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The Merits of Differential Measuring in Time and Space

Differential measuring shows several merits. Sensor offsets caused by device processing or stemming from a non-ideal reference electrode can be cancelled. Common interfering effects, e.g., from temperature, are eliminated. In order to successfully design a differential sensor system, a theoretical introduction is needed and presented in this paper. In this part, the concept of space and time differential measuring is treated and the required sensor and actuator functions are evaluated. Subsequently, several examples illustrate the possibilities and benefits of this concept. In particular, mass flow and acid and calcium concentrations are amongst the measurands determined with by the measuring system, including an actuator function. The possible differential measuring systems that can be obtained using three types of actuators (electrochemical, thermo resistive and ion exchange) and four sensors (temperature, conductivity, amperometric hydrogen peroxide detection and potentiometric pH detection) are summarised in a table, concluding this paper.

Keywords: chemical sensor, differential sensor system, sensor-actuator system, electrochemical actuator

1. Introduction

In this paper, the advantages of differential measuring are treated, specifically in case both a sensor and an actuator function are present in one sensor system. The introduction of this concept is largely theoretical. In the second part of this paper, several examples are given to illustrate the possibilities and benefits of this concept.

2. Mathematical Generalisation of Differential Measurement Systems

A generalised set-up for differential measurements is given in Fig. 1. The picture shows a tube which has the possibility to shift a sample solution in steps or continuously along sensors and actuators. In the simplest case, two sensors and only one actuator are implemented, resulting in the set-up where a sample is measured before and after the actuator step.

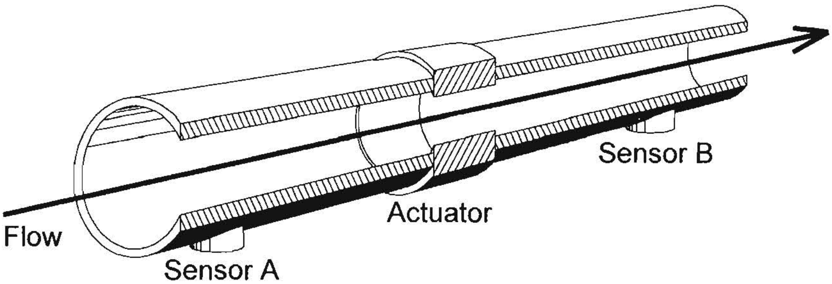

Fig. 1. Generalised set-up for spatial differential measurements using one actuator

Because of the assumed small diameter of the tube the modification by the actuator will be accomplished over the whole cross-section of this tube. When the input solution does not change (with respect to the measured variable) during a measurement, the sample measured at sensor B differs from that at sensor A only due to the modification induced by the actuator. If the modification is complete at the time the sample is at sensor B, there is no effect of time observed in the difference in sensor outputs. Therefore, one can speak of a spatial differential measurement, sampled at a single moment.

Apart from spatial differential systems, there exist time differential systems. When the flow direction of the liquid can be reversed, only one sensor is needed because then the sample can be measured before and after the actuation step using the same sensor. This requires also a composition of the input sample which is not changing due to other factors than the stimulus. When this single sensor is integrated with the actuator, as is the case with the integrated sensor-actuator device described elsewhere [1, 2], even the tube can be omitted since no controlled flow is needed. In such single sensor set-ups, one should speak of a time differential system sampled at the same location instead of a spatial differential system. Notice that this does not change the mathematical operation describing the system since in both cases a difference between the sample before and after a modification stimulus is measured.

For the generalisation of spatial or time differential systems, Figure 2 will be used. Variable x_1 is the input of interest and is modified by the actuator to x_2 which has the same dimension as x_1. The function describing the stimulus operation of the actuator is referred to as $f_\alpha(x)$, so $x_2 = f_\alpha(x_1)$. This stimulus operation will be dependent on both the actuator and the properties of the solution. If a controllable actuator is used, the controlled parameter is represented by the subscript α.

Assume that both the original sample variable x_1 and the modified variable x_2, are being sensed using two similar sensors. This means that the

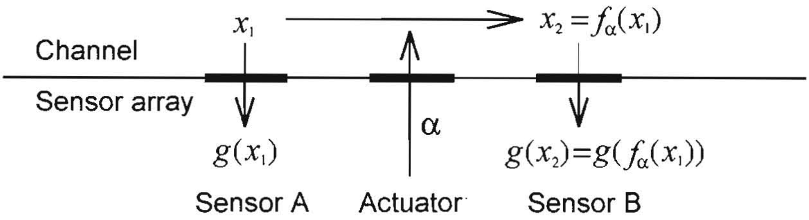

Fig. 2. Mathematical representation of a differential measurement system

sensor outputs are both given by the same operation $g(x)$ on the sensed variable. These sensors do not influence the sample.

So two operations are involved: the sensor operation function $g(x)$ and the stimulus function $f_\alpha(x)$. These operations will be discussed here separately.

2.1. Evaluation of the Sensor Operation $g(x)$

The sensor operation $g(x)$ can be any function in principle, nevertheless the number of functions observed with practical sensors is limited. Some special cases of $g(x)$ functions will be evaluated here.

Although it was assumed that both sensors have the same measurement principle, they might have a different sensitivity or offset. This results in the same $g(x)$ function, but with different parameters. The difference in the sensor operation function for sensor A and B is indicated by a superscript A or B.

For a spatial differential system, the sensors A and B are different devices and might therefore have dissimilar parameters, for example due to a not perfectly reproducible fabrication process or an unequal temperature while measuring. With a time differential system, sensor A is the same device as B, but read out at another moment. So variations in fabrication processes are cancelled out, only drift in the sensor parameters will change the function $g(x)$.

