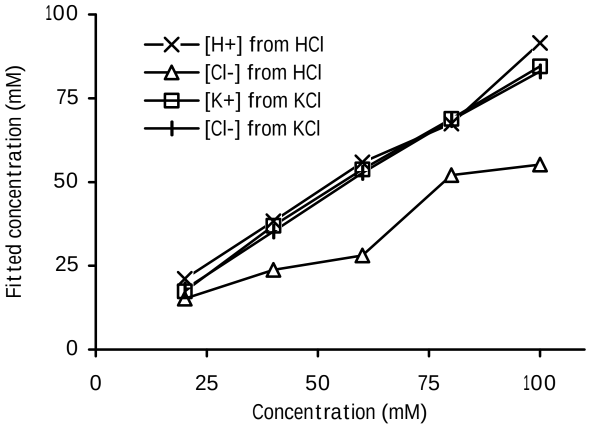


Figure 4.4: Summary of fits using the zero charge condition

4.3 Three ions

The results mentioned above are interesting because they confirm the developed theory. However, the determination of two ions can be done by a single conductivity measurement at a known temperature (with the zero charge condition in mind). The advantage of the method presented here will be in solutions having more then two types of ions.

As a test, a series of solutions was made having 25 mM sodiumchloride and 10 to 70 mM hydrogenchloride or potassiumchloride. The fitted results using the zero charge condition are presented in Figure 4.5.

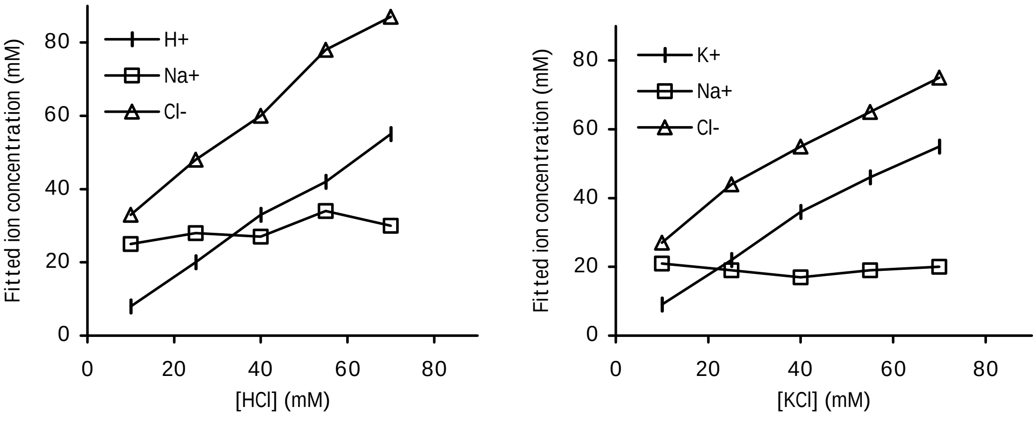


Figure 4.5: Result of fitting ions in 25 mM NaCl with various HCl (a) or KCl (b) concentrations

As could be expected, the fitted sodium concentration remains constant while the other ion concentrations do change.

4.4 A pH Measurement

In some processes a pH measurement using an ISFET or a glass electrode is not possible. These problems often come from the reference electrode, for example because:

- The sample is sensitive to chloride or potassium ions;
- The electrode dries out because it is not constantly immersed with water;
- The liquid junction is contaminated with proteins, oil or sulfide;
- Extremely high temperatures or low pH.

In these situations the fitting method can still be applied because the heater and conductivity cell can be made of a rigid conductor on a chemically inactive substrate.

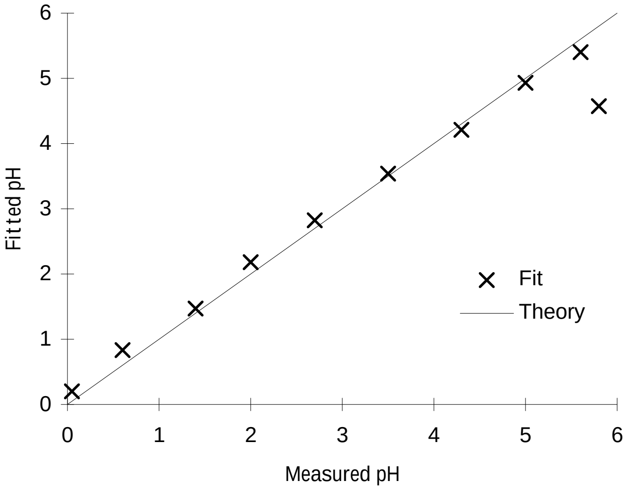


Figure 4.6: A measurement in HCl plotted as a pH determination

Starting in 0.9 M HCl and diluting down to 2 μM, a series of pH’s was created. The fitted hydrogen concentrations are presented in Figure 4.6. Coming close to pH 5.5 the determination becomes worse. The explanation is that the measured conductivity is in the order of μS/cm while the used demineralised water was of the quality 0.59 μS/cm.

Although the fitting of two types of ions is quite trivial (a single conductivity measurement with the zero charge condition in mind would give the same result), this experiment did verify the theory.

5. Conclusions

From a non-selective conductivity measurement, it is possible to find specific information like ion concentrations by recording conductivity at miscellaneous temperatures. The key to this is that every ion has its own specific limiting molar conductivity which responds uniquely on temperature.

In order to fit N ions, at least N measurements are needed. To increase accuracy, two methods were used.

First a linear estimation algorithm was introduced. This algorithm implements a least square fit for more than N measurements and gives information on the propagation of errors.

The second method is the addition of the condition that the sum of all charges is zero in equilibrium. Especially for “difficult” ion pairs (like chloride and potassium for example) this second method appeared to be essential.

For only two ions in 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 third order polynomial is required (and the third order coefficients are a factor hundred smaller then the others). So, concluding it can be said that the method is probably only of interest for systems of three different types of ions.

Future work concerning this ion-fitting method

Although some aspects concerning error propagation were handled, no conclusion was made about the detection limit. The formulas describing the error propagation should be evaluated in order to say something about what background conductivity (the sum of all ions which are not taken along in the fitting algorithm) is allowed.

Furthermore, the algorithm might give negative answers, even if charge neutrality is assumed. The fitting algorithm must be expanded to avoid negative concentrations.

As mentioned in a previous work report, the conductivity in tap water is determined for 90% by Ca^{2+}, Na^{+}, Cl^{-} and HCO_3^{-}. These ions can probably be measured using this method: this is the situation where it becomes attractive for measuring in laundromats.

Finally it should be considered what happens when on purpose three ions are chosen which are not the conductivity determining species. Does the result still give a unique fingerprint of the electrolyte?

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