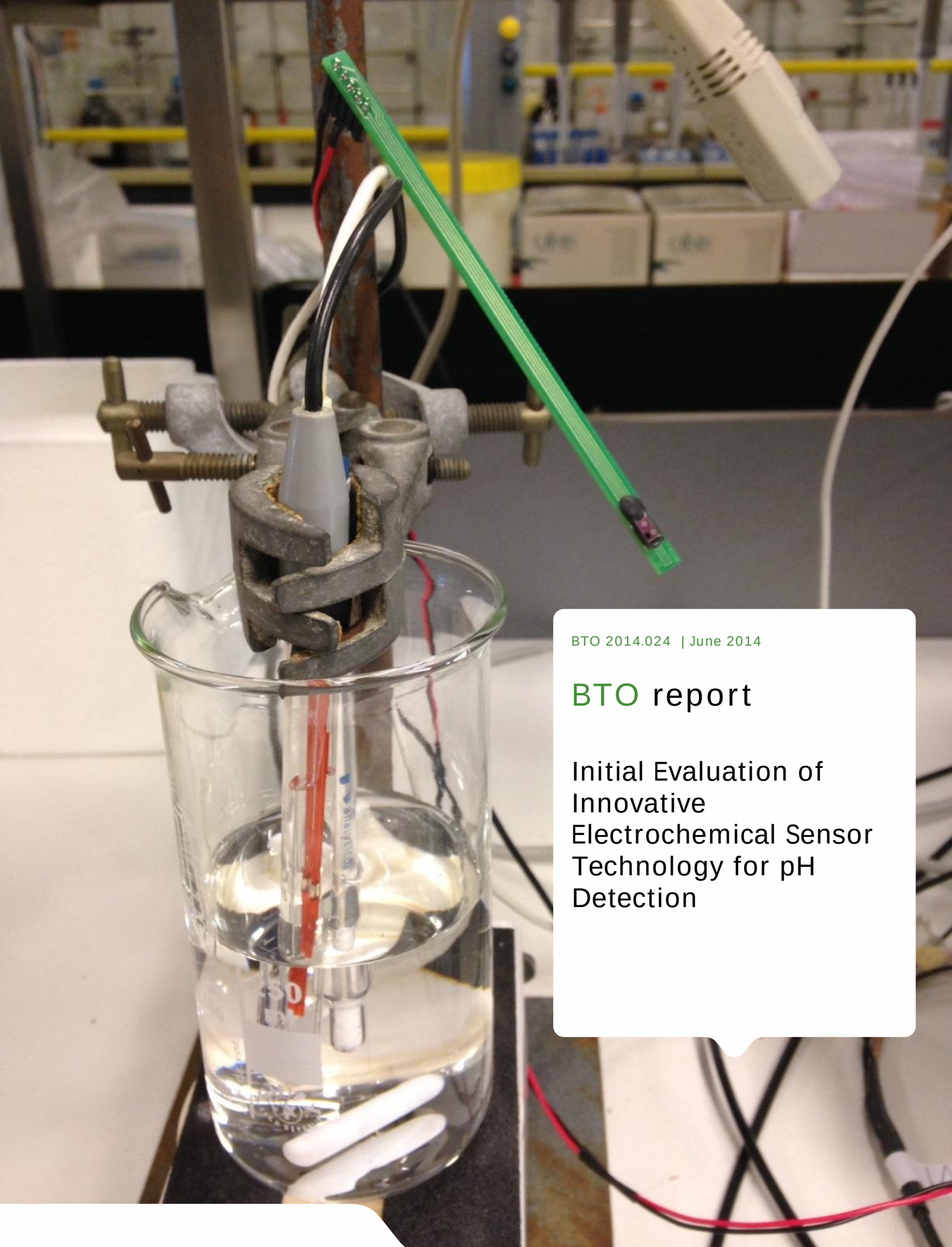




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BTO report

Initial Evaluation of
Innovative
Electrochemical Sensor
Technology for pH
Detection

BTO

Initial Evaluation of Innovative Electrochemical Sensor Technology for pH Detection

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Summary

During the project new sensor technology from the Holst Centre in the Netherlands has been tested with respect to suitability for implementation in the Dutch water sector. As a representation for the more generic ion-sensitive technology that Holst Centre develops, pH sensors were selected as a benchmark. Laboratory experiments – in small stagnant samples and in continuous flow – were performed to assess the reproducibility and stability of the pH readout.