(a) $g(x)$ is known

When the sensor operation $g(x)$ is completely known, the inverse function g^{-1} can be determined and variable x can exactly be calculated from the sensor output. In this case, the use of an actuator and a second sensor is not needed for measuring x_1. However, with practical sensors, the $g(x)$ function is only known directly after calibration since drift in both the sensitivity and the offset will change this function.

(b) $g(x)$ is a linear function with an offset
The operation of many sensors can be approximated by

$$g(x) = a_g \cdot x + b_g \tag{1}$$

for at least a certain range of x. In many sensors the drift and inter device deviation in the sensitivity a_g is much lower than the uncertainty in the offset b_g both due to drift and differences in processing. For example, when x is the pH which is measured using a pH sensor, the sensitivity is equal to about $a_g = -59\,\mathrm{mV/pH}$. This sensitivity is much more constant than the offset, which is among other things also determined by the stability of the reference electrode.

The offset b_g of the sensor is determined by two parts. The first one is the part that is common for both sensor A and B. For example, 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 equal to

$$g^B(x_2) - g^A(x_1) = a_g \cdot (x_2 - x_1) + b_g^B - b_g^A \tag{2}$$

assuming identical sensitivities a_g for both sensors. The observed offsets of the individual sensors, b_g^A and b_g^B, consist of the summation of offsets which are common for both sensors and offsets which differ from sensor to sensor. By a differential measurement, common parts in the offsets b_g are filtered out and only the non-common offsets remain. In practice, common offsets are the result of undesired external influences, while non-common offsets are constant for the individual devices.

Equation (2) shows that actually only the difference between the input x_1 and output x_2 can be measured, but when the actuator function $f_\alpha(x)$ is chosen well (for example $f_\alpha(x) = a_f \cdot x$), an absolute value for x_1 can be found as will be shown later.

(c) $g(x)$ is a logarithmic function
In case of a pH measurement using a potentiometric technique, the output of the sensor (glass electrode or ISFET) is linearly dependent on the pH. This is a linear sensing principle which has its origin in the Nernst equation [3] which expresses the linear relation between an interface potential and the pH. Actually, with all potentiometric ion selective electrodes (ISEs), the output is dependent on the logarithm of a concentration. When a concentration is the variable of interest, and not the logarithm of a concentration, the sensor output must be written as

$$g(x) = a_g \cdot \log(x) + b_g \tag{3}$$

and the differential output becomes

$$g^B(x_2) - g^A(x_1) = a_g \cdot \log\left(\frac{x_2}{x_1}\right) + b_g^B - b_g^A \tag{4}$$

assuming the same sensitivity a_g for both sensor A and B. So when using logarithmic sensors, the differential output shows the same advantage with respect to the sensor offsets. However, with respect to the variable to be measured, x_1, the difference between two logarithmic sensor outputs gives only information on the ratio between the input and output variable x_2/x_1. So, to measure the absolute value of the input variable x_1, it is not likely that a differential system based on logarithmic sensors will give the desired result[1]. Stimulus functions which can make the output useful must raise the input variable to a certain power. For example $f_\alpha(x) = x^2$ will reduce (4) to

$$g^B(x_2) - g^A(x_1) = a_g \cdot \log(x_1) + b_g^B - b_g^A. \tag{5}$$

However, such stimulus functions are not easy to realise using practical actuators.

2.2. Evaluation of the Stimulus Function $f_\alpha(x)$

A linear stimulus operation will be assumed here because this describes most of the practical observed actuator operations. Consider the stimulus function

$$f_\alpha(x) = a_f(\alpha) \cdot x + b_f(\alpha) \tag{6}$$

where the parameters $a_f(\alpha)$ and $b_f(\alpha)$ are constant at a certain chosen actuator intensity α. The constant $a_f(\alpha)$ represents an intended amplification or attenuation of the species x placed in front of the actuator, and will therefore be without a dimension. The constant $b_f(\alpha)$ is the result of an intended addition, or subtraction of the species x, which is not proportional to the amount placed in front of the actuator. This second constant will have the same dimension as x. The most common actuator operations can be identified and categorised by these constants.

Because the actuator intensity α is assumed to be constant in the following examples, the parameters $a_f(\alpha)$ and $b_f(\alpha)$ will be written from now on as a_f and b_f.

[1] One can easily confuse this set-up with the succesful acid to base titration set-up where the end point is determined by ISFETs and the titrant is generated coulometrically [4]. Although this method measures a concentration using logarithmic sensors, it is not of the generalised configuration as described here. This method uses the pH difference only as an indicator for detecting the end point of the titration. The concentration of interest is calculated from the charge supplied to the actuator when the end point is reached.

(a) Complete depletion of x: $b_f = 0$, $a_f = 0$
When both a_f and b_f are zero then (6) simplifies to $f_\alpha(x) = 0$, or in other words: the species x_1 is completely depleted by the actuator to $x_2 = 0$. An example is the effect of an ion exchanger which captures all ions of interest, when sensors are used which measure these ions selectively. Another example is an electrochemical actuator which evokes the degeneration of hydrogen peroxide into hydrogen gas and oxygen gas, and using sensors which are selective for hydrogen peroxide.

In the case of linear sensors with an equal sensitivity a_g equation (2) now gives the absolute value of input variable x_1 because x_2 equals zero. In this case sensor B is solely used as an indifferent reference sensor to filter out offsets which are common to both sensors. Notice that even if the sensors do not have the same sensitivity, the same result is obtained.

