The sensors for the intelligent micro washing system
Differential measurement systems

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Introduction

In an earlier work report it was concluded that using a substrate with only inert metal films a wide range of parameters can be measured and influenced. These parameters appeared to give a rather complete subset of the washing parameters of interest. After this technological approach an systematic overview of methods for measuring is evaluated now.

There are various ways of obtaining information from a sensor structure. A categorization can be made with respect to the signals that are supplied to the sensor structure in order to retrieve information. Examples are the application of miscellaneous frequency modes, doing dynamic measurements or choosing different inputs in a stimulus response measurement.

The concept evaluated in this report deals with methods that use the technique of spatial differential measurements in combination with a single actuator. The metal-only measurement techniques where used as a guideline for implementing this concept.

1. Overview

It can be questioned why there is a tendency towards a miniaturized sensor-actuator array approach. The answer to this question is split here into two parts. First the advantages of the combination of multiple sensors and actuators are summarized and after that the effect of miniaturization. In a third section the sensors and actuators that are the elements of the array are repeated once more.

1.1. Why using arrays?

The use of sensors in an array configuration has some advantages. With modern silicon technology the realization of more then one sensor does not necessarily result in a more complicated process ore a more expensive device. Generally the adding of a new structure is only a matter of adapting the photo lithography masks.

When more sensor principles for determining a single parameter are present on a sensor array, the combination of the obtained data may lead to more accurate data. On the other hand, measuring two different parameters of a single chemical or physical process gives the possibility of increasing the accuracy of the data. An example is the elimination of a temperature dependency by implementing a temperature sensor.

When a single structure is used to sense two parameters, which is in fact an array as well, the amount of connecting wires will be reduced. Furthermore, the data obtained from this single structure certainly came from the same sample.

Another advantage of using an array is that a pseudo reference system can be constructed. A method to be able to measure without a decent reference is by doing a differential measurement. The differential approach can be either in time (slope or trend detection) or in space (using a differential amplifier). For the first option an actuator must be used to create the slope, for the second one an actuator is necessary to have a known difference between two sensors. So, for creating a pseudo reference, a combination of sensors and actuators in an array might be necessary.

Besides the problem of creating a reference point, calibration of a sensor is an important problem in measurement system design. Calibration can be done by doing an on-line calibration using an actuator. The demands on an accurate sensor are moved then to demands on an actuator. This is possible in an array of sensors and actuators.

1.2. Why miniaturization?

The arrays meant here are more then just a box with some discrete sensors. After combining existing sensors and actuators, the next step is that of miniaturization.

Geometric miniaturization results in different weight factors of effects. While some effects may be neglected when using macro electrodes, with micro electrodes they

might be of interest. So undesired phenomena can be reduced when scaling down which might result in new parameters.
Fast responses can be expected because the "micro experiments" are performed in a local environment. For example a measurement can be repeated at elevated temperature. The heating will be fast because of the volume involved is a small chamber or a local area.
The realization of devices on a single substrate results in sensors which have an extremely good similarity. The devices in the sensor array will come from the same batch and have the same processing history.

1.3. Resuming the sensors and sensor principles

The choice was made to implement the sensor array with elements that can be manufactured by evaporating and etching metal films. Table 1.1 lists the measured parameters and the related washing parameters that can be obtained using this approach.

Table 1.1: Summary of sensors and actuators that can be realized using inert metals only

Sensors	Device	Measured parameter	Washing parameter	Principle
	Pt-100	Temperature	Temperature	Thermoresistive effect
	Flow sensor	Flow	Turbulence	Time of flight or aneamometry
	Interdigitated finger structure	Conductivity	Turbidity, water quality, rinsing effectiveness	Impedance
	Working electrode	H_2O_2 concentration	Bleach activity	Amperometry
	Bubble electrode	DST	Surfactant effectiveness	Electrochemical generation of gas bubbles
Actuators	**Device**	**Actuated parameter**	**Washing parameter**	**Principle**
	Resistor	Local temperature	Local temperature	Thermoresistive effect
	Working electrode	Local H^+, O_2 or H_2 concentration	Local H^+	Electrochemical generation of H^+, OH^-, H_2 or O_2

There are two actuators and five sensors in this table. The flow sensor however, is actually a combination of the temperature actuator and a temperature sensor. The other ones can be seen as elements with which the sensor array can be constructed. A flow measurement is in fact already a small sensor array.

