The sensors for the intelligent micro washing system

Work report 2, 16-12-94
Geert Langereis

1. The washing process

This section gives a summary of the principles of the washing process and is mainly based on the book of Jakobi and Löhr [1]. Other facts are taken from the symposium "Washing, washing process and systems: future opportunities" held at URL Vlaardingen at 24 November 1994. From this summary it will be clear what parameters in the washing process are needed to measure and control it.

1.1. Washing machines

According to a market research it became clear that most people do not buy a washing machine for better cleaning but for convenience. Although in Europe we are used to front loading washing machines, the major machine market consists of twin and simple tub washing machines (China, USA and India). The European washing machines using a vertical axis of rotation consume less water than the vertical axis (tub) types. It appears that with the European washing habits the best result is obtained.

Trends in washing machine developments are aiming at saving energy and detergent. Energy saving can be done by reducing the used amount of water. To do this the effectiveness and the volume of the tub must be adapted to the process. Some USA washing machines are using 150 litres of water, while new types do the same with 50 litres. Detergent saving aims at reduction of loss and better programming of the machine, but also reduction of water will decrease the necessary amount.

Improvement of the programming can either be done by using:

- Fuzzy control (water and detergent adjusted to the load)
- Goldstar principle (free control of rotation speed by use of direct current motor)
- Phase control (motor speed)

An interesting new design is made by A.E.G. which has introduced a two-component wash system. The advantage is that the high temperature step (required for accurate bleaching) is only performed a short time. In figure 1.1 the wash cycle is schematically drawn.

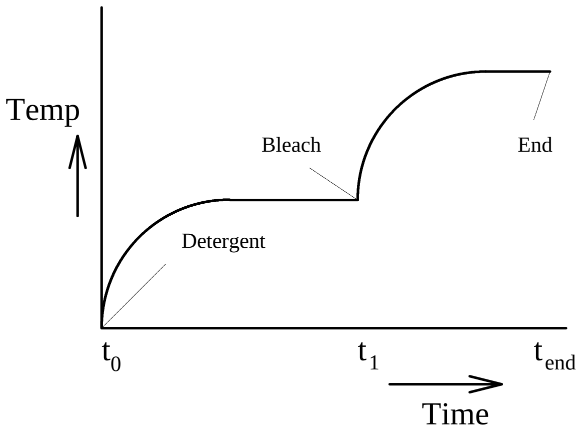


Figure 1.1: The temperature during a two component washing system

In the first period from t_0 to t_1 the temperature is relatively low (< 40°C) and only detergent is added. At time t_1 the temperature is risen to the temperature necessary for accurate bleaching. So only from t_1 to t_{end} the temperature is high which reduces energy consumption.

1.2. The water

The medium in which the whole washing process takes place is the water. The water functions as a transport medium for the detergents and must remove the released soil. To guarantee proper transport to and from the laundry, the water must wet the substrate completely. Water has a very high surface tension (72 mN/m), so wetting can only take place rapidly and effectively if this is reduced by surfactants, which thus become key components of any detergent.

The hardness of the water is defined as the amount of calcium and magnesium. The problem with these ions is that they have bad effects on the washing machines

(carbonates on heating coils) and form residues in the laundry. Another problem is that a high concentration of calcium reduces the removal of pigment soil.
Other elements present in water and decreasing washing efficiency, are iron, copper and manganese ions. These ions do catalyse the decomposition of bleaching agents. To avoid this effect complexing agents and ion exchangers are added to the detergent. One of their function is to bind multivalent alkaline-earth and heavy-metal ions through chelation or ion exchange.

1.3. Types of soil

The types of soil are here distinguished by their chemical and physical behaviour:

- Water-insoluble materials like inorganic salts, sugar, urea and perspiration.
- Pigments like metal oxides, carbonates, silicates, humus and soot (carbon black).
- Fats: animal fat, vegetable fat, sebum, mineral oil and wax.
- Proteins from: blood, egg, milk and skin residues.
- Carbohydrates (starch).
- Bleachable dyes from: fruit, vegetables, wine, coffee and tea.

A removal of soil from a surface either can be coupled with a chemical reaction (for example a redox process involving a bleach) or without chemical change. In many cases the soil consists of substances that are not removed by chemical treatment and only displacement by interfacial processes will clean the substrate. Modern detergents include this requirement and contain besides bleaches also surfactants, water soluble complexing agents and water insoluble ion exchangers.
An enhancement of soil removement is made by the increases of the mechanical input, wash time and temperature.

1.4. Physical soil removal

Physical removal of oily and pigmented soils can be done by:

- Non-specific adsorption of surfactants on the various interfaces present
- Specific adsorption of chelating agents on certain polar soil components
- Calcium ion exchange frees the calcium from soil deposits and fibres and looses remaining residues.

The principle of physical soil removement is based on the modification of the properties of the interfaces:

- Air-water: surface tension, foam generation, film elasticity, film viscosity
- Liquid-liquid: interfacial- tension and viscosity, emulsification, electric charge, active ingredient penetration
- Solid-liquid: splitting pressure, suspension stability, electric charge
- Solid-solid: adhesion, flocculation, heterocoagulation, sedimentation
- multicomponent: wetting, rolling-up processes

At washing temperatures most *oily and greasy fats* are liquid. In the first phase of washing the textile fibres and soil must be wetted as good as possible by the washing liquor. As a value for the wetting the contact angle can be taken. The Young equation gives the relation between the interfacial tensions:

$$j = g_S - g_{SL} = g_L \cos q \qquad (1.1)$$

with

j = wetting tension (N/m)
g_S = interfacial tension substrate/air (N/m)
g_{SL}= interfacial tension substrate/air (N/m)
g_L = interfacial tension substrate/air (N/m)
q = contact angle.

The contact angle is defined as in figure 1.2. If the contact angle is zero it is referred to as complete wetting and the liquid will spread spontaneously over the surface..

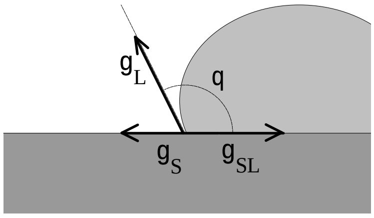
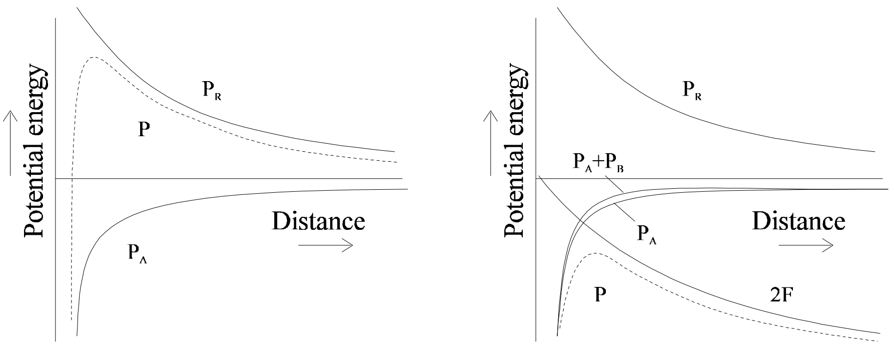


Figure 1.2: The contact angle

Only liquids with a surface tension equal or less than the critical surface tension g_C of a surface will cause thorough wetting.

Pigment soils are solid particles adhered to more or less smooth surfaces. The total potential P of particle is a summation of attraction P_A and repulsion P_R forces. This potential has a minimum at the substrate and a maximum at a certain distance. To remove the particle this potential barrier must be overcome. Adhering particles are more easily removed if the barrier is low. A soil particle in the wash liquor is less likely to contact if the barrier is large (figure 1.3a).

The potential curve for separating an adhering particle in an electrolyte solution results from a combination of the van de Waals-Born potential P_A+P_B and the free energy of formation of the electrical double layer 2F (figure 1.3b).