(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. This situation represents an incomplete ion exchange where always a fraction a_f is not being exchanged. Equation (2) becomes equal to

$$g^B(x_2) - g^A(x_1) = a_g(a_f - 1)\cdot x_1 + b_g^B - b_g^A \tag{7}$$

with a_f the fraction of depletion (< 1) or accumulation (> 1) and a_g the sensitivity of the sensors, assumed to be equal. Even when the sensors do not have an equal sensitivity, the differential output is still linearly proportional to the input variable x_1 according to

$$g^B(x_2) - g^A(x_1) = \left(a_g^B\cdot a_f - a_g^A\right)\cdot x_1 + b_g^B - b_g^A. \tag{8}$$

When the fraction a_f is always the same, and there is no drift in the differences between the sensitivities, there is no theoretical difference with the previous situation where $a_f = 0$. Again, the advantage is in the elimination of offsets which are common for both sensors.

(c) Known addition: $b_f \neq 0$, $a_f = 1$
A special situation occurs when the variable x_1 is increased by a constant value. This can be done by injecting a known amount of H^+ ions in a sample which is not buffered, while the H^+ concentration is the measured variable. The differential output (2) becomes

$$g^B(x_2) - g^A(x_1) = a_g\cdot b_f + b_g^B - b_g^A \tag{9}$$

which is not dependent on the input variable 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. The condition that the sensitivities of sensor A and B are equal is now necessary, else the difference will still be dependent on the input concentration x_1.

(d) No actuator operation: $b_f = 0$, $a_f = 1$
When the actuator does nothing, the input variable 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, but with equal sensitivities a_g, equation (2) can be written as

$$g^B(x_2) - g^A(x_1) = \left(a_g \cdot x_2 + b_g^B\right) - \left(a_g \cdot x_1 + b_g^A\right) = b_g^B - b_g^A. \qquad (10)$$

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

2.3. Summary

A generalised stimulus-response set-up is that of a flow system with two sensors and a single actuator. The sample solution is pumped along sensor A, the actuator and then sensor B. The assumption is made that the variable of interest in the supplied electrolyte is homogeneously present at both sensor A and B in the absence of a stimulus. Only then, the difference between the outputs of sensor A and B, after the stimulus is applied, can be completely ascribed to the influence of the actuator.

An alternative to this spatial differential system is a time differential system, where using a single sensor, an electrolyte is measured before and after an actuator step. Here, stability of the composition of the sample is necessary. While a difference in space can be measured at the same moment, a difference in time can be measured at the same spot in the solution.

Using a differential measurement system in combination with an actuator, data can be obtained concerning the sample as well as on the sensors itself. To get information on the sensors, the actuator must be controllable in order to select operational modes for collecting calibration data. Important is that both sensors have a similar, but not necessarily identical, operation.

3. Some Examples Based on Available Actuators

After the theoretical evaluation in the previous section, now three actuators are being categorised in these theoretical terms. The first two are the available actuator operations in the integrated sensor-actuator device as described elsewhere [1, 2]. These are the electrochemical actuator (for O_2, H_2, H^+ or OH^-) and the thermoresistive heater. In addition, an ion exchanger is taken as a third actuator. Although ion exchanger materials are not controllable actuators, an interesting intended modification of an electrolyte is made by such materials. The operation of ion exchangers can be monitored using the implemented electrolyte conductivity operation of the integrated device.

For the sensors, the three available sensor operations in the integrated sensor-actuator device are taken, being temperature, conductivity and amperometric detection. The detection of pH is evaluated as well in each subsection, because the measurement of pH shows a logarithmic sensor function which is interesting to compare with the linear operation of a conductivity sensor.

The following list of possible stimulus-response measurements does not contain all the possible options, but is more or less a brainstorm of advantages which can be expected when integrating sensors and an actuator.

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:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{11}$$

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

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-. \tag{12}$$

The reaction products H^+ and OH^- can be used for pH control. In the case of equation (11), the amount of generated protons follows from integrating the anodic current in time. However, in general, this actuator is not of the "known addition" type (c) of subsection 2.2 because the protons released will cause chemical equilibria in the solution to change. So, the measured proton concentration increase at sensor B in Figure 1 is not only dependent on the released amount in general, for example because of the influence of pH buffers and weak acids.

Weak acid concentration determination

The response on an imposed injection of protons of size ΔH^+ in a solution of a weak acid is being considered. As an example, the acetic acid equilibrium is used for the complete description of the system. This equilibrium is given by

$$HAc \leftrightarrow H^+ + Ac^-, \qquad k_a = 1.7\cdot 10^{-5} \tag{13}$$

so, before and after the addition of a ΔH^+ the acid-base equilibrium satisfies

$$\frac{[H^+][Ac^-]}{[HAc]} = k_a. \tag{14}$$

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

$$[\mathrm{Ac}^-]_{\mathrm{before}} + [\mathrm{HAc}]_{\mathrm{before}} = [\mathrm{Ac}^-]_{\mathrm{after}} + [\mathrm{HAc}]_{\mathrm{after}} = \mathrm{C}_{\mathrm{Ac}}, \tag{15}$$

$$[\mathrm{H}^+]_{\mathrm{before}} + [\mathrm{HAc}]_{\mathrm{before}} = [\mathrm{H}^+]_{\mathrm{after}} + [\mathrm{HAc}]_{\mathrm{after}} - \Delta\mathrm{H}^+ = \mathrm{C}_{\mathrm{H}}. \tag{16}$$