In addition, ion exchangers can be seen as actuators, because ions are on demand exchanged to other ions. For example, materials exist which exchange calcium ions by two protons and reverse. These materials can be used for indirect electrochemical Ca^{2+} release using a coulometric H^+ actuator. A theoretically similar operation can be obtained by using an enzyme actuator which evokes a chemical modification of the sample as well.

So the array elements that will be used are:

Sensors:
- Pt-100 thermoresistive measurement sensor
- Interdigitated finger structure for conductivity sensor
- Amperometric hydrogen peroxide sensor
- Bubble electrode for dynamic surface tension sensing

Actuators:
- Thermoresistive heater
- Electrochemical generation of either H^+ and OH^- or H_2 and O_2
- Ion exchanger (for example Ca^{2+} « $2\ H^+$) or enzyme

The sensing and actuating principles in this list are all possible to produce as micro sensors.

2. Spatial differential measurements

A general set-up for differential measurements is given in figure 2.1. The picture shows a tube approach (the opposite of a bulk system) because this allows the possibility of a shift of the sample or a continuous flow. Only then the sample measured at sensor B is identical to the one that was first at sensor A with the only difference that the actuator modified a single parameter in this sample. Because of the small diameter of the tube this modification will be of the whole cross-section of the tube.

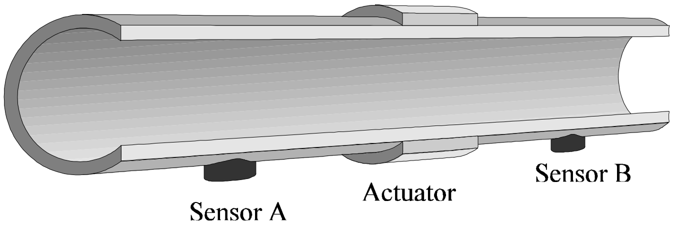

Fig. 2.1: General set-up for a spatial differential measurement using an actuator

For the generalization of systems that use this set-up the mathematical diagram 2.2 will be used. The variable x_1 is the input parameter of interest and is being modified by the actuator to $x_2 = f(x_1)$.

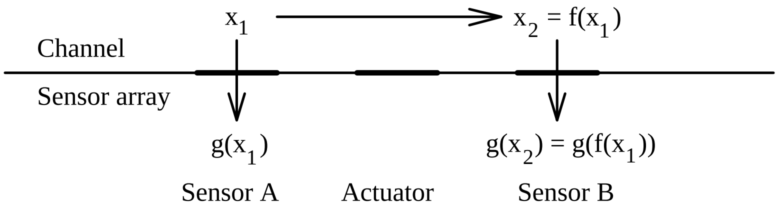

Fig. 2.2: Mathematical representation of a differential measurement system

Both the original sample condition x_1 and the modified condition x_2, are being sensed using two similar sensors. The sensor operation g(x) does not influence the sample.
So two operations are involved: the sensor operation function g(x) and the actuator modification function f(x). These operations will be discussed here separately.

2.1. Evaluation of the sensor operation g(x)

The assumption is made that sensor A and B have the same transducing operation g(x). Some special cases of g(x) functions will be evaluated here.

(a) g(x) is known

When the sensor operation g(x) is completely known, the inverse function g^{-1} can be used to determine the parameter x exactly. In this case, the use of an actuator and a second sensor is actually not necessary for measuring the parameter x. In addition, the advantage of a sensor-actuator approach can be used to study the f(x) function.

However, for realistic sensors this will never be the case because the idea of having an exact g(x) function implies that there is a perfect (absolute) reference.

(b) g(x) is a linear function with an unknown offset

The operation of a lot of sensors can be approached by:

$$g(x) = a_g \cdot x + b_{g\_common} + b_{g\_differential} \tag{2.1}$$

where the constant a_g is the sensitivity which is generally equal for both sensor A and B. The offset of the sensor is represented here by two parts b_g. The first one is the part that is common for both sensor A and B. The effect of an interfering parameter, like temperature, results in such a common offset. The second one is a constant term which is different for sensor A and B. Using a differential measurement it can be found that the output is:

$$g(x_2) - g(x_1) = a_g \cdot (x_2 - x_1) + b_{g\_differential_2} - b_{g\_differential_1} . \tag{2.2}$$

So common (and not necessarily known) offsets b_g will be filtered out when using the sensors in a differential set-up.