[a] Resultant potential [b] Removal

Figure 1.3: Potential energy of particles

Besides this energy principle, multivalent cations (which are almost always present in soils and textile fibres) show other mechanisms. *Calcium ions* can form cationic bridges which are responsible for binding soil components chemically to fibres. The linkage can be due to carboxyl groups commonly found in cotton as a result of oxidation, or to reactive centres associated with metal oxides. The problem arises with bad soluble calcium salts. The solubility is further decreased if the hardness increases.
The purpose of the detergent is to keep the calcium concentration in the water low so that a maximal concentration gradient is present between soil and water. The solubility equilibrium is displaced now in the desired direction. This is done by the capture of calcium ions by water soluble complexing agents. Then the ions are transported to insoluble ion exchangers which exchange one Ca^{2+} ion for two Na^+ ions. An example of a complexing agent is sodium-triphosphate, a common used ion exchanger is zeolite 4A.

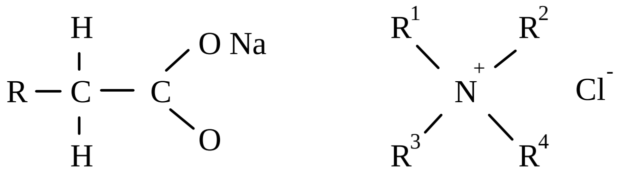
After removal of the soil an *antiredeposition* technique must be used. Already mentioned are the ion exchangers which capture the ions to an insoluble phase. Other antiredeposition agents are polymers which are being adsorbed to the substrate and become a protecting layer.

1.5. The detergent ingredients

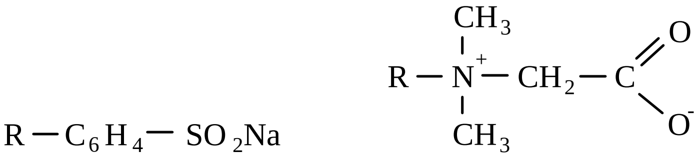
In the following section a division is made in:
- Surfactants
- Builders
- Bleaching agents
- Auxiliary agents

Each component will be evaluated.

First the *surfactants* can be devided in anionic, non-ionic, cationic and amphoteric surfactants. They are the most important group of detergent components. Some examples are drawn in figure 1.4. The most commonly used are Alkyl Benzene sulphates (LAS).



[a] Soap (anionic) [b] QAC (cationic)



[c] LAS (anionic) [d] Alkylbetaines (amphoteric)

Figure 1.4: Some surfactants

The surfactants are water soluble surface active agents. They consist of a long (alkyl) chain which is hydrophobic, and a hydrophilic functional group. In general both adsorption and wash effectiveness increase with increasing chain length. Surfactants with little branching in their alkyl chains generally show good wash effectiveness but relatively poor wetting characteristics, whereas more highly branched surfactants are good wetting agents but have unsatisfactory detergency.

The functions of *builders* are supporting detergent action and eliminating calcium and magnesium ions.
The first category is that of the *specific alkaline substances* like sodium carbonate and sodium silicate. Their activity is based on the fact that soil and fibres become more negatively charged as the pH increases, resulting in increased mutual repulsion. Alkali also precipitates ions that contribute to the hardness.
Secondarily there are *complexing agents* which form water insoluble complexes with alkali elements and heavy metals. This has a lowering effect on the water hardness. Example are ethylenediaminetetraacetic acid (EDTA), sodium diphosphate and citric acid.
Ion exchangers were mentioned before because of their effect on the water hardness and their relation to complexing agents. Examples are sodium triphosphate and zeolite 4A (sodium aluminium silicate).

Bleaches are added to the detergent to get a lighter shade in the colour of an object. Physically this implies increase of the reflectance of visible light at the expense of absorption. The physical bleaching are the processes described before. Here, however, the chemical bleaching components are meant. Chemical bleaching is the removal of non-washable soils by reductive or oxidative decomposition of chromophoric systems. The oxidative bleaches are more common in washing processes. In laundry, components are present that become colourless if they are bleached reductively and return to their coloured forms if they are oxidised by air.
In many countries outside Europe the bleaching component is sodium-hypochlorid. In Europe the dominant bleaches are peroxide based. The active bleaching component is

the intermediate hydrogen peroxide anion which is converted from hydrogen peroxide in alkaline medium.

$$H_2O_2 + OH^- \Leftrightarrow H_2O + OH_2^- \qquad (1.2)$$

The most important source for hydrogen peroxide is sodium perborate ($NaBO_3 \cdot 4H_2O$) which is present in the crystalline form as the peroxodiborate ion. This ion has excellent dry life time and hydrolyses in water to hydrogen peroxide.

The peroxide is most active at 90°C because of the dependency of equation 1.2 on temperature. To wash at lower temperatures (<60°C) a bleach activator is added. When present in wash liquor of pH 9-12, these activators react preferentially with hydrogen peroxide to form organic peroxy acids which have a higher oxidation potential than hydrogen peroxide. An example is TetraAcetylEthyleneDiamine (TAED).

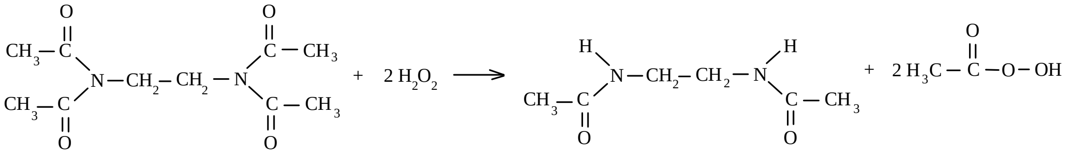


Figure 1.5: Reaction of TAED and hydrogen peroxide to peroxyacetic acid

A more new approach is the lowering of bleaching temperature by bleaching catalysis. The bleaching power of sodium perborate is increased by some heavy metal chalates.

The last group of detergent compounds are the auxiliary agents which are added in small amounts. They all have a quite specific function.

Enzymes are used to cleave proteins (proteolytic enzymes) from sources like milk, cocoa, blood and grass. The effectiveness of enzymes is based on enzymatic hydrolysis of peptide and ester linkages. Because properties of the washing liquor, enzyme must remain stable in environments containing alkaline (pH between 9 and 11), high temperatures (90°C), hydrogen peroxide, complexing agents and surfactants. Also, the enzyme must be storable so having a little autolysis tendency.

Antiredeposition agents deposit on fibres and soil in order to avoid contact between free soil particles and clean laundry. An example is carboxymethyl cellulose (CMC).

In history, foam was a good indication of the washing effectiveness. With modern synthetic surfactants foam is not required because loss of the detergents by foaming out of the system will be the case. So in drum type washing machines, foam is inhibited by *foam regulators*. This type of regulator is called foam inhibitor. With hand washing the consumer wants to generate lots of foam so foam boosters are added.

Various machine components are made of metals. To prevent corrosion of these parts, modern detergents are supplemented with *corrosion inhibitors* in the form of water glass. This material deposits an inert layer on metallic surfaces to prevent attack by hydroxide ions.

After bleaching a yellowish tinge remains. In detergents often *fluorescent whitening agents* (FWA) are added. They can be devided in cotton-, chlorine resistant-, polyamide- and polyester whiteners.

Fragrances are added to the detergent to give both the powder and the clean laundry a nice smell. In addition it masks the unpleasant odours produced during the washing.
To sell a product that can be distinguished from other products, the powder is coloured by *dyes*. The preferred colours for both powders and liquids are blue, green and pink.
In powdered detergents *fillers* are present. These inorganic salts (sodium sulphate) give the detergent a good flowability and flushing properties, high solubility, little caking of the powder under humidity and prevent dusting. In liquid detergents phase separation and precipitation due to temperature changes are prevented by *formulation aids*.

