Differential measuring using an ion exchanger applied to Ca^{2+} ion concentration determination

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Abstract

In this paper, differential measuring with chemical sensors is illustrated. The advantages of differential measuring are listed, followed by a practical example of such a chemical sensor system, consisting of a column filled with ion exchanger. The inlet and outlet of this column are provided with electrolyte conductivity (ec) sensors. Differential measuring of the electrolyte conductivity and the proper choice of the ion exchanger allows the absolute determination of specific ion concentration, present in the solution that passes the column. It is thus shown that Ca^{2+} ion concentrations in the mM range can be determined.
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1. Introduction

Differential measuring aims at obtaining relevant information from subtracted sensor output signals. The subtraction can be carried out either on signals obtained from two sensors at different positions (spatial differential measuring) or on signals from one sensor at different moments (time differential measuring). This distinction turns out to be irrelevant for the mathematical generalisation of differential measuring, presented elsewhere [1]. Nevertheless, the illustrations and the experiments are restricted to spatial differential systems. An impression of such a system is shown in Fig. 1.

In Fig. 1, a tube is shown through which a sample solution can be transported along the sensors A and B. Obviously, spatial differential measuring in one and the same solution does not yield relevant information of that solution (at best of the sensor itself). Therefore, a certain action is required to obtain relevant data, i.e. sensors A and B should measure in solutions with different compositions. This action is effected by the actuator, shown in Fig. 1. When the composition of the incoming solution at sensor A 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. This

paper aims at illustrating the functional integration of differential measuring by physical integration of an actuator with the sensors in order to achieve the aforementioned action.

There are several advantages of differential measuring:

- *Cancellation of sensor and sensor system offsets*: Sensors are rarely totally identical after having been processed, or they operate with respect to a non-ideal common reference. Subtraction of true constants or varying but truly common signals by differential measuring cancels in that case the interfering effect.
- *Elimination of common effects*: Many sensors are not uniquely sensitive for their measurand, but respond also to temperature, light, humidity, etc. By differential measuring, the interfering effect is common to both sensors and cancels after subtraction.
- *Retrieval of absolute information*: Differential measuring can yield absolute information of the measurand. By a properly designed system, as shown in this paper, absolute data can be obtained.

The favourable use of differential measuring is illustrated with a chemical sensor system, capable of the determination of the concentration of a specific ion from a response of the conductivity to a specific ion exchange operation. The ion exchanger (the actuator in Fig. 1) replaces the ions of which the concentration has to be determined by other ions, e.g. protons. This causes a difference in conductivity of the

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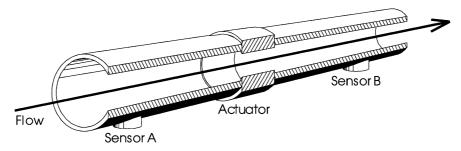*E-mail address:* w.olthuis@el.utwente.nl (W. Olthuis).

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

solution before and after contact with the ion exchanger. These conductivities are measured with two electrolyte conductivity (ec) sensors (sensors A and B in Fig. 1).

An ion exchanger can reversibly exchange ions between a solid and a liquid in which there is no substantial change in the structure of the solid [2–4]. An ion exchanger is a system where the following chemical equilibrium holds:

$$M^-A^+ + B^+ \Leftrightarrow M^-B^+ + A^+ \tag{1}$$

Here M^- is the network of the ion exchanger (e.g. a polymer) and A^+ and B^+ are both cations. Anions in solution do not partake in the exchanging process in this example. Further the network M^- is in principle insoluble, immobile, and not conductive.

In most cases the network is initially filled with protons, which means that the network will catch the present cations in solution in exchange for protons. Taking calcium as an example, for every calcium ion taken up, two protons will be released into the solution, which thus becomes more conductive. After use, the ion exchanger contains more calcium than protons and the ion exchanger can not be used anymore for catching calcium ions. However, it is possible to 'reset' the ion exchanger by putting it in a solution containing a high concentration of protons. So the process can be reversed and the ion exchanger can be recycled.

The principle is illustrated with an example: the commercially available ion exchanger Dowex® CCR-2 is originally saturated with H^+ ions, but will release two of these when one Ca^{2+} ion is captured. The ion exchanger is used in the so-called *column operation* mode: a column in which the ion exchanger is fixed and the solution is allowed to flow through. Experiments are conducted to prove the feasibility of the proposed approach. Both the expected behaviour and the practical use in ion concentration determination, using ion exchangers and conductivity sensors, will be shown with these initial measurement results.

2. The ion exchanger as actuator in a differential measurement system

The actuator function of an ion exchanger is of the type "fractional depletion or accumulation", because a constant percentage of incoming species is being captured for a certain constant contact time with the ion exchanger. 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. This type of operation is illustrated in Fig. 2.