Equation (2.2) shows that actually only the difference between the input and output parameters can be measured, but when the actuator function f(x) is chosen well (for example $f(x) = a_f \cdot x$), an absolute value for x_1 can be found.

2.2. Evaluation of the actuator function f(x)

A linear actuator operation will be assumed here. Consider the actuator operation function:

$$f(x) = a_f \cdot x + b_f \tag{2.3}$$

where the parameters a_f and b_f are constant. The most common actuator operations can be identified and categorized by these constants.

(a) Complete depletion of x: $b_f = 0, a_f = 0$

When both a_f and b_f are zero then (2.3) simplifies to f(x) = 0, in other words: the parameter x is completely depleted by the actuator. An example is the effect of an ion exchanger which captures all ions of interest. Another example is an electrochemical actuator which catalizes the degeneration of hydrogen peroxide into hydrogen gas and oxygen gas.

In the case of linear sensors equation (2.2) now gives the absolute value of input parameter x_1 because x_2 equals zero.

(b) Partial depletion or accumulation of x: $b_f = 0, a_f \neq 0$

In the case of a fractional depletion or accumulation of species x, the situation resembles the previous one a lot. This situation represents an incomplete ion exchange where always a fraction $1\text{-}a_f$ is being exchanged. Equation (2.2) becomes:

$$g(x_2) - g(x_1) = a_g(a_f - 1) \cdot x_1 \tag{2.4}$$

with a_f the fraction of depletion (<1) or accumulation (>1) and a_g the sensitivity of the sensors. When this fraction is always the same there is no theoretical difference with the previous situation where $a_f = 0$.

(c) Known addition: $b_f \neq 0, a_f = 1$

A special situation is when parameter x is enlarged by a constant value. This can be done by injecting a known amount of H^+ ions in a sample or by heating a known number of degrees. The differential output (2.2) becomes:

$$g(x_1) - g(x_2) = -a_g \cdot b_f \tag{2.5}$$

so the differential output becomes independent of the input parameter x_1. This method which can be referred to as known addition can be used to determine the sensitivity a_g of the sensors involved.

(d) No actuator operation: $b_f = 0, a_f = 1$

When the actuator does nothing, the input parameter x_1 is exposed to both sensor A and B. Examples are an inactive electrochemical actuator, an inactive heater and a saturated ion exchanger. For non-equal sensor offsets b_g equation (2.2) can be written as:

$$g(x_2) - g(x_1) = \left(a_g \cdot x_2 + b_g{}^B\right) - \left(a_g \cdot x_1 + b_g{}^A\right) = b_g{}^B - b_g{}^A. \tag{2.6}$$

This means that the differential offset due to non equal sensors can be found (and eliminated afterwards) by inactivating the actuator.

2.3. Conclusions

Using a differential measurement system in combination with an actuator a lot of data can be obtained. Therefore the actuator must be controllable in order to select operational modes from which calibration data can be obtained. Important is that both sensors have a similar operation.

A convenient set-up is that of a flow system with a small volume so that the measured samples are equal except for the parameter that is being influenced by the actuator.

3. Evaluation of actuators

After the theoretic evaluation of the previous chapter, now three actuators are being categorized in these theoretic terms. The chosen actuators are the electrochemical actuator (O_2, H_2, H^+ or OH^-), the thermoresistive heater, and the ion exchanger. This choice is made because the product of these actuators is sensitive by sensors that can be realized in the sensor array using only metal films.
Although it can not simply be done using metal films, the detection of pH is evaluated as well in each subsection. This is done because the measurement of pH shows a logarithmic sensor function which is interesting to compare with the linear conductivity sensor.