1.6. Sequential dosing and interfacing

After measuring the situation the system is adapted by adding detergent. The most accurate way of controlling is by adding the detergent components separately. In nowadays washing processes a total washing powder is applied containing all detergent elements. The amount of detergent is dosed by the user according to the water hardness. In this way not only the builder dosage is increased but also the amount of surfactant (which does not have a lot of effect because the surfactant effectiveness is a matter of time rather than concentration). This ineffective way of dosing does not fit with the intelligent washing system.
For effective sequential dosing some restrictions must be made. For example if bleaching elements are already supplied, the proleatic enzymes are destroyed at the moment they are added. So the bleaching must be after the enzymatic cleaning.
At URL the following sequence is proposed:

1. Builder
2. Enzymes: - prolease
   - lipase
3. Surfactants
4. Bleach

First the builder is dosed according to the water supply and must be applied during the washing to capture Ca^{2+} ions. The enzymes are added in an early stage to avoid the "burn in" effect, which is the unremovable adherence of reduced (by bleach) peptides like blood contaminants. Then the surfactants are added. This leaves the possibility to raise the temperature in the last phase of the washing as mentioned in section 1.1.

Besides the possibility of controlling the dosing (chemical interfacing) it can be considered to control the physical parameters (physical interfacing):

- A *non-interfacing* washing system
  In this case the intelligent washing cassette has no influence on the washing program. The user chooses the accurate program and the cassette must do it's dosing in the pre-defined program steps. The advantage of this method is that the machine does not have to be changed.
- An *interfacing* washing system
  This requires a special machine that allows to be controlled by the cassette. The user must only choose some parameters that can not be measured like white or coloured laundry. The cassette can now change the length of a cycle according to the measured soil level. The interfacing must be an improvement, this means that

the length of the washing process may not be increased, that the amount of used detergent must be decreased and that the result should be better.

2. The μTAS concept

The continuous monitoring of chemical parameters is not only important in washing industry but also in for example medical diagnosis, chemical production and environmental analysis. The tendency is to measure as many parameters as possible, which results in a lot of equipment. The tendency is to combine analysis setups in order to reduce space and costs. Another aim is to build an automatic evaluation system in order to get a total analysis system (TAS).

The miniaturised total analysis system (μTAS) is a concept for on-line monitoring combining classical techniques and photolithographically defined micro structures. The ultimate μTAS is drawn in figure 2.1, it combines channels, pumps and sensors in one chip. The control supplies for the pump and the valve are not in the figure.

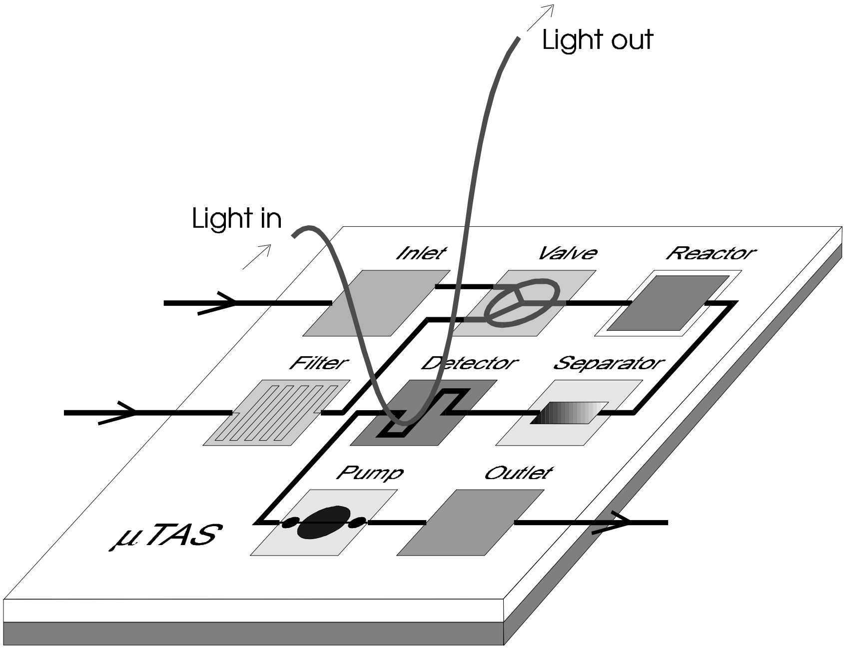


Figure 2.1: Example of an ultimate μTAS

The advantages of such systems are numerous [2]:

- The system becomes portable, sometimes even implantable.
- One is measuring at the location of the sample. This has advantages on the accuracy of the measurement.
- The silicon technology is a well established technique and can be used to realise the μTAS. Both micromechanical, microplumbing and sensing devices were in the past implemented in silicon. The silicon technology can be used for (inexpensive) large scale production.
- Access to new types of analysis techniques (electrophoresis for example).
- Lower consumption of analyte than with conventional techniques (samples of μl).

- Faster operation because only a small sample is taken. If evaluated in a small volume (a mTAS with a flow system) with sizes smaller than the diffusion length of the used solvents, an elimination of the diffusion constant is obtained which results in an improved behaviour.
- No expert necessary because system takes care of chemical skills like titration and other chemical handling.

The mTAS-concept is mentioned here because the system to be developed for the washing control in fact is such a system. The washing system consists of a number of sensors and a dosing system controlled by an electrical circuitry. Maybe, in first instance, the tube system is not necessary. An array of bare sensors situated in the washing tub may give accurate information to make the necessary decisions.

3. Measurement methods

This section states some considerations about the integration of sensors. By combining sensors the system can get more capabilities than the separate sensors would give. Also, by using a single sensor in different ways more information can be obtained.

3.1. Getting more from one single sensor

A sensor (for example a silicon structure primarily meant as ISFET) can give more information by using different modes. This modes can be:

a - *Frequency modes.* An ISFET can be used as conductivity sensor when a high frequency is applied [3]. In the low frequency range (DC) the device still is a pH electrode. Those two frequency modes can be used at the same time or at separate times.

b - *Connecting mode.* As seen in the previous work report, some bipolar modes are present in an ISFET. To get data from such a mode the transistor must be connected in a different way. So the use of these modes must be at separate times.

3.2. Combining sensors

There are two possibilities in combining sensor structures to sensor functions. These two are sometimes hard to distinguish:

a - *Functional integration*. The technique called "connecting mode" of the previous paragraph is a special case of this, where one structure is used for two functions.

b - *Geographical integration*. The second option is that one sensor structure is used for different tasks. Some structures can be used as a part of another measurement setup. For example by combining two ISFETs (primarily used for pH measurements) with two metal electrodes (present as a reference or for a dynamic surface tension measurement), a new setup can be made which measures conductivity in a four points method [4].

3.3. Mathematical improvements

Consider the measurements from the sensors as a vector of data. This vector contains information on for example pH, temperature, conductivity and concentrations. These are direct measurable values. From this data it is possible to know more than with the separate values.

a - *Eliminating undesired dependencies*. For example a temperature dependency in the pH can be eliminated simply because the absolute temperature is known.

b - *Verification*. Two methods for measuring conductivity were mentioned: a four points method using two ISFETs and a high frequency method using one ISFET. The measured values together give a more reliable view on the actual conductivity.

c - If vector **a** is being measured (containing direct measurements) and vector **b** is wanted (containing the desired physical and chemical data), a calculation must be made because **b** = f(**a**) need to be solved. For example the value $\mathbf{a}_1$ containing the load weight and $\mathbf{a}_2$ containing the pCa results in factor $\mathbf{b}_1$ which can be the amount of calcium per load unit and is calculated from $\mathbf{a}_1$ and $\mathbf{a}_2$.

In fact, options a and b are special cases of option c.