The results of the current study demonstrate that mainly the sensor-to-sensor reproducibility and the stability of the sensors are in need of improvement for foreseen implementation in the (Dutch) water sector for real-time monitoring purposes. Encouraging results that demonstrated the potential of the technology have been obtained, with sensors reproducing correct pH levels and stability of the readout over hours. However, variations in the detailed characteristics rendered a different set of identical sensors even less fit for implementation. This variation in the characteristics limits the intended implementation of the technology as a whole.

The current status of the technology is not mature enough for implementation in the (Dutch) water sector. However, from the current study clear areas for improvement have been identified and new research and development initiatives can be streamlined. Identified areas for improvement are the reproducibility and stability as mentioned before, as well as incorporation of temperature correction and additional validation experiments on renewed sensors prototypes.

This study has identified the potential of the pH technology and, as the pH example was initiated as a benchmark of the generic underlying technology, the ion-sensitive technology developed by Holst Centre. While not mature yet, the potential for the (Dutch) water sector is high. Therefore, the sector should remain closely involved to monitor and assist in development and characterization of new prototypes in order to further streamline (Dutch) water sector *sensing*-needs into applied research and development.

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1 Introduction

1.1 Sensoring

Sensors are emerging as a disruptive technology to gain (near-) real-time information of the water cycle within drinking water utilities, as well as the wider water cycle. Application areas can be categorized in various categories such as *'Early Warning'* and *'Rapid Response'*, dealing with the (real-time) determination of water quality and the response to signs of abnormal behavior. Water quality is of course key priority for the delivery of immaculate drinking water. Categories as *'Process Control'* and *'Asset Management'* deal more with the business side of water utilities where optimization of the operations is key, resulting in a reduction of costs. Technologically, sensors and data management are generally not yet robust enough for widespread implementation. Therefore, effort has to be put in the development and evaluation of new technologies to solve these issues.

The Vitens Innovation Playground and the SenTec center of WLN are sensor demonstration sites that illustrate the effort of the Dutch water sector to evaluate new sensor technology. KWR, within the renewed vision on sensor research developed within the new Joint Research Programme (BTO – Bedrijfstakonderzoek), aims to be of added value within this area by (i) scouting and testing new technologies and (ii) connecting technology, data and organization, leading to (iii) validation and implementation of sensors. To this end, collaborations with abovementioned demonstration sites are foreseen. In order to successfully scout and validate new technologies, strong links with national and international technology providers are a prerequisite and actively pursued. Within this framework, in the *'Verkennd Onderzoek'* of the BTO, the opportunity was taken to test new technology from the Holst Centre in the Netherlands.

1.2 Holst Centre Technology

The Holst Centre in Eindhoven, the Netherlands, is a leading open-innovation technology research and development institute. Holst Centre is a collaboration between Imec in Leuven, Belgium and TNO in the Netherlands. Holst Centre develops generic technologies for Wireless Autonomous Sensor Technologies and Flexible Electronics. Within the programme Ultra-low Power Sensors, accommodated in the Imec part of Holst Centre named Imec-nl, innovative technologies are being researched for the development of sensors for a broad range of applications such as gas sensing, ion-sensing and electronic noses.