3.1. Electrochemical actuator

Consider an inert metal working electrode at which the oxidation of water to protons and oxygen gas is controlled by an applied anodic current:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (3.1)$$

or water is reduced to hydroxyl ions and hydrogen gas by a cathodic current:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- . \qquad (3.2)$$

The reaction products H^+ and OH^- can be used for pH control. For the case of equation (3.1) the amount of generated protons follows from integrating the anodic current in time. However, this actuator is not of the "known addition" type (c) because the protons released will cause chemical equilibia in the solution to change so the measured proton concentration at sensor B (figure 2.2) is not proportional to the released amount.

As an example a single weak acid equilibrium is used for the complete description of the system:

$$HAc \leftrightarrow H^+ + Ac^- \qquad k_a = 1.7 \cdot 10^{-5} \qquad (3.3)$$

Before and after the DH^+ the acid-base equilibrium satisfies:

$$\frac{[H^+][Ac^-]}{[HAc]} = k_a . \qquad (3.4)$$

Two equations can be written which describe the continuity of the total amount of Ac^- and H^+ respectively:

$$[Ac^-]_{before} + [HAc]_{before} = [Ac^-]_{after} + [HAc]_{after} = C_{Ac} \qquad (3.5)$$

$$[H^+]_{before} + [HAc]_{before} = [H^+]_{after} + [HAc]_{after} - \Delta H = C_H . \qquad (3.6)$$

From equation (3.4) the proton concentration before and after the release of H^+ can be found:

$$[H^+]_{before} = -\frac{k_a}{2} + \frac{1}{2}\sqrt{k_a{}^2 + 4k_aC_{Ac}} \qquad (3.7)$$

$$[H^+]_{after} = -\frac{k_a + \Delta H}{2} + \frac{1}{2}\sqrt{(k_a + \Delta H)^2 + 4k_aC_{Ac}} . \qquad (3.8)$$

Both the conductivity sensor or a potentiometric pH sensor can be used for determining a shift in the equilibrium.

Differential pH measurement
Two pH sensors will measure:

$$\Delta pH = -\log[H^+]_{after} + \log[H^+]_{before} \qquad (3.9)$$

which can be expressed in terms of the constants C_{Ac}, k_a and DH$^+$ using (3.7) and (3.8). However, this results in a complicated expression. In this report no numerical evaluation will be given on whether this leads to interesting information on C_{Ac} or k_a.

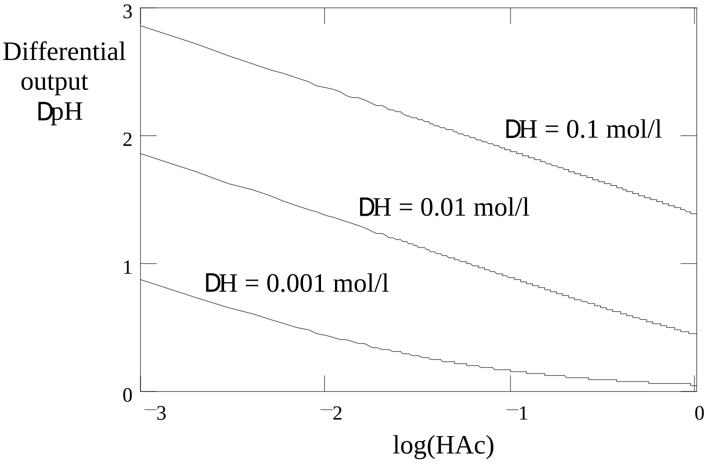

Fig. 3.1: Dependency of the differential pH on a "proton step" as a function of the weak acid concentration

Figure 3.1 shows a plot of equation (3.9) for an acetic acid concentration range of three decades and using three different H^+ steps. It appears that the dependency is linear unless the DH^+ is much smaller than the weak acid concentration. The lowest curve shows a deviation from a linear behaviour because of a too low DH^+.

Differential conductivity measurement

From a differential conductivity sensing the output will be:

$$\Delta\kappa = \kappa_{\mathrm{after}} - \kappa_{\mathrm{before}} \tag{3.10}$$

with

$$\kappa = [H^+]\lambda_{H^+} + [Ac^-]\lambda_{Ac^-} \tag{3.11}$$

where l_i is the limiting molar conductivity for ion i.
Substituting (3.7) and (3.8) the Dk can be found which again can be written in terms of the constants C_{Ac}, k_a and DH. Just like the pH measurement this conductivity measurement gives a very complicated expression.