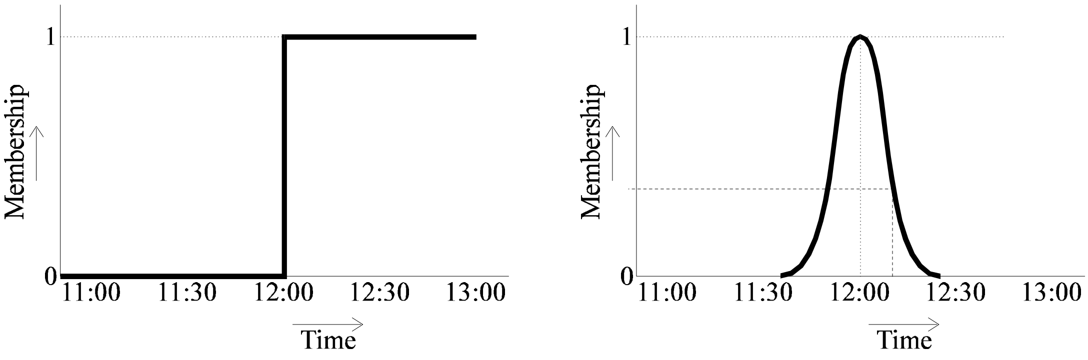
The implementation of the mentioned function f giving the relation between vectors **a** and **b** can be done in two ways. If a suitable model is present the desired value can directly be calculated from components of vector **a**. For example if the temperature dependency of the output of an ISFET is known explicitly, it is possible to eliminate it. A second method is the usage of fuzzy logic. With fuzzy logic in combination with fuzzy control a decision can be made towards the control from measured data that is not completely stated. A short impression of fuzzy control is given in the following section. It is not the aim of this project to design the complete control logic, but the usage of fuzzy logic might have its consequences on the demands on the sensors.

4. Fuzzy logic

In conventional logic (Boolean) it is said that statement A is true or not true. With fuzzy logic it is possible to express the uncertainty of a statement in its *membership-function* [5].

4.1. The membership function

The membership-function can be explained by formulating the Boolean algebra slightly different. With Boolean algebra, statement A is either in the set of "true" or "not true", or in other words: statement A is a member of the set "true" or not (figure 4.1a). A fuzzy membership-function however describes the validity of the phrase "statement A is true" depending on an input variable. Different from Boolean algebra is that in fuzzy logic a statement like "this is for 20% certain" is allowed.



[a] Boolean statement: "It's afternoon" [b] Fuzzy statement: "It's about noon"

Figure 4.1: Membership functions

For example the statement "it is about noon" is a subjective phrase. At 12:00 this statement is absolutely true, but at 12:05 the validity depends on the opinion. Figure 4.1b shows a possible membership function for this statement. An interpretation can be that at 12:10 only 30% of the people say it's about noon.

A formal notation is as follows: given situation x_i, the membership of statement A is written as $\mu_A(x_i)$. For example, in figure 4.1b the situation x_i = 12:00 with the statement A = "It's about noon" results in a membership of $\mu_A(x_i) = 1$.

4.2. Fuzzy algebra

The next step is making algebraic rules. A Boolean example is:

IF (A AND B) THEN C (4.1)

Which states that C can be concluded only if the condition (A AND B) is met. This condition is true only if both A and B are true. Now consider two fuzzy statements A and B, both having a membership function like figure 4.1b. Now, it is no longer possible any more to decide simply whether the condition (A AND B) is met. Figure 4.2 gives the two membership functions μ_A and μ_B, and it will be clear that the condition (A AND B) will never be true in the Boolean sense. Formal formulated:

$$[\mu_A(x_i) = 1] \text{ AND } [\mu_B(x_i) = 1] = \text{TRUE} \qquad (4.2)$$

can not be solved for a realistic x_i (see figure 4.2).

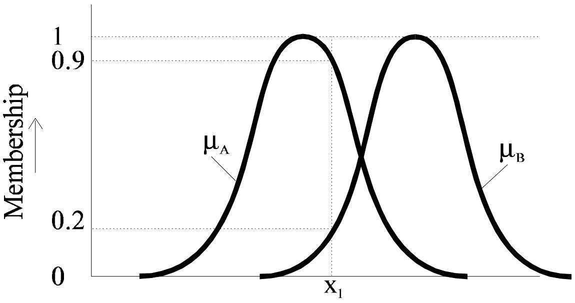
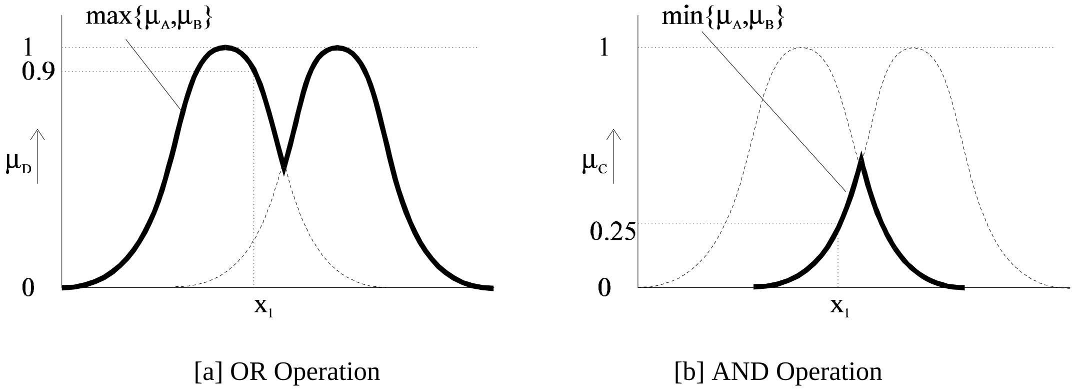


Figure 4.2: Two membership functions

So for fuzzy decisions it is necessary to define new fuzzy algebra which allows uncertain answers. The definitions are based on the mathematical set theory. For AND operations the *min* statement is used and for OR operations the *max* statement.

AND: $\mu_C(x_i) = min\{\mu_A(x_i), \mu_B(x_i)\}$ (4.3)
OR: $\mu_D(x_i) = max\{\mu_A(x_i), \mu_B(x_i)\}$ (4.4)

This simply states that the AND membership function $\mu_C(x_i)$ can be found from the functions μ_A and μ_B by taking the smallest value from these two. This is graphically illustrated in figure 4.3.



[a] OR Operation [b] AND Operation

Figure 4.3: Fuzzy decisions

From figure 4.3a it can be seen that with input x_1 the change that (A OR B) is true is 90%. Figure 4.3b shows that (A AND B) is 25% then.

Also other operators can be defined. For example the NOT function can be:

NOT: $\mu_E(x_i) = \{1-\mu_A(x_i)\}$ (4.5)

Other fuzzy operators can give a fuzzy set that does not fit with our experience. It is possible to make a conclusion based on the product:

$\mu_F(x_i) = \{\mu_A(x_i) \cdot \mu_B(x_i)\}$ (4.6) without knowing the exact meaning of this product, but it can be shown that $\mu_F(x_i)$ will be between the OR and the AND result.

4.3. Fuzzy control

After defining variables and operators it is possible to make conclusions and use these in an adapting system. An example can be the system consisting of the sentences:

"If it's too cold turn the heater higher"
"If it's too hot turn the heater lower"

The subjective experience "too cold" results in an adaptation of the heater now, which is the desired result. If it was a wrong decision, the next experience will be a situation that is too hot which probably results in a lowering of the heater.

In most fuzzy systems the experience has several discrete values, for example "very cold", "cold", "warm", "hot" and "very hot". The adaptation also can have several stages. This is why fuzzy is sometimes seen as the mathematics between Boolean (binary) and analogue.

A fuzzy control system is schematically drawn in figure 4.4. The system does not significally differ from conventional control systems. An error signal can be defined from the input signal, some measured values and the output signal. A control unit adapts the process according to this error signal.