Electrochemical sensors have great potential for detecting gases and ions in solution. Already, Holst/Imec electrochemical sensors have been successfully applied in so-called body-area networks (BAN) applications. Integrated pH and Cl⁻ sensors were applied for the real-time analysis of sweat, with foreseen applications in areas such as sports and elderly care. Studies have demonstrated the applicability of micro-sensors in real-time monitoring of milk acidity as an early warning system for milk deterioration as well. Together with the Flexible Electronics programmes at Holst, developments are aimed at the incorporation of sensors on thin flexible foils. The possibility to fabricate sensors on foil can substantially reduce the cost of fabrication of sensors since high-throughput technologies, such as roll-to-roll printing, can be used. Low-cost and mechanical flexibility can substantially lower the barrier for replacing sensors employed in the field that have run out of specifications or have been damaged.

Ion-sensitive sensors in development at Holst/Imec are micro-fabricated on chip/foil. In addition, an compatible electronics platform is developed for read-out, data processing and communication. The approach is modular with the potential future possibility to add various sensor capacities to the underlying basic concept and electronics. The total size of sensor chips are few square millimeters (Figure 1).

Figure 1: Picture of a pH-microsensor printed on plastic foil



The current project was aimed at evaluating the status of the new sensor technology of Holst/Imec with specific focus on the applicability within water technological and environmental settings that thus far has not been demonstrated. The technology potentially provided the opportunity to effectively gather hydrochemical data at rather inaccessible locations, such as distribution networks or underground water infrastructure and soils, with minor interference on the medium to be sampled. Moreover, developments for printing ion-sensitive sensors on foil or other materials, make them (more) cheaply producible and easily replaceable. These innovations can be highly profitable for the Dutch drinking water sector as large(r) volumes of hydrochemical data can be gathered at low(er) costs. The project was foreseen to be a step towards validation of the pH technology at a larger scale (e.g. Vitens Innovation Playground) and towards differentiation to new parameters that the technology is capable of (e.g. other ions such as chloride). Furthermore, the project is a basis for a collaborative development of more integrated and sophisticated sensor solutions together with the Holst/Imec.

1.3 pH Sensors

For specific applications, such as monitoring of (underground) water treatment or monitoring of the chemical and microbiological stability of water, various parameters can be used as indicators. The technology developed by Holst/Imec is adaptable towards different (ionic) parameters. For practical reasons, the current study uses pH-sensors as a benchmark of the current status of the sensor technology. Measurements of the pH of drinking water are, amongst other, of interest for the determination of the calcification potential of water. This is especially relevant in distribution networks where water from multiple sources with different original basicity are mixed. Depending on the amount of mixing the resulting pH can change, leading to consumer (dis)satisfaction regarding the amount of limestone deposition in washing machines or water cookers. Within the BTO project 'Soft sensors for water quality monitoring' this issue is being tackled from a modeling perspective by developing a method to predict parameters at every site in the distribution network. In ecohydrological and environmental research, pH is used as a general indicator of process rates and water quality. In general, data availability currently is a major constraint in mathematical modeling of hydrochemical processes and in the optimized operation of underground technologies. New pH sensing technologies may provide a cost effective solution for subsurface data acquisition, thereby providing new spinoff for e.g. environmental risk assessments, optimization of subsurface technologies and ecological restoration.

Current pH measurements in the water sector, partly still performed in the laboratory, are mainly based on measurements using a combination of glass- and reference electrodes or gel-based electrodes. In addition to these classical methods, Ion-Sensitive Field Effect Transistors (ISFETs) are used. These types of pH sensors currently suffer from stability and robustness of the devices. The sensors therefore need to be recalibrated regularly in order to

yield reliable measurements, which is relatively labor-intensive. An additional specific problem for ISFETs, is that the lifetime of these sensors is limited by leakage of ions from the reference system into the water sample. Sensors that require significantly less recalibration and maintenance therefore are interesting for more reliable measurements and cost reduction. Consequently, it will become more feasible to implement sensor technology into a wider application area and develop more sophisticated monitoring technologies and strategies.