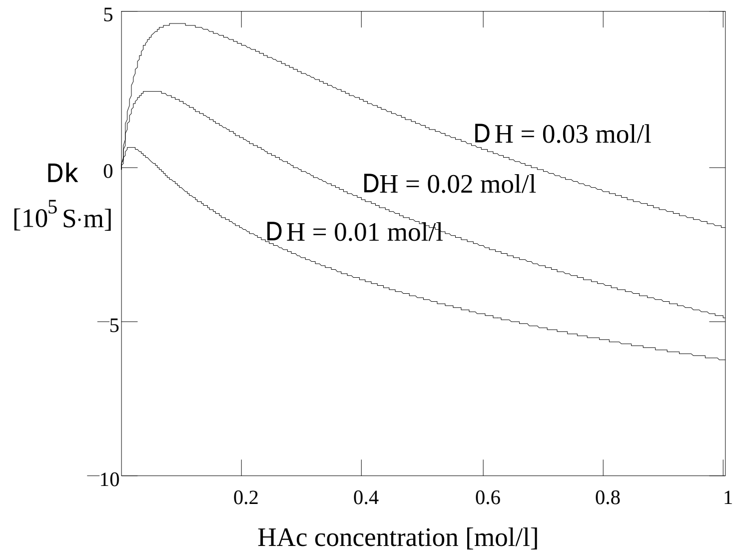

Fig. 3.2: Dependency of the differential conductivity on a "proton step" as a function of the weak acid concentration

Figure 3.2 shows the simulated relation between the conductivity change and the weak acid concentration. It will be hard to find a useful sensor operation from this type of measurement.

Summarizing it can be said that by generating a known amount of H^+ ions, the measured difference between two sensors (either pH or conductivity) changes with a complex function due to the displacement of equilibria in the solution. The measured difference gives information on the contamination of the sample solution. For the interpretation of the mentioned complex function a range must be chosen in which it simplifies or a smart actuator function must be chosen in order to reduce this function to an easier one.

Differential temperature measurement

The measurement of temperature is only of interest when an endo- or exothermic reaction is evoked by injecting oxygen gas, hydrogen gas, protons or hydroxyl ions. At first sight no such reactions are likely in the washing system.

Differential DST measurement

Recently Alex Volanschi showed that the output of the dynamic surface tension sensor is not a function of the pH [1]. This independency is necessary for the accurate operation of this sensor. So neither the sensor operation nor the sample solution is sensitive to the DH^+ action. The differential output will be zero.

Differential amperometric H_2O_2 detection

In the presence of hydrogen peroxide, the oxidation of water at the actuator will not occur before all hydrogen peroxide is oxidised:

$$2H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- . \qquad (3.12)$$

This gives the possibility of the electrochemical capturing of all available hydrogen peroxide at the actuator. The difference measured by two H_2O_2 sensors is equal to the absolute amount of H_2O_2. Under this condition the actuator function is of the type (a) "complete depletion".

3.2. Thermoresistive heating

The thermoresistive heater is a metal strip with a certain resistance. The heat being produced when a current flows through it will be used to put thermal energy in the system.

Acid base equilibria, for example equation (3.4), are dependent on temperature because the acid constant k_a is temperature dependent.

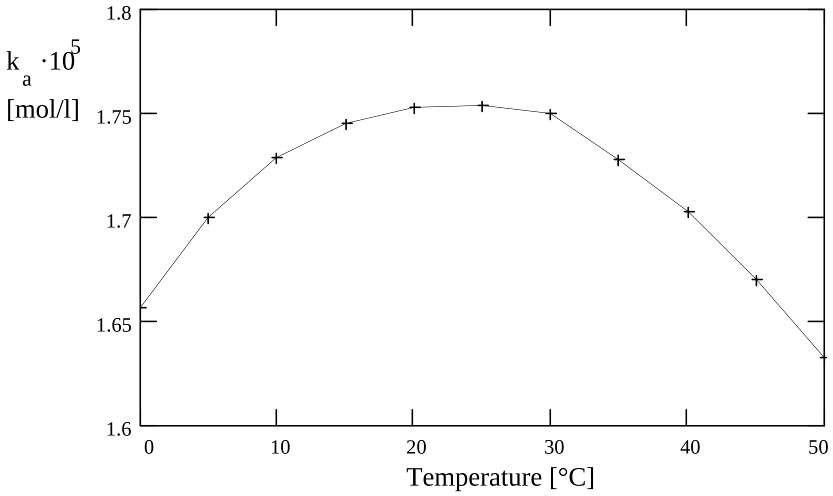

Fig. 3.3: Dissociation constant of acetic acid at various temperatures
From: CRC Handbook of chemistry and physics, 74th edition