The operations on the proton and calcium concentrations are

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

$$[H^+]_{out} = 2(1 - a_f)[Ca^{2+}]_{in} + [H^+]_{in} \tag{3}$$

where $0 < a_f < 1$. A complete exchange is characterized 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 is calcium and the measurement will consequently give information on the water hardness.

The difference in conductivity induced by the ion exchanger is equal to

$$\begin{aligned}\Delta\kappa &= \Delta[H^+]\lambda_{H^+} + 2\Delta[Ca^{2+}]\lambda_{Ca^{2+}} \\ &= 2(1 - a_f)[Ca^{2+}]_{in}\lambda_{H^+} + 2(a_f - 1)[Ca^{2+}]_{in}\lambda_{Ca^{2+}} \\ &= 2(1 - a_f)(\lambda_{H^+} - \lambda_{Ca^{2+}})[Ca^{2+}]_{in} \end{aligned} \tag{4}$$

where λ_i is the limiting molar conductivity of ion i. Eq. (4) shows that the output is linearly dependent on the calcium ion concentration. Note that it is no longer necessary to know the proton concentration to obtain the calcium ion concentration via $\Delta\kappa$.

The determination of pH before and after the ion exchange is also an option. However, calculations show that
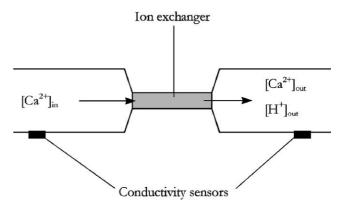

Fig. 2. Illustrating the column operation using two conductivity sensors.

on one hand the initial proton concentration must be relatively low to obtain a measurable ΔpH for a given calcium concentration, and moreover, for a proper concentration determination, the absolute initial pH must be known, which requires a conventional reference electrode. Such an electrode is not planned to be included in the measurement system and therefore we focus on the electrolyte conductivity detection.

3. Experimental

3.1. The ion exchanger

Experiments are performed with the Dowex® CCR-2 ion exchanger from Fluka, which is a weak acid cation exchanger with carboxyl acid as active group. The dry resin consists of spherical beads with mean particle size of approximately 0.5 mm with a density of 0.76 kg/dm^3. This exchanger is particularly mentioned for its outstanding capacity to take up cations, related to alkalinity, and is as such applied for the demineralisation (softening) of water in the pH range 5–14.

3.2. The set-up for the column operation

In the column operational mode, a column is filled with ion exchanger through which the solution is allowed to flow. Paper filters prevent the exchanger to flow out. It was decided to fabricate a provisional column of 12 cm length, divided into four segments of 3 cm each in order to change the total exchange capacity, if required. The segments were made from Perspex®, by drilling a hole with a diameter of 6 mm in each segment. Each segment, thus has a column volume of ca. 0.85 cm^3, which can contain maximally 0.65 g exchanger. Two similar Perspex blocks with a 6 mm diameter channel serve as inlet and outlet of the column and are equipped with planar interdigitated electrolyte conductivity sensors, specifically designed for this purpose. These low-cost ec sensors consist of etched copper structures on a printed circuit board. A photograph of the system is shown in
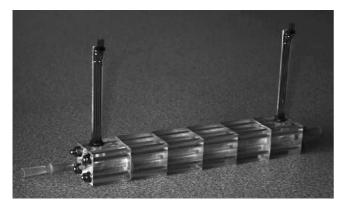

Fig. 3. Photo of the system showing the Perspex® blocks with the ion exchanger-filled column, and the ec sensors at the inlet and outlet.

Fig. 3. The area of the sensor that actually will be in contact with the solution is electroplated with gold.

The ec sensors consist of five fingers per electrode with a finger width of 0.2 mm, spaced apart 0.16 mm. The total ec sensor size was defined by casting the area with Hysol® two component resin and measures 2 mm × 2 mm. Thus, an ec sensor was fabricated with a theoretical cell constant of 2.3 cm^{-1} [5,6]. After experimental characterization, this sensor could very well measure KNO$_3$ solutions in the concentration range between 0.5 and 100 mM KNO$_3$ at a measuring frequency of 150 kHz, which corresponds with a conductivity range from 0.06 to 10 mS/cm.

The flow of several solutions through the column was obtained by pressurizing bottles containing these solutions via an Omnifit gas flow controller. Thus, a constant flow of ca. 2 cm^3/min was obtained for all solutions.

3.3. Measurement protocol

The ion exchanger in the column was pre-conditioned by flowing through a 10 mM HCl solution for 1 min. Next, the column was flushed for 5 min with demi-water. In order to characterize the system, a solution of 10 mM KNO$_3$ was led through the column. During this experiment, the conductance at the inlet and outlet of the column was determined every 0.2 s with the ec sensors as described for a total of 500 measurements per sensor. The measurements were performed by a HP 33120A function generator and two HP 34401A digital multimeters, all PC-controlled by HP-Vee software.