The Holst/Imec pH sensors are based on an IrO_x electrode and a quasi-reference electrode of AgCl. The potential of the IrO_x electrode depends on the pH of the environment (concentration of available H^+ ions), while the potential of the quasi-reference electrode in this setup is dependent on the Cl^- concentration as well. With a stable background Cl^- concentration the changes in pH can therefore be determined from the potential difference between the two electrodes. The potential difference between the electrodes is easily measured with a simple electrometer / voltmeter. For the present study, rigid chips (Figure 2) instead of sensors on foil were used to study the inherent characteristics of the sensor technology.

Figure 2: Picture of provided pH sensors from Holst/Imec. On the left, the micro-fabricated sensor chip is visible with the two different (circular) electrodes.



The pH sensors that were provided for this feasibility study were initially characterized by Holst / Imec. The two specifically interesting parameters in the analysis are the absolute offset potential between the different electrodes (independent of pH) and the change in potential difference upon varying the pH. The relation between electrochemical potential and pH, in itself actually dependent on temperature as well, is described by the Nernst equation, yielding a theoretical slope of -59.2 mV/pH at 25°C . The initial characterization of the sensors yielded an average offset potential of 283 mV and an average slope of -61.1 mV/pH , close to the expected theoretical value.

1.4 Current Project

Within the current project a feasibility study of the Holst/Imec pH sensors was performed for future implementation in the water sector. The detailed characteristics of the pH measurement itself, its short-term stability and longer-term drift were determined, aimed at characterizing the expected timeframe for (re-)calibration. In the original project proposal, application of the sensors in representative target environments was planned, foreseen to give indications of the robustness of the pH-sensors in realistic application environments and the amount of maintenance necessary for proper functioning. However, since stability of the measurements was uncovered as a main barrier, additional laboratory experiments were performed instead.

2 Experimental

2.1 Research Plan

The evaluation started with a batch-wise ‘true value’ calibration of the pH sensors against reference pH measurements by using standardized buffer solutions of varying pH and by spiking drinking water with amounts of acid and base to modify the pH. From this, the sensitivity as well as the initial stability of the signal were assessed. Additionally, a small continuous flow process imitation setup (Sensibel) was used to evaluate continuous flow measurements. Drinking water was used as matrix and the setup was monitored for more prolonged periods of time, with spiking experiments performed to assess the sensitivity of the sensor to rapid pH changes, and the stability of the sensors assessed by the variation of sensor signals during the course of the continuous experiment.

2.2 Experimental Setups

2.2.1 Batch Measurements

Holst Centre provided 15 pH sensors on chip with read-out electronics (Keithley 617 Electrometers) and software to address the electrometers and monitor the output potential difference. Two pH sensors were simultaneously read out. The instruments were installed at KWR and measurements were performed initially in simple beakers (Figure 3). Calibrated IUPAC buffer solutions (Radiometer Analytical) were used as well as drinking water. Dosing experiments to increase or decrease the pH of the medium were performed with HNO_3 and NaOH . Reference pH measurements were taken using temperature-corrected KCl-based combined pH and reference electrodes (Radiometer Analytical GK2401C). These readings were taken manually.

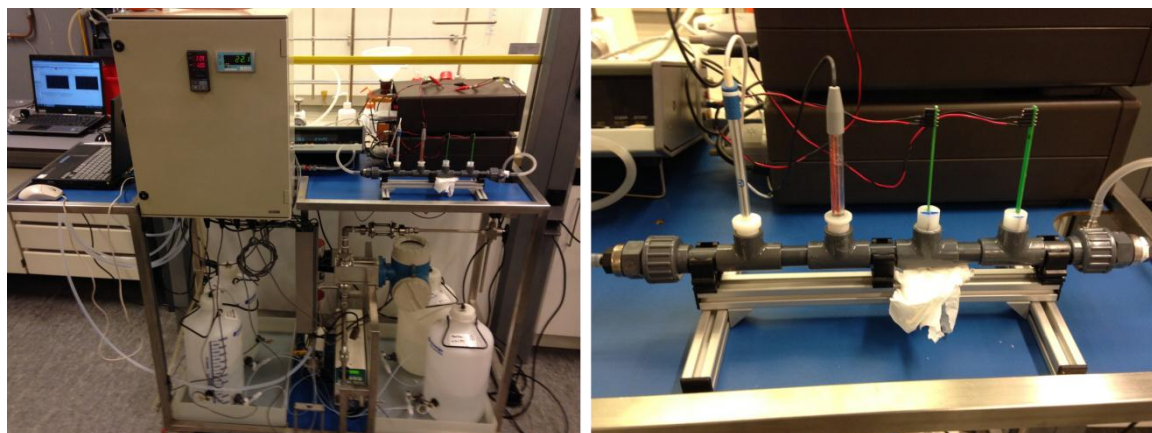
Figure 3: Batch Measurement setup with beaker, sensors, read-out electronics and PC.