The maximum in figure 3.3 arises from two opposing effects. First, as the temperature increases there is a tendency for the undissociated acid molecule to split into two parts (the proton and the anion) due to kinetic energy. However, as the temperature increases further, the dielectric constant decreases and so the electrostatic forces between anion and proton increase [2].

Starting from the equations (3.4) and (3.5) and assuming equal proton and anion concentration it can be found that:

$$[H^+] = \frac{k_{a,T}}{2}\left(\sqrt{1+\frac{4C_{Ac}}{k_{a,T}}}-1\right) \qquad (3.13)$$

with C_{Ac} the total amount of acetic ions in the sample and $k_{a,T}$ the dissociation constant at temperature T.

Differential pH measurement

The proton concentration as given by equation (3.13) can be differentially sensed using pH sensors as:

$$\Delta pH = -\log[H^+]_{T_2} + \log[H^+]_{T_1}$$

which results in:

$$\Delta pH = \frac{1}{2}\log\frac{k_{a,T_1}}{k_{a,T_2}} \qquad (3.14)$$

using $k_a << C_{Ac}$. So a differential pH measurement where at one sensor the temperature differs from the other gives information on the dissociation constant of the acid involved.

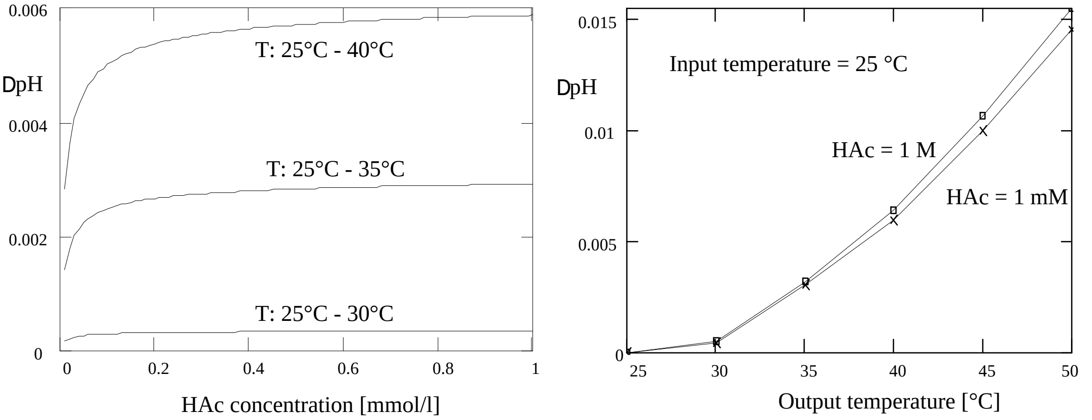

Fig. 3.4: Dependency of the pH on a temperature step as a function of the weak acid concentration (left) and the final temperature (right)

According to the left graph of figure 3.4 the variation of the ΔpH as a function of the acetic acid concentration (at a constant temperature step) becomes significant for concentrations below 0.1 mM. From a graph like the right one the dissociation constant can be determined using equation (3.14).

Differential conductivity measurement

The displacement in the acid-base equilibrium will result in a variation in the conductivity as well. Equations (3.11) and (3.13) yields:

$$\begin{aligned}\kappa &= [H^+]\lambda_{H^+} + [Ac^-]\lambda_{Ac^-}\\ &= [H^+]\cdot\left(\lambda_{H^+} + \lambda_{Ac^-}\right)\\ &= \frac{k_{a,T}}{2}\left(\lambda_{H^+} + \lambda_{Ac^-}\right)\left(\sqrt{1+\frac{4C_{Ac}}{k_{a,T}}} - 1\right)\end{aligned}$$

Using $k_a << C_{Ac}$ the differential output can be written as:

$$\Delta\kappa = \Delta k_a \frac{\lambda_{H^+} + \lambda_{Ac^-}}{2}. \qquad (3.15)$$

which indicates that the change in conductivity is proportional to the change in the dissociation constant.