From equations (14), (15) and (16) the proton concentration before and after the release of H^+ can be found:

$$[\mathrm{H}^+]_{\mathrm{before}} = -\frac{\mathrm{k_a}}{2} + \frac{1}{2}\sqrt{\mathrm{k_a^2} + 4\mathrm{k_a}\mathrm{C}_{\mathrm{Ac}}}\,, \tag{17}$$

$$[\mathrm{H}^+]_{\mathrm{after}} = -\frac{\mathrm{k_a} + \Delta\mathrm{H}^+}{2} + \frac{1}{2}\sqrt{(\mathrm{k_a^2} + \Delta\mathrm{H}^+)^2 + 4\mathrm{k_a}\mathrm{C}_{\mathrm{Ac}}}\,. \tag{18}$$

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

$$\Delta\mathrm{pH} = -\log[\mathrm{H}^+]_{\mathrm{after}} + \log[\mathrm{H}^+]_{\mathrm{before}} \tag{19}$$

which can be expressed in terms of the constants C_{Ac}, k_a and ΔH^+ using (17) and (18). However, this results in a complicated expression. In this paper no numerical evaluation will be given on whether this leads to interesting information on C_{Ac} or k_a. Instead, a graphical method is used.

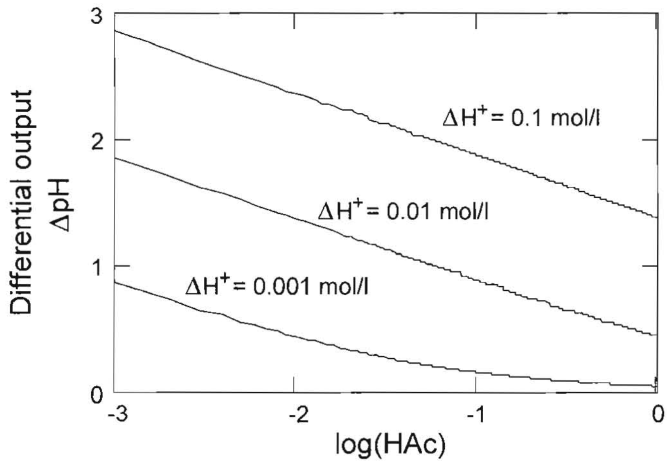

Fig. 3. Dependency of the differential pH on a "proton step" as a function of the weak acid concentration using the acid constant of acetic acid

Figure 3 shows a plot of equation (19) for an acetic acid concentration range of three decades and using three different H^+ steps. It appears that the dependency on the logarithm of the weak acid concentration is linear unless the ΔH^+ is much smaller than the weak acid concentration. The lowest curve shows a deviation from a linear behaviour because of a too low ΔH^+. The dependency on the chosen H^+ addition shows that the output signal is only useful in a certain range.

In the parts of the curves in Fig. 3 where the curves are linear, the added amount of H^+ ions is apparently an excess, resulting into a pH which is only dependent on this added excess. Therefore, the pH difference is determined by the pH of the original acetic acid concentration and the pH caused by the excess of H^+ ions. So, the principle of operation is that the pH after the addition of a sufficient amount of H^+ ions (which results into an acetic acid independent "reference" pH) is compared to the pH of the original acetic acid. This method comes the closest to the type complete depletion (a) with b_f not equal to zero.

In fact this method is a part of a coulometric titration which is only sampled at two points, and where the measured information is in the pH change (and not in the supplied amount of titrant). This successful application of a differential measurement system based on logarithmic sensors seems an exception to the conclusion which was drawn from equation (4). However, since the logarithm of the acetic acid concentration is measured, the used sensors are actually linear sensors.

Using a differential conductivity determination the output will be:

$$\Delta\kappa = \kappa_{\text{after}} - \kappa_{\text{before}} \tag{20}$$

with

$$\kappa = [H^+]\lambda_{H^+} + [Ac^-]\lambda_{Ac^-} \tag{21}$$

where λ_i is the limiting molar conductivity for ion i. The difference in the conductivity $\Delta\kappa$ before and after the injection of the ΔH^+ can be calculated by evaluating equation (21) in both situations. To express the observed $\Delta\kappa$ in terms of the acetic acid concentration C_{Ac}, the acid constant k_a and the injected amount of protons ΔH^+, equations (14), (17) and (18) must be substituted into (21) for the situation before and after the H^+ injection. Just like the pH measurement this conductivity measurement gives a complicated expression.

Figure 4 shows the simulated relation between the conductivity change and the weak acid concentration. At a zero acetic acid concentration, the injected protons are not captured by acetate ions Ac^-, and the measured change in conductivity is caused by the conductivity of the ΔH^+ only. Since the curves are not linear, the acetic acid concentration corresponding to a measured $\Delta\kappa$ is harder to determine for a higher acetic acid concentration. Therefore, it is more practical to find the necessary amount of ΔH^+ resulting into a $\Delta\kappa$ equal to zero. Empirically, using theoretically obtained data, it