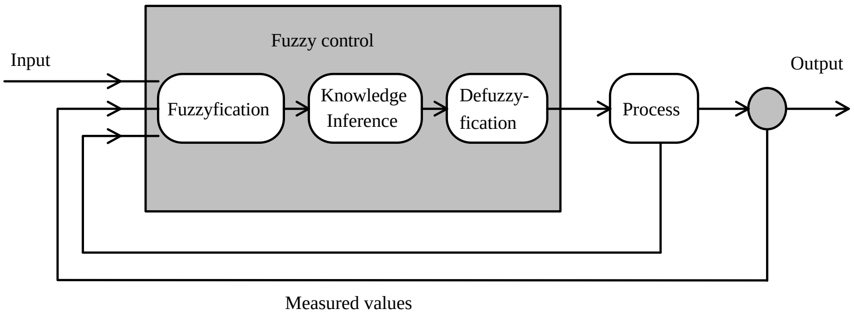
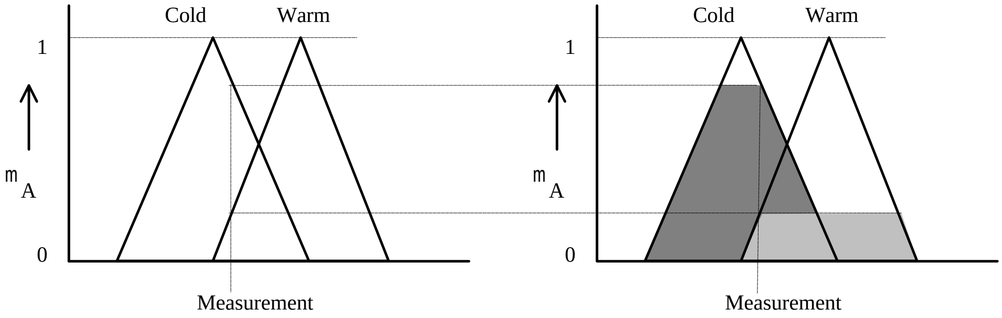
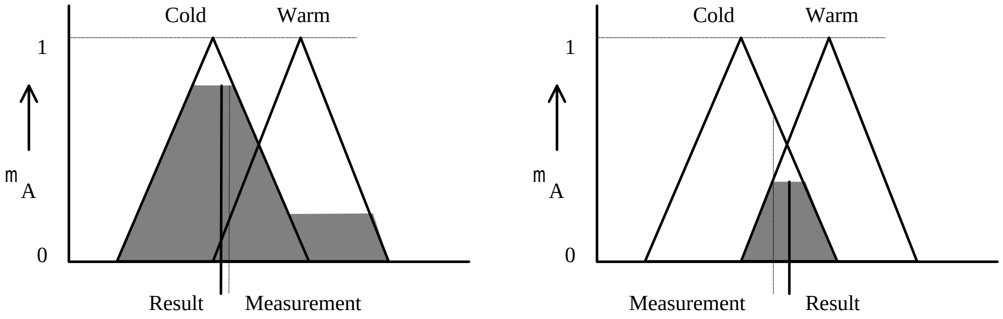


Figure 4.3: Fuzzy control system

In the control unit the physical values are first fuzzyficated, which is the translation of a signal to a membership function. Based on these membership functions decisions are made in the inference block using programmed knowledge. To use the conclusion in the process, the fuzzy signal must be defuzzyfied.



[a] Fuzzyfication of a measurement [b] Representation in fuzzy terms



[c] OR area and defuzzyfication [d] AND area and defuzzyfication

Figure 4.4: Fuzzy decision system

Figure 4.4 gives an example. The membership functions are here triangular shaped and there is one for the subjective term "cold" and one for "warm". Figure 4.4a shows a measurement that can be evaluated as about 30% warm and 75% cold.

In figure b this signal is fuzzyfied and represented as an area consisting of subsets of the membership functions "cold" and "warm". Now it is possible to make a decision. The OR operation was defined as the maximum of the two operators, this is the surface of figure c. The AND operation results from the minimum op the subsets shown in figure d.

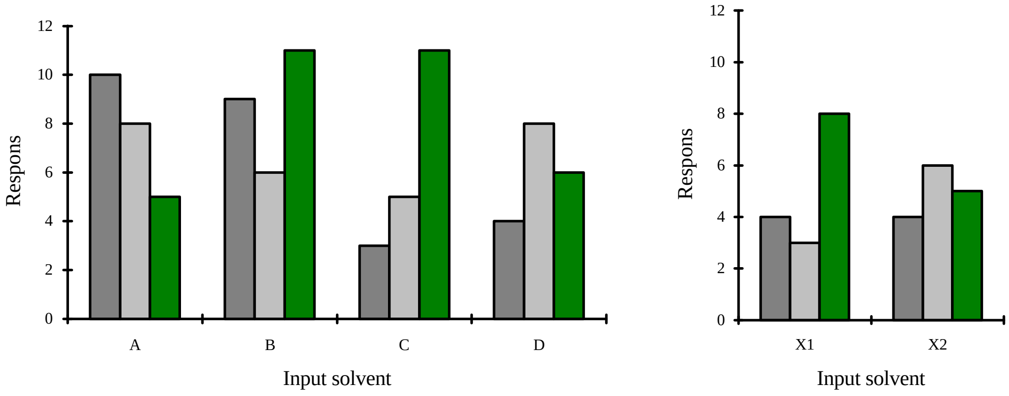
The results of the operations are fuzzy signals (represented as surfaces), to get a single value the weighted middle is taken. This is the defuzzyfication.

4.4. Requirements of a fuzzy system on the sensors

Fuzzy control can be used to make decisions about inputs that are not completely stated. This has its consequences towards the signals. A signal used in fuzzy systems does not have to change analogous with the value to be measured, some discrete stages are allowed. The discrete stages might be fuzzy defined. This means that drifting of a sensor does not have to be a problem for the accuracy of the system.

In washing systems the watching of trends is sufficient rather than the absolute measured values. A fuzzy system is able to handle this kind of signals.

An application can be a recognition system containing three ISFETs. The sensors are coated with different membranes so they have a different sensibility. The profiles are drawn in figure 4.5.



[a] Profiles to calibration gases

[b] Unknown gases

Figure 4.5: The recognition of gases

In figure 4.5a well defined solvents A, B, C and D are applied. The resulting sensitivities are different so the profile can in future be used to identify liquids A, B, C and D. However, if an unknown solvent is applied, a completely new profile arises (figure 4.5b profiles X1 and X2). After measuring these profiles once, it is possible to identify these liquids also.
To do this identification fuzzy logic will be useful. The pattern recognition gives information about:

- classification
- identification
- quantification

of test liquids. There is however always an uncertainty in the conclusion, which becomes less if there are more sensors and if these sensors are more selective.

5. The amperometric hydrogen peroxide measurement

In most European detergents, the bleaching component is hydrogen peroxide. With the process:

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \qquad (5.1)$$

(which has an redox potential E^0 of 0.68V) the available peroxide can be reduced. By integrating the current over the time, the total reduced amount of peroxide can be calculated.

5.1. Cyclic voltammetry

To study the charge transfer reactions the current-voltage relationship is used. This technique is called voltammetry. The cyclic voltammetry (CV measurement) is defined as the current behaviour with a triangular voltage applied [6].
If only one species is reversibly reduced,

$$O + ne^- \Leftrightarrow R \tag{5.2}$$

the surface concentration of O will change according to the Nernst equation:

$$\frac{[O]}{[R]} = e^{\frac{nF}{RT}(E-E^0)} \tag{5.3}$$

with E^0 the redox potential. The supply of O will be under diffusion control so a maximum will be obtained at a certain peak voltage E_p. A characteristic CV curve is drawn in figure 5.1.