However, the limiting molar conductivity λ_i is temperature dependent itself, according to:

$$\lambda_i = \frac{z_i^2 Fe}{6\pi a}\frac{1}{\eta(T)} \qquad (3.16)$$

with

z_i: the charge number of ion i,
F: Faraday's constant,
e: the charge of an electron,
a: the radius of the ion and
$\eta(T)$: the viscosity of the medium,

the last one is dependent on temperature by $e^{Ea/RT}$. This results in an increase of λ_i with temperature of 2 to 3% per degree for typical ions as the temperature increases from 25°C [3]. This is in the range of the temperature dependency of the dissociation constant k_a.

Differential temperature measurement

Unlike the example of the electrochemical actuator, the direct measurement of the released quantity itself does give information on the system now. When the raised temperature is measured at one of the sensors, the time delay between generation and measurement gives information on the direction and size of the mechanical flow of the sample.

Differential DST measurement

Because the dynamic surface tension is quite an energetic phenomenon, it is not surprising that it depends on temperature. The surface tension γ_w decreases linearly with increasing temperature. From literature a decrease of 1.08 J/m^2 per 10°C was found [4].

The actuator will therefore be of the type (b) "Partial depletion or accumulation". Equation (2.4) shows that the measured differential output is proportional to the absolute surface tension of the sample solution in this case. At first sight, this does not give new information because the single DST sensor did the same already.

Differential amperometric H_2O_2 detection

Hydrogen peroxide is in equilibrium with the HO_2^- ion under the dissociation of a proton:

$$H_2O_2 \leftrightarrow H^+ + OH_2^-. \qquad (3.17)$$

When measuring using an amperometric sensor this equilibrium is not important because this reaction is fast in relation to the diffusion controlled measurement. What is being measured is the actual hydrogen peroxide concentration which is independent of the temperature.

3.3. Ion exchangers or enzymes

The actuator function f(x) for an ion exchanger is of the type "partial depletion or accumulation" (b) because a constant percentage of species x_1 is being captured. The operations on the proton and calcium concentrations are:

$$[\mathrm{Ca}^{2+}]_{\mathrm{out}} = a_f [\mathrm{Ca}^{2+}]_{\mathrm{in}} \tag{3.18}$$

$$[\mathrm{H}^{+}]_{\mathrm{out}} = 2 \cdot (1 - a_f) \cdot [\mathrm{Ca}^{2+}]_{\mathrm{in}} + [\mathrm{H}^{+}]_{\mathrm{in}} \tag{3.19}$$

where $0 < a_f < 1$. A complete exchange is characterised by $a_f = 0$ and no operation results in $a_f = 1$. The last one can be the result of a saturated ion exchanger.

Which ion exchange couple should be chosen can be concluded from the field of application and the available sensors. The ion to be captured should be calcium while this might give information on the water hardness in washing processes. For miniaturized sensors and actuators the exchange of these calcium ions to protons is desired because protons are measurable ions and it leaves the possibility of reversing the exchange action by electrochemically generating H^+. So an interesting ion exchange couple could be the cation-exchange $2H^+$ « Ca^{2+} which generally is done by zirconium phosphate based resins [5]. Because only cations are being exchanged, the pH is changed by this material.

The operation of an enzyme actuator can be compared to the operation of an ion exchanger because a certain percentage of species is being catalized. The result is a partial depletion operation. The examples in this paragraph use the ion exchange principle.

Differential pH measurement

The measurement of the pH before and after the ion exchange results in:

$$\begin{aligned}\Delta \mathrm{pH} &= -\log[\mathrm{H}^{+}]_{\mathrm{out}} + \log[\mathrm{H}^{+}]_{\mathrm{in}} \\ &= \log\left(\frac{[\mathrm{H}^{+}]_{\mathrm{in}}}{2 \cdot (1 - a_f) \cdot [\mathrm{Ca}^{2+}]_{\mathrm{in}} + [\mathrm{H}^{+}]_{\mathrm{in}}} \right)\end{aligned} \tag{3.20}$$

So for a significant measured pH change, the proton concentration must not be very large in relation to the calcium concentration. Secondly for determining the calcium concentration, the absolute proton concentration must be known.