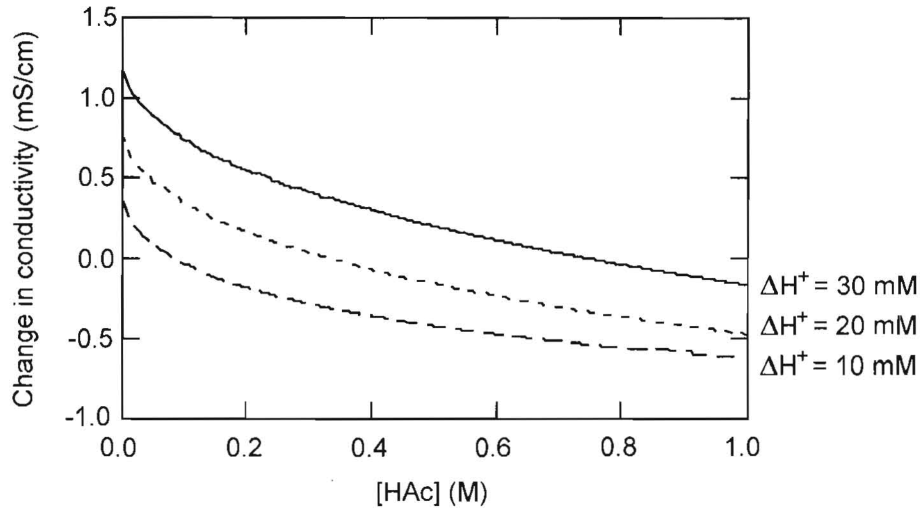

Fig. 4. Theoretical dependency of the differential conductivity on a "proton step" as a function of the acetic acid concentration

was determined that then the corresponding acetic acid concentration can be approximated by $C_{HAc} = 0.84 \cdot 10^3$ litre/mole$\cdot(\Delta H^+)^2$ over quite a large range of acetic acid concentrations.

Differential temperature measurement

Now the measurement of pH and conductivity is used as an example of differentially monitoring the effect of an electrochemical actuator, also the other two sensors are described in combination with this actuator. 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, such reactions are not likely in a washing system.

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:

$$2H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- . \tag{22}$$

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" which has the advantage that common offsets in the sensors are filtered out.

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.

Equilibria, observed in acid-base systems like equation (13) and precipitation systems, are dependent on temperature because the equilibrium constants k_a and k_s are temperature dependent in general. However, a concentration determination based on an imposed disturbance of such an equilibrium will be difficult. An interference is the dependency of the ion mobility on temperature which will complicate the interpretation of a conductivity measurement. Although this is not observed with a differential pH measurement, the logarithmic nature of pH sensing completely suppresses the very small changes in the H^+ concentration.

Differential conductivity measurement

The limiting molar ionic conductivity λ_i is indirectly temperature dependent, according to [5]

$$\lambda_i = \frac{z_i^2 \mathrm{Fe}}{6\pi a} \frac{1}{\eta(T)} \tag{23}$$

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,

where the last one depends exponentially on temperature. This results into an increase of λ_i with temperature of 2 to 3% per degree for typical ions around room temperature. The corresponding stimulus function describing the effect of heating on a conductivity measurement, is of the type (b) "accumulation of x" with $a_f(\alpha) > 1$, and $b_f(\alpha) = 0$ in equation (6). The parameter α represents the imposed temperature change.

In general, a fitted polynomial temperature dependency for the limiting molar ionic conductivity is more practical than the use of equation (23). Elsewhere, it is shown that using such polynomials, the separate ion concentrations can be calculated of an assumed set of present ions [6]. Therefore, this stimulus-response measurement will not be evaluated here.

Differential pH measurements

In terms of section 2, the effect of heating will change the sensitivity a_g of the sensors, since in general a pH measurement has a sensitivity proportional to temperature. The process of interest, the influence of the stimulus function

$f_\alpha(x)$, can not be studied separately because pH sensors are temperature dependent.

Differential amperometric H_2O_2 *detection*
Hydrogen peroxide is in equilibrium with the HO_2^- ion under the dissociation of a proton:

$$H_2O_2 \leftrightarrow H^+ + HO_2^-. \tag{24}$$

When measuring, using two amperometric sensors, this equilibrium is not relevant because whether H_2O_2 or HO_2^- is measured, in both cases the number of electrons released per measured molecule is equal. What is observed as a response on a heating stimulus when doing chrono amperometry, is probably the effect of a small change in the diffusion coefficient.

Differential temperature measurement
By measuring temperature differentially while heating, the system is of the type "known addition" (c) which does not give any information on the input, but only on the system. An example is the use of the time delay between stimulation and sensing for determining the speed of flow. This is described in section Additional results, where a flow measurement is described based on the transport time of a heat marker from the actuator to a temperature sensor.

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 [7]. It makes a difference whether sensors are used which can measure selectively the captured/released species or the used sensors are not selective (like electrolyte conductivity sensors).

For example, the commercially available ion exchanger Dowex® CCR-2 is originally saturated with H^+ ions, but will release two of them when one Ca^{2+} ion is captured. The operations on the proton and calcium concentrations are

$$[Ca^{2+}]_{out} = a_f[Ca^{2+}]_{in}, \tag{25}$$

$$[H^+]_{out} = 2\cdot(1 - a_f)\cdot[Ca^{2+}]_{in} + [H^+]_{in} \tag{26}$$

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

From the field of applications and the available sensors this couple of ions ($2H^+ \leftrightarrow Ca^{2+}$) is very interesting. The ion to be captured should be calcium while this might give information on the water hardness in washing processes. For miniaturised sensors and actuators the exchange of these calcium ions to protons is desired because protons are relatively easy measurable ions and it leaves the possibility of reversing the exchange action by electrochemically generating H^+.

The operation of an enzymatic actuator can be compared to the operation of an ion exchanger because a certain percentage of species is being catalysed while a product is released. This results into a partial depletion operation. All examples in this paragraph use the ion exchange principle.

