Tap water hardness estimated by conductivity measurement to reduce detergent dosing

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1. Abstract

The amount of detergent which is supplied to a washing machine for a single washing process, should be adjusted to the hardness of the tap water to ensure optimal washing conditions. On the other hand, this amount should be limited in order to reduce the residues which are drained afterwards. So, optimal dosing requires a hardness sensor. A problem is, that the implementation of an absolute hardness determining element in a washing machine is not simply possible at this moment. However, by using the large correlation between the hardness and electrolyte conductivity of tap water, the hardness of tap water can be estimated based on the measured conductivity. This is an advantage since the incorporation of a conductivity cell for the long time use in a washing machine is not very difficult.

2. Introduction: the dosing of detergent

The dosing of detergent in a washing machine should be based on the hardness of the tap water and the amount of laundry in the tub. While the adjustment to the amount of laundry can be performed quite exactly by the operator, the hardness of the tap water can not simply be determined without implementing sensors. For choosing the amount of detergent necessary to accomplish a good removal of hardness ions (builder action), an indication table is printed on the package defining about three categories of tap water hardnesses with their corresponding dosing volumes. However, these dosing volumes always result in an excess of applied detergent. In order to reduce the amount of chemicals which will consequently be flushed into the environment after washing, it is inevitable to optimise the applied volume of detergent.

With respect to the builder, optimal dosing should be based on the measured tap water hardness. However, the determination of hardness requires a calcium sensor. Calcium sensors use potentiometric techniques in general, which require a reference electrode. Both devices are rather vulnerable, however, and therefore not useful for the incorporation in a washing machine.

In this short note, it is proven that it is in principle possible to estimate the tap water hardness based on an electrolyte conductivity measurement. Such a measurement does not require a reference electrode and uses a cheap device which does not need calibration because of the intrinsic stability of conductivity sensors.

3. Tap water hardness and conductivity

The hardness of water is defined as the concentration of multivalent ions, with calcium and magnesium ions the most dominating. The problem with these ions is that they have bad effects on washing machines since they can precipitate as carbonates on heating coils. In addition, they form residues in the laundry, which requires the addition of softener to prevent stiff fabrics. Another problem is that a high concentration of calcium reduces the efficiency of detergents.

Figure 1 shows the distribution of the hardness ions in the tap water of 44 Dutch cities as determined in 1986 [1]. The calcium concentration, which is significantly larger than the magnesium concentration, appears to be normally distributed around 1.4 mM.

Other elements present in water which decrease the washing efficiency, are iron, copper and manganese ions. These ions catalyse the decomposition of bleaching agents. To avoid this effect complexing agents and ion exchangers are added to the detergent. One of their functions is to bind multivalent alkaline-earth and heavy-metal ions through chelation or ion exchange.

An impression of the most important ions present in tap water is obtained by observing the electrolyte conductivity. The conductivity distribution of tap water coming from the same Dutch cities as used for figure 1, is plotted in figure 2. The normal distribution curve with an average of 0.49 mS/cm and a standard deviation of 0.16 mS/cm is drawn as well. The ions that contribute to the overall observed electrolyte conductivity can be found in figure 3. It appears that Ca^{2+}, Na^{+}, Cl^{-} and HCO_3^{-} determine the conductivity of tap water for almost 90% on the average.

4. The correlation between hardness and conductivity

Figure 3, which is based on a statistical analysis of the tap water in 44 Dutch cities in 1986 [1], shows also that the hardness ions, calcium and magnesium, determine the conductivity for 40%. The question rises whether it will be possible to approximate the tap water hardness by measuring the water conductivity.

In figure 4 a plot is given with the measured water conductivities on the horizontal axis, and the measured hardnesses on the vertical axis. The data is obtained from the same data source of the composition of Dutch tap water. The tap water hardness is expressed here as the total concentration of multivalent ions. To convert this to the more common calcium carbonate equivalent, the factor 100.1 g/mole must be used.

Using a least square algorithm, a line could be plotted in this figure. The observed correlation between hardness and conductivity appears to be 0.85. So, based on the measured conductivity, the hardness can be guessed using this line. The average error in the guessed hardness is 13% while the observed maximum error is 50%.

Any knowledge on other ions will increase the accuracy of the estimated hardness. For example, the concentration of sodium is easier to measure than the calcium ion concentration. By placing a sodium sensor in the same water as in which the conductivity is measured, the conductivity contribution due to sodium can be subtracted from the total observed electrolyte conductivity. The result is a corrected conductivity which will have a larger correlation to the water hardness.

In figure 5, the conductivities after subtracting the calculated conductivity contributions due to the measured sodium concentrations are plotted on the horizontal axis for the same set of data which is used in figure 4. The new correlation has become 0.94, which is obviously much larger than in the case without a correction for the sodium concentration. Also the average error in the approximated hardness has reduced to 7.8% and the maximum error is 38.4% now.

5. Discussion

Although the observed errors in the estimated hardness appear to be quite large, the estimated value can be used to reduce the excess amount of detergent dosing. Without a conductivity measurement, the dosing should be adjusted to the largest possible water hardness which is about 3.0 mM. By a single conductivity measurement the dosing can be reduced, even without using a sodium sensor for correction. For example, when a conductivity of 20 mS/m is observed, the hardness will not be larger than 1.2 mM using the correlation line with 50%

overdosing compensating for the maximum error. Therefore, the conductivity measurement in tap water results in a reduction of applied detergent of more than 50%.

Using the information from the sodium sensor, the overdosing can be reduced even more. This example uses sodium, but knowledge concerning other ions will also increase the correlation. What can be seen from figure 3, is that HCO_3^- has an even larger contribution to the conductivity of tap water than sodium. Therefore, knowing the concentration of this ion will increase the accuracy much stronger.