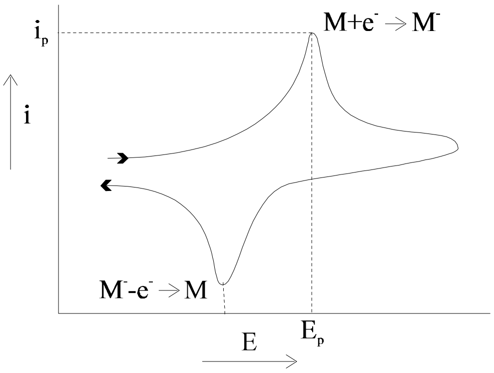


Figure 5.1: Typical CV-profile

This is for the positive slope of the potential E, at the negative slope the re-oxidation results in an equal peak current. This peak is defined by the Randles-Sevcik equation.

$$i_p = -0.4463 nFC_0 \sqrt{\frac{nF}{RT} Dv} \tag{5.4}$$

With:

n: the number of electrons transferred between oxidant and reductant
C_0: the bulk concentration
D: the diffusion coefficient.

So from the peak current the concentration can be obtained.

5.2. Practical application

The applications of amperometric peroxide sensors can be found in glucose sensors were the H_2O_2 is being measured that is catalysed from glucose by peroxidase. The principle of the amperometry is drawn in figure 5.2.

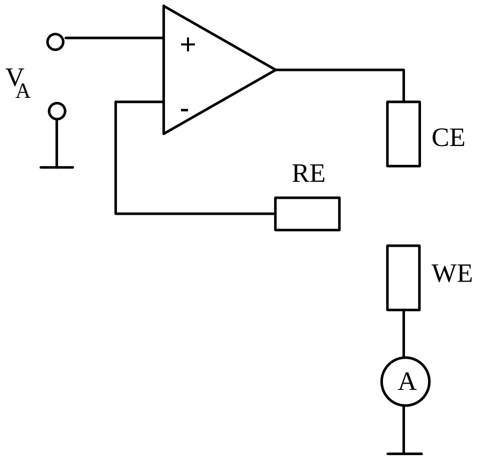


Figure 5.2: Amperometry setup

The applied voltage V_A comes totally across the working electrode WE because the reference electrode RE operates without current. The operational amplifier guarantees that the RE electrode is at the same potential as the applied voltage, the current is available from the counter electrode CE. So the potential across WE is known and the current can be measured.
An interesting example is one where the reference is set by an ISFET [7]. The ISFET showed here an offset towards the SCE of -1.7 V. Between hydrogen peroxide concentrations of 0.01 and 1 mM the circuitry showed a linear dependency, the current varied between 0.1 and 10 µA.

6. The coulometric acid/base titrator

In the hydrogen peroxide amperometric sensor actuator system H^+ ions were generated. In combination with a normal ISFET these ions can be used to perform an acid/base titration. In practice two other coulometric reactions can be used [8] the anode and cathode respectively:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (5.5)$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \qquad (5.6)$$

For the first E^0 is 1.229V, and for the second -0.83V. In figure 5.3 the coulometric reactions are controlled by the current source and the end of the titration pH is detected by ISFET 2. The bulk pH is measured with ISFET 1 and is a reliable reference.

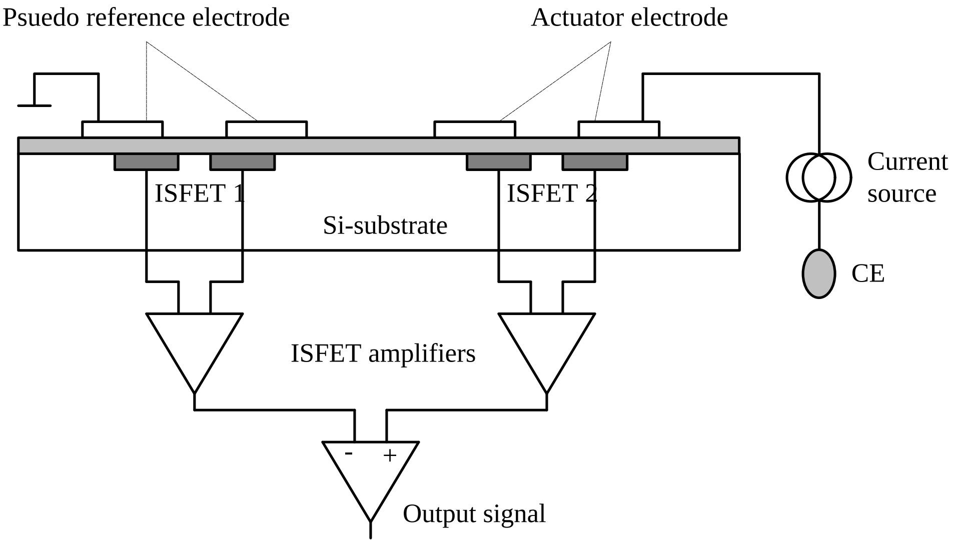


Figure 5.3: The coulometric device

The largest disadvantage of this device is that the end of the titration is dependent on the diffusion coefficient of the acid D_{acid}:

$$t_{end} = \frac{\pi D_{acid} F^2 C_{acid}{}^2}{4 j_c{}^2} \qquad (5.7)$$

where j_c is the cathodic current density through the actuator, F Faraday's constant and C_{acid} the acid concentration.

7. Controlling a complete washing system

Now the washing process is summarised and some sensors are mentioned, it is possible to combine them. In the first subsection, the washing process is splitted into four phases, each giving other information.

7.1. The parameters to measure

During the washing process the parameters that are important are not the same. In this subsection a division is made in four phases: examining the dry load, just after wetting, during the main wash and during rinsing. This division is made after a poster used at URL.

Examining the dry load

There are several parameters to obtain from the dry load:

- A "sniff chip" can identify the soil that comes with the fabrics.
- The amount of laundry can be measured by evaluating the weight.
- It should be nice if it was possible to identify the load itself, but because this appears to be very difficult the user must choose a program.

After applying the water

- The hardness of the water can be measured. This is necessary to decide how much builder must be applied. The hardness is exactly determined by measuring the Ca^{2+} and Mg^{2+} concentrations.
- Again a "sniff chip" can be applied to get an impression of the soil. This wet sniff method can include other sensors.

During the main wash

- The dynamic surface tension gives an indication of the amount of surfactants.
- Measuring pH is important because at a higher pH the washing is better. As seen in a previous section the bleaching activity can be measured by an amperometric sensor.
- The temperature is important as long as the washing is done at elevated temperature. When in future the washing is done at room temperature, this sensor can be omitted.
- In a parallel project a peptide sensor system is developed. It seemed that by sensing the concentration of stain selective peptides an indication is obtained of the amount of stain.
- The acid/base titrator can give information about the enzymes in the washing system. However, the evaluation of the output is very complicated.

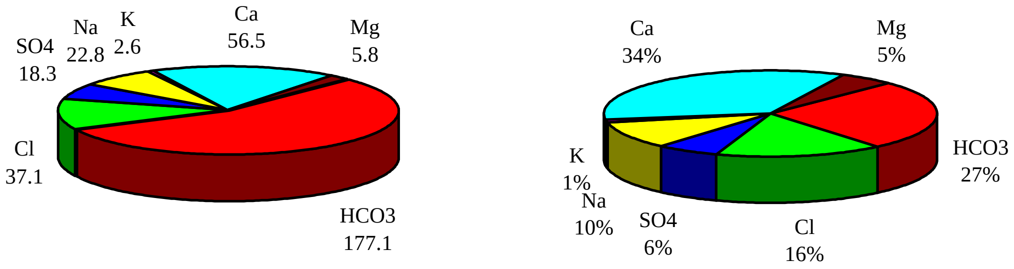
During rinsing

- The conductivity gives information during rinsing about the effectiveness.
- The pH sensor which is present anyway can give similar information.

Measuring the process is only half of the work, a measurement is only important if it gives information about a parameter that we want to know and that is controllable.