Differential pH measurement

Measurement of the pH before and after an ion exchange results in

$$\begin{aligned} \Delta \mathrm{pH} &= -\log[\mathrm{H}^+]_{\mathrm{out}} + \log[\mathrm{H}^+]_{\mathrm{in}} \\ &= \log\left(\frac{[\mathrm{H}^+]_{\mathrm{in}}}{2\cdot(1-a_{\mathrm{f}})\cdot[\mathrm{Ca}^{2+}]_{\mathrm{in}} + [\mathrm{H}^+]_{\mathrm{in}}}\right). \end{aligned} \tag{27}$$

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 equal to

$$\begin{aligned} \Delta\kappa &= \Delta[\mathrm{H}^+]\cdot\lambda_{\mathrm{H}^+} + 2\cdot\Delta[\mathrm{Ca}^{2+}]\cdot\lambda_{\mathrm{Ca}^{2+}} \\ &= 2\cdot(1-a_f)\cdot[\mathrm{Ca}^{2+}]_{\mathrm{in}}\lambda_{\mathrm{H}^+} + 2\cdot(a_f-1)\cdot[\mathrm{Ca}^{2+}]_{\mathrm{in}}\lambda_{\mathrm{Ca}^{2+}} \\ &= 2(1-a_f)(\lambda_{\mathrm{H}^+} - \lambda_{\mathrm{Ca}^{2+}})[\mathrm{Ca}^{2+}]_{\mathrm{in}} \end{aligned} \tag{28}$$

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

Differential temperature measurement

The ion exchange process most probably does not influence the temperature of the sample. Therefore it can not be expected that differentially measured temperature changes will occur.

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 with protons might disturb the amperometric H_2O_2 measurement at sensor B with respect to sensor A.

3.4. Additional Results

Some additional techniques can be performed, using the same set-up as shown in Fig. 1, or the time differential equivalent, but which do not satisfy the generalised measurement technique. An example is the coulometric sensor-actuator device for performing acid-base titrations [4]. Although this set-up consists of two sensors and one actuator, the determination is done by recording a titration curve instead of using a single differential measurement. In this subsection, two methods are presented where the output is also not determined by simply taking the difference between two sensor outputs.

Coulometric precipitation titration of calcium
Besides the already mentioned acid-base equilibria like described in equation (13), also precipitation reactions can be evoked using a H^+ or OH^- stimulus. In that case, the stimulus function $f_\alpha(x)$ is not one of the linear examples of subsection 2.2, since in this case $f_\alpha(x)$ describes the non-linear disturbance of a solubility equilibrium. Therefore, the interpretation of a single differential measurement will not be easy. An alternative to get useful information from this stimulus-response measurement, is to control the actuator until the differential measurement indicates an end point. This will be explained with the precipitation of calcium hydroxide as an example.

The bad solubility of calcium ions in an alkaline medium is given by

$$\mathrm{Ca(OH)_2} \leftrightarrow \mathrm{Ca^{2+}} + 2\mathrm{OH^-}, \qquad k_s = 1.3 \cdot 10^{-6}\,\mathrm{mol^3 l^{-3}} \tag{29}$$

with k_s the solubility constant of calcium hydroxide. Precipitation of calcium hydroxide can be monitored using a conductivity sensor since an imposed addition of for example sodium hydroxide does not result in the expected conductivity increase when some of the added hydroxyl ions have precipitated with calcium ions.

The measurement of calcium ions is very interesting for qualifying the builder action when monitoring washing processes. The builder effect consists of both exchange and precipitation of calcium ions. While ion precipitation during washing can be monitored by measuring the electrical conductivity of the water, the exchange of ions will not result into a significant electrolyte conductivity change. Therefore, a calcium detection method is desired for monitoring building by means of ion exchange.

The typical shape of a volumetric conductimetric precipitation titration can easily be constructed [8]. Consider a solution containing calcium ions and where all other charged particles are not likely to precipitate. By adding volumes of a sodium hydroxide solution, sodium will introduce a conductivity increase proportional to the added volume and the other ion concentrations will be constant. So, only Ca^{2+} and OH^- will account for a non-linear change in the observed conductivity since they have a certain interaction. Normally, with precipitation titrations, the first addition of titrant is already enough to reach the saturation point and will therefore result into a minimal precipitant.

When adding a small amount of sodium hydroxide, all added hydroxyl ions will precipitate and the remaining effect is the replacement of calcium ions by two sodium ions. The conductivity will slightly decrease since the molar conductivity of sodium ions is higher than that of calcium ions. After all calcium ions are captured completely, the conductivity will increase because of the added free hydroxyl and sodium ions. So, the end point of the titration, which is a measure for the calcium concentration, can easily be determined from the turn over point where the calcium ions are just exhausted. A theoretical plot of a volumetric precipitation titration with a conductivity measurement as an end point detection is drawn in Fig. 5.

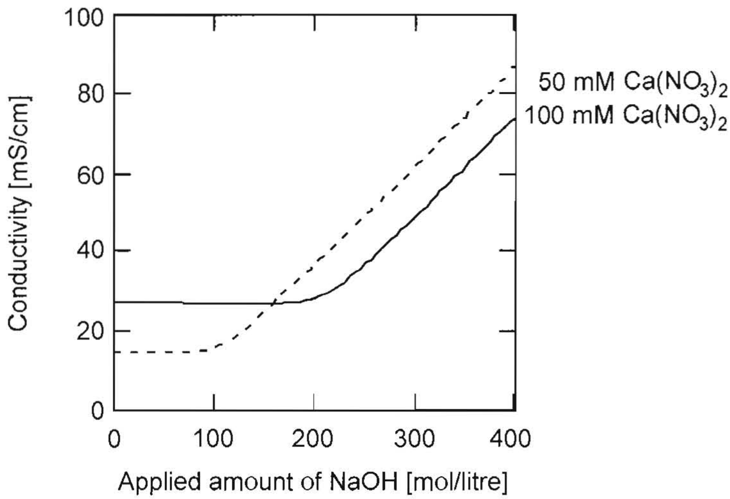

Fig. 5. Volumetric conductimetric precipitation titration of calcium nitrate with sodium hydroxide

From this figure it can be seen that a fixed addition of sodium hydroxide will not result into an unambiguous change in conductivity, since one does not know whether the end point in the titration curve is passed. A method using a controlled titrant addition (a titration), while monitoring the conductivity as an end point detection, does give more information on the success of the determination. Therefore, it is preferred to measure a precipitation reaction not using the generalised measurement technique of section 2.