2.3 Flow Measurements

After the batch measurements the so-called Sensibel platform at KWR was used to perform continuous flow measurements. The platform can be used to test and validate sensors (on location) where a continuous sample stream is supplied to the sensors. The flow rate of the stream can be chosen and up to 4 different solutions can be added with varying rates to the main stream to perform dosing experiments. The platform was adapted by incorporating two pH sensors and the pH reference and temperature probes into simple plastic flow cells that were watertight sealed with Zwaluw Hybrifix elastic sealant. These flow cells were connected in series onto the main sample stream (Figure 4). Experiments were performed with drinking water at a flow of 12L/h and solutions of HNO_3 and NaOH . The flow system and the electronic readout of the sensors were separately operated by different software, while the readout of the reference pH electrode was done manually.

Figure 4: (adapted) KWR Sensibel platform for continuous flow measurements of the Holst/Imec pH sensors.



3 Results

3.1 Batch Measurements

3.1.1 Initial Remarks

The initial characterization of sensors involved calibration in IUPAC buffers of predetermined pH, reproducing the initial characterization results performed by Holst/Imec on the sensors that were delivered to KWR. Initial experiments were performed using buffer solutions of pH = 1.7, 4.0, 7.0 and 10.0. Sensors were immediately used without any pretreatment. From the start of the measurements a relative large spread in the behavior of the various sensors was observed. Holst/Imec consider the sensor signal stable when the mV signal changes < 0.1 mV for a period of ~10 seconds. With a large subset of sensors unstable and slow responses were observed, with sensor readings drifting and/or no linear characteristics. Especially high pH calibration points were off. After consultation with Holst/Imec, the drifting and subsequent non-linearity was an effect that resulted from a plausible change in electrode surface properties upon exposure to pH > ~9. Furthermore, pre-conditioning of the sensors with the medium of interest was proposed as solution for drifting problems, indicating the sensor surfaces need to equilibrate with the surroundings before experiments.

3.1.2 Calibration in Buffer Solution

In subsequent experiments overnight pre-conditioning of sensors in buffer solution (pH = 7.0) was performed and higher pH levels were avoided as much as possible. With these protocols, stable calibration measurements were obtained for the pH sensors. Linear calibration curves were obtained that were employed to extract parameters describing the pH sensor electronic characteristics, *i.e.* the slope and offset potential of the measurements. The outlined experiment was performed with sensors #8 and #9 as shown in Figure 5, and was repeated using the sensors #5 and #18. From these experiments a comparison was made between the characterization results at Holst/Imec and at KWR (Table 1).

Figure 5: Measurement curves of two sensors in buffer solutions 1.7, 4.0 and 7.0 - The graphs show the potential difference readout when placed in the different solutions - and Calibration curves of Sensors #8 and #9. From the curves the offset potential difference and the slope versus pH are obtained.