7.2. Interpreting the conductivity

The conductivity itself is not a useful measurement but it gives information about the components in the washing liquor. The hardness of the water is defined as the concentrations of Ca^{2+} and Mg^{2+}. These ions are together with other ions (Na^+, Cl^- and HCO_3^- for example) responsible for the conductivity. The assumption is that by measuring the conductivity an impression of the hardness can be obtained.
From a statistical research of the ions in the water of 45 Dutch cities in 1986 [9] some graphs were made. In figure 7.1a the average concentration of the seven most dominant ions are shown. It appears that HCO_3^- has the highest mass concentration: 177.1 mg/l.



[a] Concentration [mg/l]   [b] Contribution to the conductivity

Figure 7.1: The average of the ions in Dutch drinking water

From the concentrations the conductivity can be calculated [10]. The conductivity k of a solution depends on the number of ions present (molar concentration c) in relation to the molar conductivity L_m:

$$k = c \cdot \Lambda_m \qquad (7.1)$$

In strong electrolytes the molar conductivity of the complete solution is the sum of the limiting molar conductivities l_i with respect to the ratio's n_i. The limiting conductivity is defined as the partial conductivity where no interaction with other ions is present.

$$\Lambda_m = \sum n_i \cdot l_i \qquad (7.2)$$

In table 7.1 the contribution to the total conductivity of the ions of figure 7.1a is calculated. The results in the last column are plotted in figure 7.1b. It can be seen that the concentration of Ca^{2+} has a contribution to the conductivity of 34%.

Table 7.1: Calculation of the partial conductivities of the most important ions

	Molar mass [g/mol]	Lim. conduct. [$S\cdot cm^2/mol$]	Average [mg/l]	Partial conduct. [mS/m]
HCO_3^-	61.02	44.5	177.1	12.92
Cl^-	35.45	76.35	37.1	7.99
SO_4^-	96.07	160	18.3	3.05
Na^+	22.99	50.1	22.8	4.97
K^+	39.1	73.5	2.6	0.50
Ca^{2+}	40.08	119	56.5	16.77
Mg^{2+}	24.3	106	5.8	2.54
			Total average conductivity:	48.74 mS/m

In figure 7.2 the measured hardness of the water is plotted against the measured conductivity. It can be seen that the correlation is large: 0.852. The line is drawn with the least square algorithm.

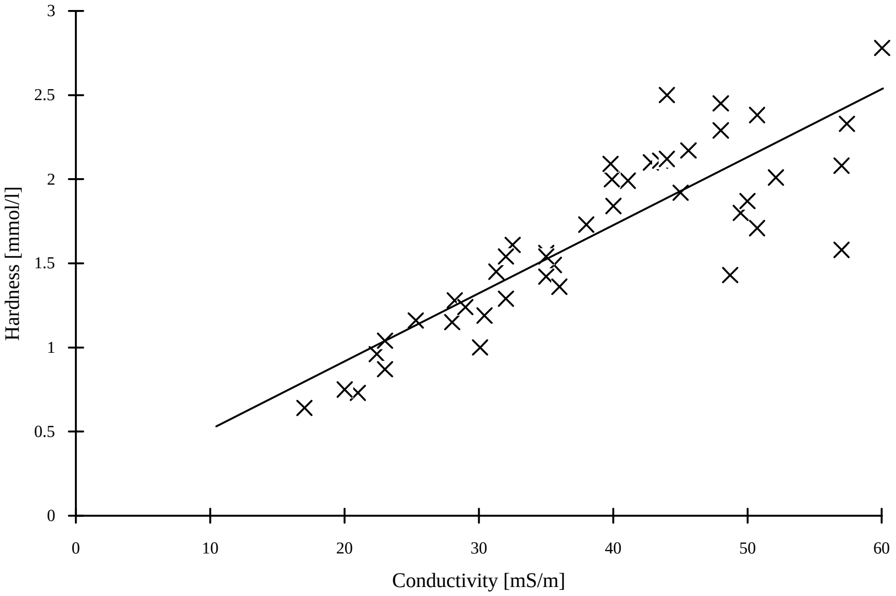


Figure 7.2: The correlation between the water hardness and conductivity

If a Na^+ sensor is available, it is possible to eliminate this factor in the conductivity. This adapted conductivity has a larger dependence on the Ca^{2+} and Mg^{2+} concentrations. With the data of table 7.1 a new correlation was calculated between hardness and corrected conductivity, the correlation coefficient was increased to 0.936.
From figure 7.1b it can be seen that the HCO_3^- concentration is the largest error in the relation between hardness and conductivity. Eliminating this concentration would give a much larger improvement of the correlation.

After applying the builder it is certainly not possible any more to determine the hardness by measuring the conductivity while using a pre-defined slope. An exchange of one mole of calcium to two moles of sodium gives hardly a change in the conductivity of the liquid (an increase of 2×50.1 mS for the sodium and a decrease of 119 mS for the calcium) but the hardness decreases with one mole.

7.3. Combining the titrator and the amperometric device

Both equation 5.1 and 5.5 show that the number of used electrons is equal to the amount of produced acid, so the current can be used to calculate the end point of the titration no matter which reaction takes place. For the hydrogen peroxide measurement only reaction 5.1 is allowed. Fortunately the redox potential of 5.1 is lower than that of 5.5 (0.68V respectively 1.229V) so it is possible to control this.
In figure 5.4 a first idea for the combination of the two devices is drawn. ISFET 1 is used as reference electrode for both measurements. The counter electrodes are also common. The working electrodes however are not the same: for the coulometric device WE is located near ISFET 2 and for the amperometric device the grounded electrode near ISFET 1 is used. The input for the coulometric actuator is the current source and for the amperometric actuator V_A.

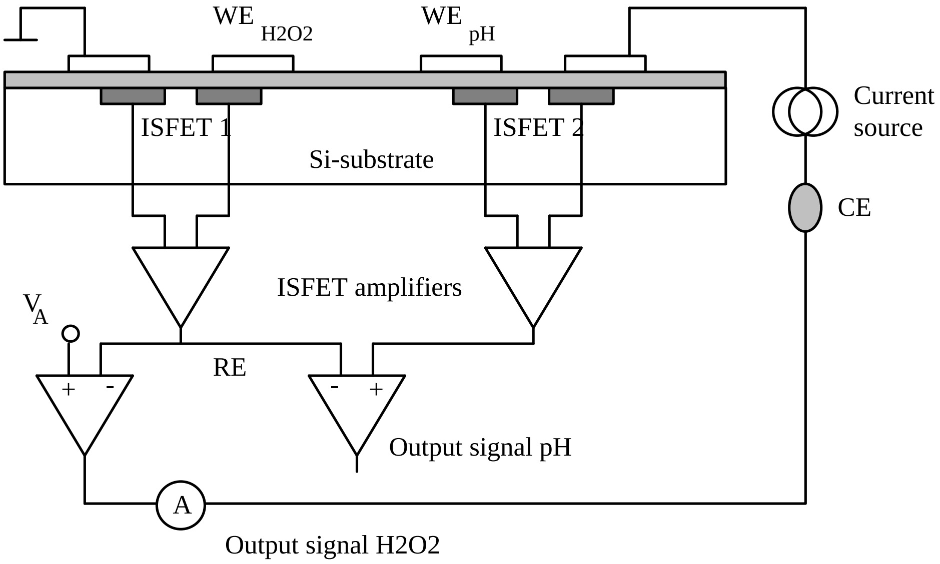


Figure 7.3: Combination of the amperometric and coulometric devices

To prevent electrolysis of water the potential V_A must be held below 1 V during amperometric measurements.

7.4. A complete washing evaluation system

The following measurements were evaluated in this report and workreport 1:

Table 7.2: Parameters to measure

Sensor	Sensor principle	Parameter	
Temperature	pn-junction	T	Rep1 5
Conductivity	4-points with ISFETs	Hardness, end of rinsing	Rep1 7
pH	ISFET	pH	Rep1 6
H_2O_2-concentration	amperometric	Bleach activity	Rep2 5
Acid/base titration	ISFET/metal electrode	Peptides	Rep2 6
Dynamic surface tension	bubbles	Surfactants	Rep1 8
Peptide sensor	stain selective peptide	blood etc.	Rep2 7.1

The last two sensors are not available yet in a reliable version, so in the next section only the first five are implemented.