Differential conductivity measurement

The difference in conductivity induced by the ion exchanger is:

$$\begin{aligned}\Delta\kappa &= \Delta[\mathrm{H}^+]\lambda_{\mathrm{H}^+} + \Delta[\mathrm{Ca}^{2+}]\lambda_{\mathrm{Ca}^{2+}} \\ &= 2\cdot(1-a_f)\cdot[\mathrm{Ca}^{2+}]_{in}\,\lambda_{\mathrm{H}^+} + (a_f-1)[\mathrm{Ca}^{2+}]_{in}\,\lambda_{\mathrm{Ca}^{2+}} \\ &= (1-a_f)\left(2\lambda_{\mathrm{H}^+} - \lambda_{\mathrm{Ca}^{2+}}\right)[\mathrm{Ca}^{2+}]_{in}\end{aligned} \qquad (3.21)$$

which means that the output is linearly dependent on the calcium concentration.

Differential temperature measurement

The ion exchange does probably nothing with the temperature of the sample. Differentially measured temperature results in zero output.

Differential DST measurement

The combination of lipophilic ion-exchanger resins with samples containing surfactants gives problems. By extracting fatty components from the resin, the surfactant will destroy the ion exchanger.

When this problem can be avoided, the DST-measurement will not be affected by a cation exchange because the effect of cations on the surface tension is very low. The pH change will have no effect either as was mentioned earlier. So differentially measured dynamic surface tension will give zero output.

Differential amperometric H_2O_2 detection

For an ideal ion exchange the presence of H_2O_2 will have no effect. However the pH change due to the exchange of calcium by protons might disturb the amperometric H_2O_2 measurement.

3.4. Summary

Using three actuators and five sensors, fifteen combinations for building a differential measurement system. Table 3.1 gives a summary of the possible combinations for implementing the set-up of figure 2.1.

Table 3.1: Summary of the sensor/actuator combinations

Sensor Actuator	**Pt-100** Temperature	**Finger structure** Conductivity	**Working electrode** Amperometric H_2O_2	**Bubble electrode** DST	pH
Thermoresistive heating	Flow	Dependency of the dissociation constant on temperature	0	Surface tension	Dissociation constant
Electrochemically generated H^+, OH^-, O_2 and H_2	0	Weak acid conc. Dissociation constant	H_2O_2	0	Weak acid conc.
Ion exchanger	0	Ca^{2+}	0	0	Calcium when absolute pH is known

Some of the applications were evaluated with a weak acid as a sample solution. For more complicated sample solutions the response on the actuator is not a simple change in the acid equilibrium any more.

4. Conclusions

The materials and technology that are the most likely for implementing a sensor array were evaluated in a previous work report. A next logical step is to develop a concept for array-type measurements.

In the first chapter of this report the advantages of miniaturized sensor arrays were evaluated. It was stated there that differential measurements in combination with an actuator would probably solve calibration and reference problems.

The combinations of three actuators and five simple sensors gave fifteen set-ups for implementing a measurement system. Some of them showed promising concepts.

Measuring differentially conductivity while exchanging calcium ions by two protons gives absolute information on the calcium concentration of a sample. In the special case where the ion exchanger is completely saturated with calcium ions there is no exchange operation so calibration data is available. The ion exchanger can be re-used after displacing calcium ions by electrochemically generated H^+ ions.

Differential (chrono) amperometric hydrogen peroxide detection while depleting hydrogen peroxide oxidatively gives information on the hydrogen peroxide concentration.

By heating a sample containing a weak acid both a differential pH measurement and a differential conductivity measurement is dependent on the temperature sensitivity of the dissociation constant. For an acid with a large dissociation constant the output is concentration sensitive as well.

When injecting a known amount of H^+, the measured pH change is a function of the weak acid concentration. The same seems to be possible using a conductivity measurement. This method is closely related to a coulometric acid-base titration

With all methods the offset of the used sensors is filtered out by the differential measurement. When the differential systems are set to zero when the actuator is inactivated, common noise will not appear on the output.
The geometrical similarity of the measurement systems in combination with the small number of array-elements results in a simple realization process.

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