After applying the builder it is 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 into two moles of sodium gives hardly a change in the conductivity of the liquid (in one litre an increase of 2×50.1 ❍S·cm^{-1} for sodium and a decrease of 119 ❍S·cm^{-1} for calcium) but the hardness decreases with one mole. Therefore, it is not likely that the hardness can be guessed during washing based on the measured conductivity.

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

Legends:

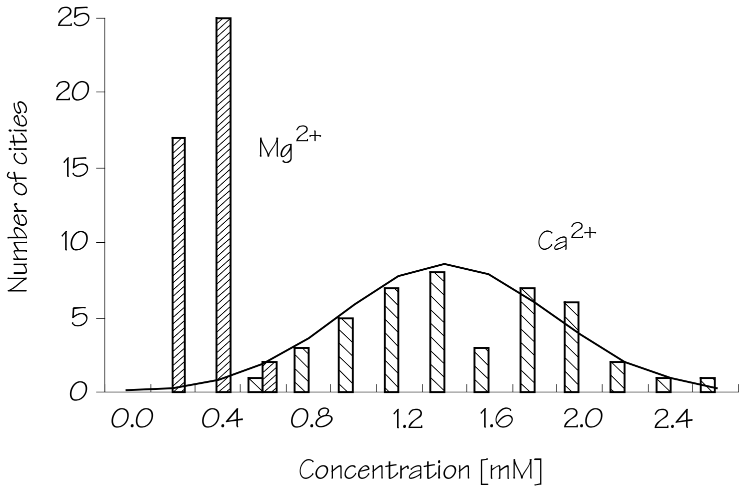
Figure 1: Concentration distribution of hardness-ions in tap water of 44 Dutch cities in 1986 [1]

Figure 2: Distribution of conductivity in Dutch tap water in 44 cities

Figure 3: The average contribution of the separate ions to the conductivity

Figure 4: Correlation between water hardness and conductivity in 44 Dutch cities in 1986

Figure 5: The same as figure 4, but after the mathematical elimination of the contributions of sodium to the conductivities



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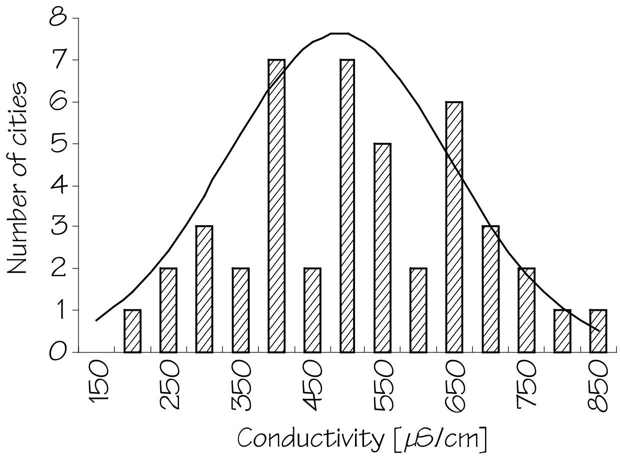

Figure 2: Distribution of conductivity in Dutch tap water in 44 cities

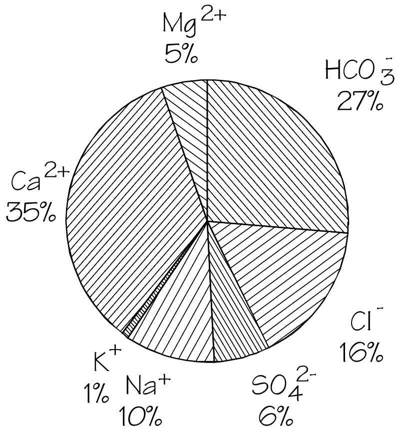

Figure 3: The average contribution of the separate ions to the conductivity

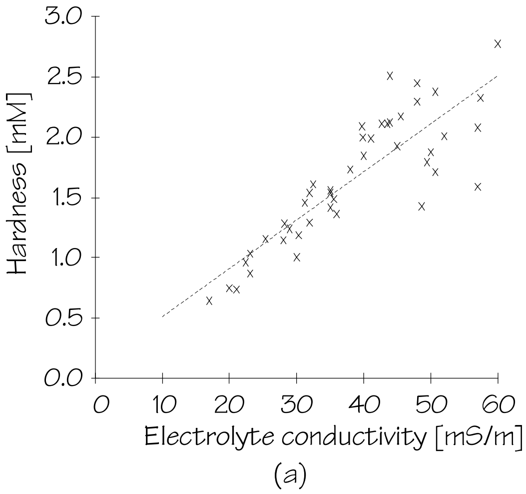

Figure 4: Correlation between water hardness and conductivity in 44 Dutch cities in 1986

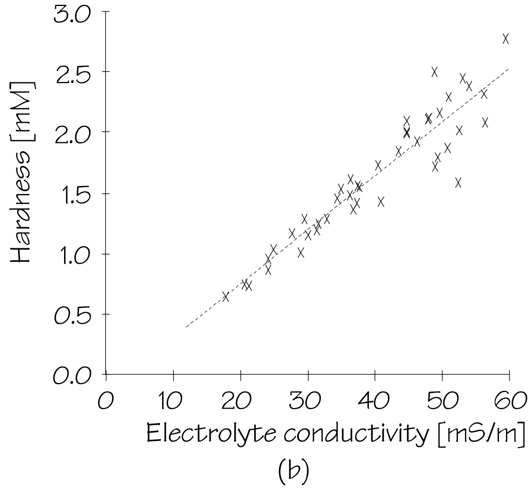

Figure 5: The same as figure 4, but after the mathematical elimination of the contributions of sodium to the conductivities