To control the system a microcontroller can be used. A popular one is the 83C552 of Philips which combines low costs with a lot of functions. Some on chip functions are:

- 8051 based instruction code
- 16 MHz clock
- 256 bytes of RAM
- 8k byte EEPROM on chip
- power down mode (low power consumption if not used)
- five 8 bit ports from which at least one is left for binary I/O functions
- an 8-input 10 bits ADC (» 10 kHz at 16 MHz)
- RS232 port for communication with a computer

- I^{2}C port for a two-wire communication with other I^{2}C chips

With only one data latch chip, 64k RAM can externally be accessed, but the internal 256 bytes will be sufficient in most of the cases. The TDA 8444 is an octal DA chip which supports the I^{2}C protocol, so an 8-input and 8-output system controlled by a processor can easily be realised.

In figure 7.4 the basic elements of a mivrocontroller system are drawn. The personal computer is added to program the system and to watch it during the test phase.

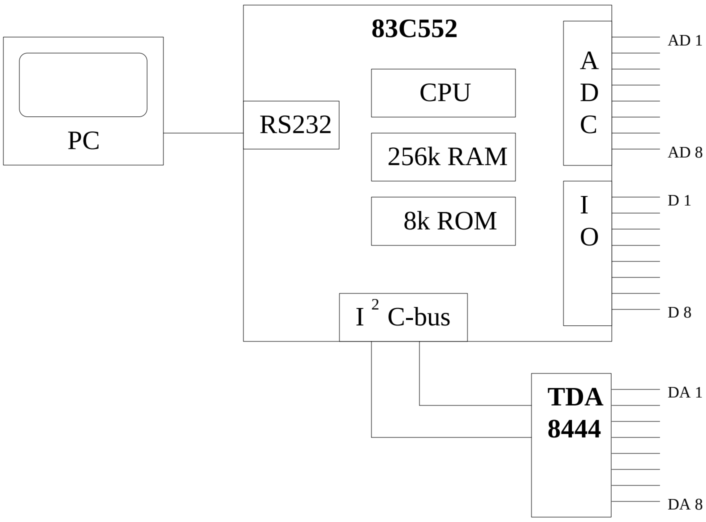


Figure 7.4: A microcontroller system

Consider the structure of figure 7.5. The two outside ISFETs form together the coulometric and amperometric devices as drawn in figure 7.3. The metal electrodes can be used as the actuator electrodes for a four points conductivity measurement as evaluated in work report 1 in section 7.

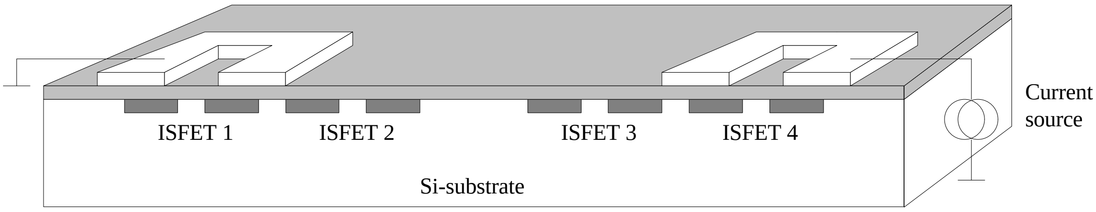


Figure 7.5: A sensor array for measuring several parameters

An electronic circuitry for measuring the conductivity can be as in figure 7.6.

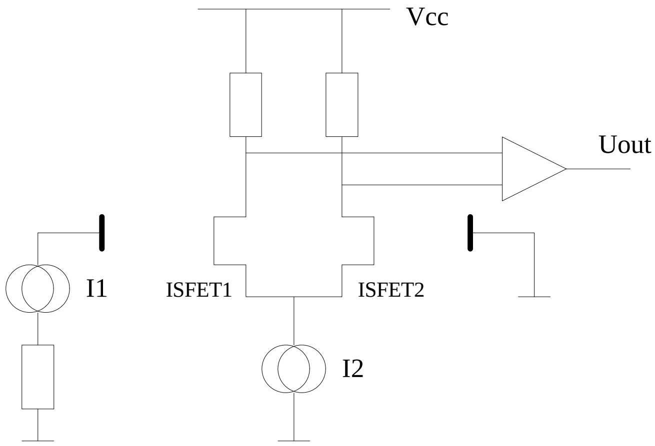


Figure 7.6: Four points conductivity measurement

For the temperature measurement one of the four ISFETs can be used. The pH signal is available from the coulometric device.

By using the accurate circuitry, the first five parameters of table 7.2 can be measured. To do this, the sensor array must be supplied with the next elements:

	Fig 7.6	Fig 7.3
Controlled I source	1	1
Controlled V source		1
I measurement		1
V measurement	1	1
ISFET amp		2
OpAmp	1	2

The controlled current sources can be conbined as the current source in figure 7.5. If the ISFET amplifier is the one using one opamp as given in report 1, the total system must contain the following elements:

- 2 DA-converters
- 3 AD-converters
- 5 opamps

So 6 DA-converters and all of the binary IO-ports of the microcontroller system are left for the dosing system. It can be seen that by using a simple sensor structure combined with a few integrated circuits a measurement part of the intelligent washing control system can be obtained.

In section 4 of work report 1 two methods of measuring were mentioned. The first method uses complete electronic circuitry which delivers the desired signal, the microcontroller only has to sample this signal. With the second method the microcontroller has to find the operation poit itself. This gives a more flexible and smaller system. The system described in this section is obviously one of the first kind.

It is possible to make a system of the second kind but this uses a lot more AD-converters, which is expensive. As seen above the electronic circuitry for a system of the first kind should not be a problem.

8. References

[1] G. Jakobi and A. Löhr, Detergents and textile washing, principles and practice, VCH Verlagsgesellschaft mbH, Weinheim, Germany 1987

[2] A. van der Berg and P. Bergveld, Micro total analysis systems, Proceedings of the mTAS '94 workshop, Kluwer Academic Publishers 1995

[3] A. Volanschi, W. Olthuis, P. Bergveld, Electrolyte conductivity measured with an ISFET, Proc. Conf. Trends in Electrochemical Biosensors, Trieste, Italy, 1992

[4] A. Volanschi, W. Olthuis, P. Bergveld, Design of a miniature electrolyte conductivity probe using ISFETs in a four point configuration, Sensors and Actuators B, 18-19 (1994), page 404-407

[5] U. Schulte, Fuzzy logic, een introductie, Kluwer Techniek, Deventer, Nederland, 1994

[6] E.A.H. Hall, Biosensors,Open University Press, Buckingham 1990

[7] T. Murakami, S. Nakamoto, J. Kiruma, T. Kuriyama and I. Karube, A micro planar amperametric glucose sensor using an ISFET as a reference electrode, Proc. Bio Fair, Tokyo, Japan, Marcel Dekker NY,1986

[8] W. Olthuis and P. Bergveld, Performance of the coulometric sensor actuator device improved by mTAS, Micro total analysis systems, Proceedings of the mTAS '94 workshop, Kluwer Academic Publishers 1995

[9] Statistiek wateronderzoek 1986, Vereniging van Exploitanten van Waterleidingbedrijven VEWIN, Rijswijk, 1986

[10] P.W. Atkins, Physical chemistry, fifth edition, Oxford University Press, Oxford, 1994

Distribution list:

Prof.dr.ir. P. Bergveld (UT BIO)
Dr.ir. W. Olthuis (UT BIO)
A. Volanschi, M.Sc (UT BIO)
Dr.ir. R.T.J.M. van der Heijden (URL)