While a volumetric titration requires a burette for adding the titrant, an alternative is to add the titrant by coulometric generation. Hydroxyl ions for the titration can be generated by the reduction of water according to equation (12). A coulometric precipitation titration of calcium with conductivity sensing as the end point detection, seems an ideal method since it can be implemented very simply using solid state components. The precipitation can easily be reversed by subsequently lowering the local pH using an anodic current. The shape of the curve will be different from Fig. 5 since only OH^- is added without a positive counter ion. Charge neutrality is accomplished by migration of positive ions to the working electrode. However, in practice, the precipitation appears to be less controllable than might be expected from equation (29). When the solution is supersaturated, the solubility constant k_s can be exceeded and the theoretical behaviour in the conductivity is not observed. Therefore, in analytical chemistry, a nucleation core is used to prevent supersaturation. How this technique can be applied to a coulometric actuator is not yet clear.

Flow measurement

For the application of the generalised set-up, the assumption was made that there is a flow along the sensors of an input electrolyte which is not changing in composition, and an immediate and complete modification of the electrolyte is generated at the actuator. Only in that case, the measurement is continuous and the distance between sensors and actuator is not of interest. However, when the actuator is switched on and off, the time delay between the actuator and one of the sensors can be observed. This delay is directly proportional to the flow speed of the sample.

In the alternative set-up consisting of an integrated sensor actuator structure, a flow measurement can also be performed. The actuated species will be removed proportionally to the flow speed. This is already in use in case a continuous supply of heat is injected into an electrolyte while the temperature is monitored. A lowering of the observed temperature indicates movement of the medium.

Considering the actuators of section 3, two markers for determining flow speed are available. Either a heat pulse or an electrochemically generated H^+ or OH^- cloud can be used, since also the sensors for detecting these pulses are available. When using a generated H^+ cloud as a marker, appropriate sensors are the conductivity cell and a pH sensor. The other option is to use a heat pulse and measure this with a temperature sensor.

The difference between time of flight using ions and time of flight using a heat pulse is in the diffusion effect. The diffusion constant of heat in water is equal to $1.455 \cdot 10^{-7}\,m^2 \cdot sec^{-1}$, the diffusion constant of protons in water is equal to $9.311 \cdot 10^{-9}\,m^2 \cdot sec^{-1}$ [9]. So, when using ions as a marker, the spreading of this marker is much smaller than when using a heat pulse. In addition, while heat can leak out of the channel by thermal conduction through the walls, particles like H^+ can not. Therefore, the use of a H^+ marker is preferred, especially for determining very low flow rates.

With time differential systems, using an integrated sensor-actuator structure, the same advantage of an ionic marker will be observed. In correspondence with flow measurement, the movement of a generated H^+ cloud due to flow of the medium can be measured as a decrease in the observed conductivity. In this case the same advantage to the thermal equivalent is observed since no absorption by the substrate material of the generated stimulus is possible.

3.5. Summary

Using three actuators and four sensors, twelve combinations for building a differential measurement system are possible. Table 1 gives a summary on the possible combinations for implementing the set-up of Fig. 1.

Table 1. Summary of sensor-actuator combinations

Sensor / Actuator	Pt-100 temperature	Finger structure conductivity	Amperometry H_2O_2	Potentiometry pH
Electrochemically generated H^+, OH^-, O_2 or H_2	0	weak acid conc. mass flow Ca^{2+} concentration	H_2O_2	weak acid conc. mass flow
Thermoresistive heating	mass flow	ion concentrations (with assumed set of ions)	diffusion constant	dissociation or acid constant
Ion exchanger	0	Ca^{2+}	0	Ca^{2+} (if pH is known)

The use of a time differential or spatial differential system does not make any difference for the mathematical background of the stimulus-response measurements, with the exception of the flow measurements. However, the spatial differential system measures at one single moment at two different sensors, while a time differential system measures at two different moments at the same spot in the electrolyte.

For the application of temperature sensors in a differential set-up, only mass flow can be detected. The reason is that no heating due to the electrochemical actuator and the ion exchanger is assumed.

The differential conductivity measurement appears to be the most universal technique for measuring. This advantage comes from the non-selectivity, resulting in a difference in conductivity after all three actuator steps.

Unless a logarithmic value, like pH of pCa, is desired, the linear nature of sensing of a conductivity cell shows the advantages of linear sensing described in section Mathematical generalisation of differential measurement systems.

A hydrogen peroxide measurement using an amperometric technique, shows little new information. Although a cancellation of offsets can be observed when using an electrochemical actuator, either thermoresistive heating or an imposed ion exchange does not show any promising new results.

Using potentiometric pH sensors, the results do not compete with the coulometric acid-base titrator as was published before [4]. Probably, due to its selectivity and logarithmic dependency on concentrations, the practical application of pH measurements in differential set-ups will give results which do need smart additional manipulation in order to retrieve useful electrolyte information.