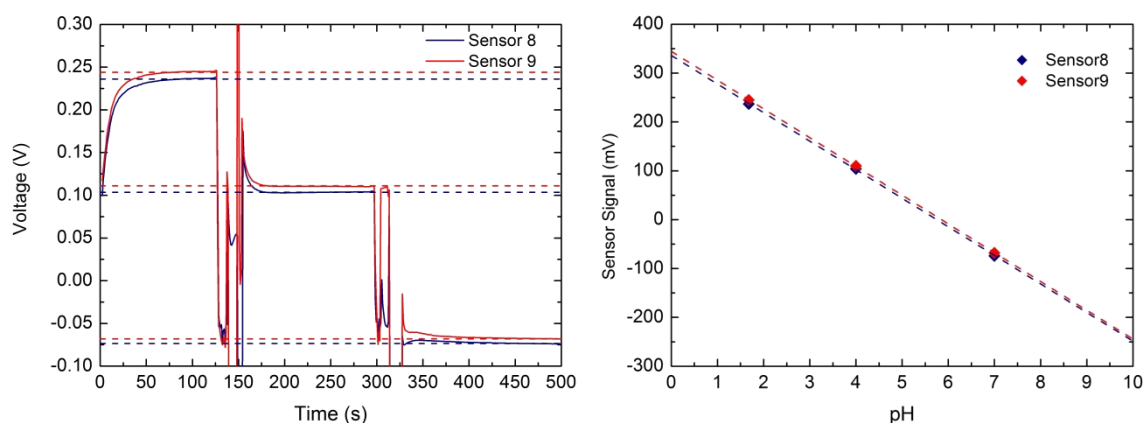


Table 1: Comparison of sensor Characteristics calibrated in buffers at Holst/Imec and KWR.

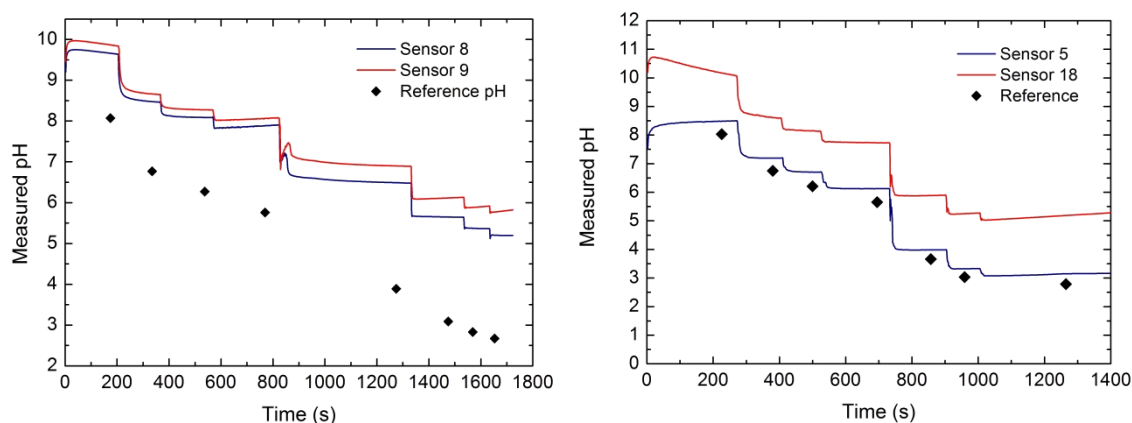
Sensor	Offset @ Holst (mV)	Offset @ KWR (mV)	Slope @ Holst (mV/pH)	Slope @ KWR (mV/pH)
#8	207.9	336.0	61.8	58.5
#9	196.1	344.4	61.4	58.9
#5	362.8	290.9	62.1	55.3
#18	272.5	256.9	59.4	55.1

For this particular set of sensors the electrical characteristics are aptly reproduced between the two laboratories of Holst/Imec and KWR. The mV/pH response of the sensors is consistently lower when measured at KWR compared to Holst/Imec. However, as briefly explained, this parameter is temperature dependent so a discrepancy in the temperature of the surrounding can be a cause of this. Nevertheless, for detailed measurements of the pH in real applications, a temperature correction should be applied and incorporated in a complete measurement system. The absolute potential offset between the laboratories are slightly different but within expected distribution window of the measurements at Holst/Imec. Slight deviations in the chemical composition of the environment (buffer) can be the underlying reason for deviation per sensor. The average offsets of the combined subset of sensors amount to 259.8 and 307.1 mV at Holst/Imec and KWR respectively, versus 283.0 ± 75.8 mV averaged over the complete set of 15 sensors characterized at Holst/Imec. Therefore, the measured potential offsets at KWR are within the sensor-to-sensor distribution.