4. Results and discussion

4.1. System characterization

Fig. 4a shows the expected measured conductivities using the column set-up. At the start at $t = 0$, the initial flow of demi-water is considered to be replaced by potassium nitrate, indicated by the rise in conductance of the upper curve of Fig. 4a, determined by the ec sensor at the inlet of the column. As the solution with constant KNO$_3$ concentration passes the ion exchanger the calcium ions will be replaced by protons. Consequently, a certain time after the increase in conductance at the inlet is measured, a rise in conductance at the outlet will be measured. The equivalent conductivity is higher due to the higher mobility of the protons and so the conductance measured at the outlet is higher than the one measured at the inlet, as shown in Fig. 4a, second curve. If the difference in conductance is plotted, one thus expects the curve as shown at the lower curve of Fig. 4a.

This expected result is experimentally verified by leading a 10 mM KNO$_3$ solution through the column. The upper curve of Fig. 4b shows the measured conductance at the inlet of the column and the second curve reflects the measured conductance at the outlet. Fig. 4b, lower curve, shows the
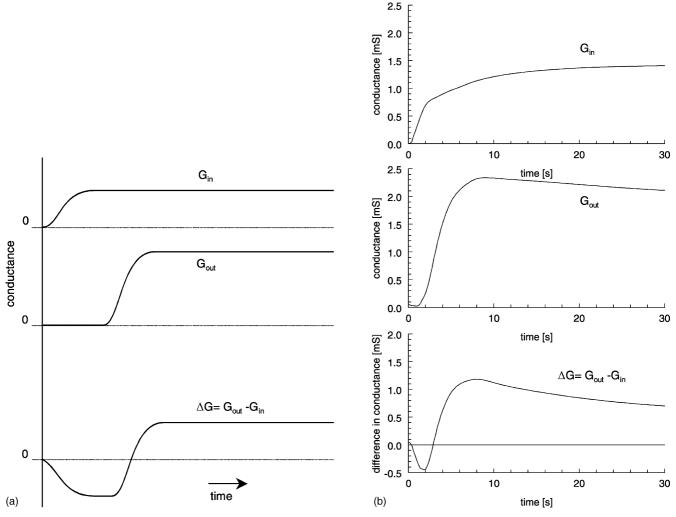
Fig. 4. (a) Expected conductance at the inlet G_{in} (upper curve) and the outlet G_{out} (second curve) of the ion exchanger column and the resulting difference in conductance, ΔG (lower curve). (b) Measured conductance at the inlet and outlet of the column (first and second curve, respectively) and the resulting difference in conductance (lower curve) in 10 mM potassium nitrate.

result of the difference of the measured conductivities at the inlet and at the outlet of the column. It can be concluded that this shows all features as predicted by the curve of Fig. 4a, lower curve. The decay of the curve of Fig. 4b after its maximum can be caused by either the (slow) kinetics of the exchange reaction or the saturating process of the ion exchanger.

4.2. Calcium ion concentration determination

Similar experiments were carried out but for different calcium nitrate concentrations. The maximal difference in conductance between the inlet and outlet (i.e. the maximum of the lower curve of Fig. 4b) was regarded as the measurand. Between each measurement, the column was pre-conditioned according to the procedure described in Section 3. The thus determined difference in conductance as a function of the calcium nitrate concentration is plotted in Fig. 5.

The total relative error for these initial experimental results was estimated to be ca. 17% due to small differences

in temperature and concentrations, and the conductance read-out procedure. This determination of the conductance turned out to be relatively inaccurate due to poor mixing of the solutions at the inlet and outlet compartment of the
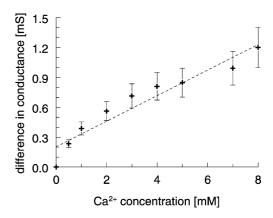

Fig. 5. The measured difference in conductance at the inlet and outlet of the column as a function of Ca^{2+} concentration passing the ion exchanger.

column in which the ec sensors are placed. Taking this error into account, the linear relation between the difference in conductance and the Ca^{2+} concentration, as predicted by Eq. (4) reasonably holds.

Future work will thus be the optimisation of this provisional design, resulting in smaller dimensions and a better integration of the ec sensors with the inlet and outlet compartment of the column. Proper processing in plastics or glass enables the fabrication of many of such columns in one system which can be placed either parallel or in series. Thus, specificity for more than one ion or increased selectivity for one ion can be obtained.

5. Concluding remarks

The application of an ion exchanger in combination with conductivity sensors in a column operational mode illustrates the use and some of the advantages of differential sensor systems for calcium ion sensing. It was shown that an ion exchanger which exchanges one calcium ion by two H^+ ions, gives a conductance change which is proportional to the absolute calcium ion concentration.

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