For mass flow measurements, the choice of a spatial or a time differential set-up does make a difference. With the sensors and actuator placed in a row, the time of flight of a marker is measured. This results in the restriction that only linear flow can be measured and no turbulent flow. When, however, an integrated sensor-actuator structure is used, there is no time delay due to the geometry, and the flow information is obtained from the dilution of a marker. An example of the second technique can be shown with heat as the marker.

4. Conclusions

The mathematical impact of subtracting sensor signals was demonstrated in the first section of this paper. Promising results could be expected from linear actuators, before and after a stimulus measured by linear sensors. In that case, sensor offsets will cancel out and absolute information on a certain input variable will be present in the differential signal.

This rather theoretical evaluation was illustrated by brainstorming on the combinations possible with three actuators and four simple sensors, resulting into twelve set-ups for implementing differential measurement systems. Some of them resulted into useful ideas.

Weak acid concentration determination was mentioned more than once. Although the used weak acid model solution acetic acid is of course not present in a washing machine, hydrogen peroxide shows also an acid-base behaviour with the anion HO_2^-.

Determination after the addition of H^+, created by an electrochemical actuator, can be done by both a differential pH or conductivity measurement. Although these methods resemble acid-base titrations, the information is in the measured sensor difference and not in the added amount of titrant (indicated by the end-point). The differential pH method gives information on the logarithm of the weak acid concentration, while a differential conductivity sensing gives the weak acid concentration immediately. For efficient use of the second one, the injected current through the actuator before the end-point (defined as the moment where the difference in conductivity equals zero) can be used. However, the conventional coulometric titration with pH as the end point detection is still much more established and requires a similar set-up.

Weak acid concentration determination by measuring either pH or conductivity while applying a temperature step in order to change the acid equilibrium was suggested. But the practical use of this method is not easy since a temperature step will change much more parameters like the ion mobility and sensor slopes. Moreover, the use of a logarithmic sensor for measuring a concentration is not optimal since a non-linear operation is applied to the signal of interest.

Measuring calcium could not be done using single sensors up to now. Three options where found using stimulus-response measurements. Although it is not a one-spot differential measurement, the most elegant method would be a precipitation titration with conductivity sensing as an end point detection. The measurement of calcium by a precipitation technique is preferred because the possibility to precipitate is the reason that this hardness ion must be measured. Practical use of this titration method might fail, however, since precipitation is slow and furthermore hard to control.

Another method is to compare the conductivity at two temperatures. For this method, the pH must be increased first in order to assure that calcium is partially precipitated, since only then a change in the solubility constant due to the temperature difference can be measured. But now, the same problems will be encountered as with the other calcium precipitation method while in addition the problems with all the other parameters varying with temperature will show up.

What is probably possible for calcium sensing, is the application of an ion exchanger in combination with conductivity sensors. It was shown that an ion exchanger which exchanges one calcium ion by two H^+ ions, gives a conductivity change which is proportional to the absolute calcium concentration which is supplied to this system. Notice that this is an example of a method using linear sensors in combination with a linear actuator. The selectivity of the ion exchanger is used to sense calcium using non-selective conductivity sensors. The advantage of ion exchangers is that they can be reversed. An example is the use of an exchanger for the couple $Ca^{2+} \leftrightarrow 2H^+$, which can simply be reversed using electrochemically generated H^+ ions. A completely saturated ion exchanger gives calibration data on the sensors because the same sample solution is supplied to both sensors.

Since the ion exchanger material needs a certain path-length in order to exchange ions, the sample solution must be pumped through a column. This pumping and the use of a column will limit the advantages of the "all in one" sensor-actuator device. In addition, the use of a tube introduces a source of possible system break downs since obstructions might occur easily in dirty washing water.

What is interesting is the comparison of flow detection methods based on indicators. When using a cloud of ions as a marker (preferably H^+ since this can be generated electrochemically), this marker can not diffuse out of the tube. A heat pulse instead, can be conducted by the tube material or the substrate of the sensor-actuator, and will be lost for time of flight detection purposes. In addition, because the diffusion of heat is faster than the diffusion of ions, very low flow rates can be determined with a low spreading of the marker. With an integrated sensor-actuator device, the same advantages of an ionic marker will be observed, since there is also no sink via the bulk material.

One method was not worked out, but only mentioned superficially in this paper. This is the ion concentration measurement by interpreting the change in conductivity after changing the temperature. This method is described in detail in [6].

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Zasady pomiarów różnicowych w czasie i przestrzeni

Pomiar różnicowy ma wiele zalet. Można np. skompensować wywołane w procesie przetwarzania sygnału lub nieidealnością elektrody odniesienia, oraz elektrody powodowane zmianami temperatury. W celu prawidłowego zaprojektowania czujnika różnicowego należy przeprowadzić jego analizę teoretyczną przedstawioną w artykule. Najpierw rozważono zasadę przestrzennego i czasowego pomiaru różnicowego oraz przeanalizowano wymagania odnoszące się do czujników i bloków wykonawczych. Następnie rozpatrzono kilka przykładów obrazujących zalety rozważanej metody. W szczególności przedstawiono systemy pomiarowe przepływu masy oraz stężenia kwasów i wapnia. Możliwe różnicowe systemy pomiarowe składające się z trzech bloków wykonawczych (elektrochemicznych, termorezystywnych i jonowymiennych) i trzech czujników (temperatury, przewodności, amperometrycznych nadtlenku wodoru i potecjometrycznych pH) są przedstawione w tablicy podsumowującej wyniki artykułu.