3.1.3 Drinking Water Assessment after Buffer Calibration

After calibration of the sensors in the reference buffer solutions, the sensors were immediately transferred to drinking water to assess the ability to recover the correct pH levels of the (acid- and base-dosed) drinking water using the initial calibrations. Figure 6 summarizes the experiments using the sensors for which the calibration was described above. The results demonstrate the reproducibility of the sensor readings. Only with sensor #5 an adequate agreement could be obtained with the reference pH determinations, while readings of the other sensors were significantly off.

Figure 6: Drinking water experiments using sensors calibrated in buffer solutions. *ph* is recalculated from the readout of the sensors using the calibration parameters. reference *ph* measurements were performed manually.



From Figure 6 two different cases are discerned that lead to false pH readings concerning changes in the offset potential and the slope of the millivolt signals versus pH. In the experiment with sensors #8 and #9 the response to a change in pH (slope mV/pH) is not equal to the calibration value while concurrently a change in offset potential is observed. In the experiment using sensors #5 and #18 the slope is equal to the calibration slope while only, and most noticeable for #18, an offset in the absolute value of the pH level (offset in the mV signal) is observed.

Both cases represent the impact of the different environments to the sensors readings. However, both cases are distinguished by the ability to relatively easily re-adjust the sensor readings to yield a proper value. In the experiment where only the offset is changed, the complete pH readings are fairly quickly reproduced without detailed re-calibration, *i.e.* only a single pH reference measurement would be required. In the case of sensors #8 and #9 a more elaborate sensor calibration sequence with multiple pH level references would be required.

Both effects are adequately explained by the difference in the calibration medium and measurement medium. Specifically, the effects are assigned to different concentrations of ions, especially Cl^- , which will have a large impact on the detailed potential of the two electrodes of the sensors.

Since the sensor readings of sensor #5 fairly reproduced the specific pH levels set in the experiments, a longer term stability experiment was performed after the initial dosing experiment with sensors #5 and #18. Figure 7 shows the sensor readings during the experiment. The batch setup was left unattended overnight with the pH sensors actively generating readings. The next morning the stability of the water matrix was verified by reading the reference pH level manually.

Figure 7: Overnight stability of measured pH signal in batch experiments. The pH of the matrix was constant during the experiment as determined with the control measurements.

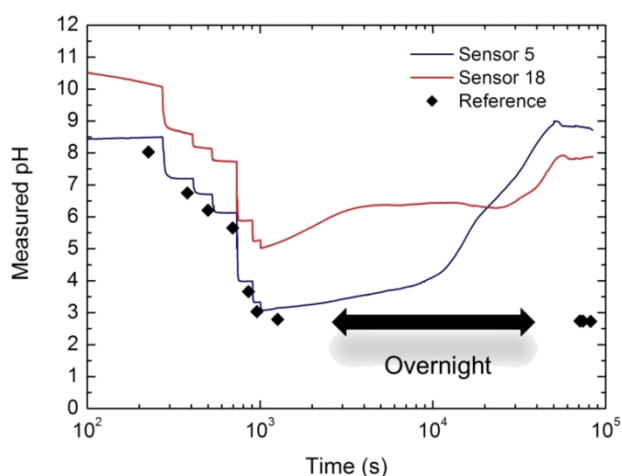


Figure 7 demonstrates that the sensor readings are vastly drifting while the water matrix was constant overnight as an identical pH level was measured by the reference electrodes before and after the longer stability experiment. Remarkably, the detailed behavior of the two sensors is profoundly different while in an identical environment. From this experiment it can be concluded that the combination of the current pH sensors and the calibration protocol in buffer solution is not optimal for reproducible pH reading over shorter and longer periods.

The main inference from the batch experiments based on calibration of the sensors in buffer solutions concerns therefore that equilibration of the sensor surfaces with the surroundings seems necessary to produce consistent, adequate and potentially longer-term stable readings. Sensors need to be calibrated in the medium of interest to minimize differential effects between the media. Furthermore, non-equilibration of the sensor surfaces with the surrounding environment leads to instability of the sensor signal after the transfer from buffer calibration solutions into drinking water.

3.1.4 Calibration in Drinking Water

Based on the abovementioned conclusions that calibration of sensors in buffer solutions do not yield optimal performance, experiments were performed investigating the possibility of calibration of the sensors directly in drinking water. Drinking water was taken from the tap and dosed with either HNO_3 or NaOH to vary the pH level. With this procedure a calibration protocol was established. Figure 8 demonstrates the successful adaptation of the calibration protocol. The initial measurement matrix in the experiment here is tap water at Nieuwegein exhibiting $\text{pH} = 7.9$. Stable sensor reading and linear calibration curves were obtained.

Figure 8 shows the results of the sensors #8 and #9, sensors that were used in the previous buffer calibration experiment as well. By using the identical sensors that were used for calibration curves using buffer solutions – sensors #5 and #18 were used once more as well – a comparison can be made between calibration parameters in buffer solutions and in drinking water. Furthermore, additional drinking water calibrations were performed using sensors #1,#2,#11 and #12. Table 2 summarizes the calibration parameters of the various sensors calibrated in drinking water and, where appropriate, compares the obtained values with parameters from buffer solution calibrations. Stable calibrations were obtained for all sensors while insight in the pH-sensitivity of the sensors (mV/pH slope) demonstrates that this parameter changes slightly compared to calibration in buffer solutions. On average 1.2 mV/pH change is observed, resulting in an under- or overestimation of up to ~0.2 pH points. For the water sector this might not be high enough sensitivity, however, calibration in the medium of interest can potentially mediate this difference. The offset potential of the sensors, however, can change dramatically up to 265 mV (average of the subset ~200 mV), as expected from the earlier experiments. Such a large change in offset potential will lead to a complete collapse of the determination of the correct pH. The result highlights the influence of the medium that affects the calibration parameters leading to the clear recommendation that calibration in the medium of interest is critical for successful operation.

Figure 8: calibration curves for sensors #8 and #9 in Drinking water.

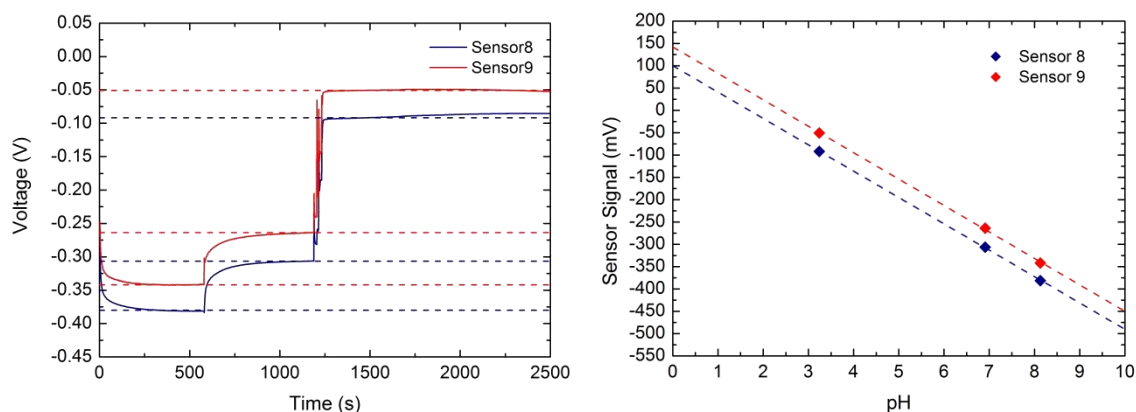


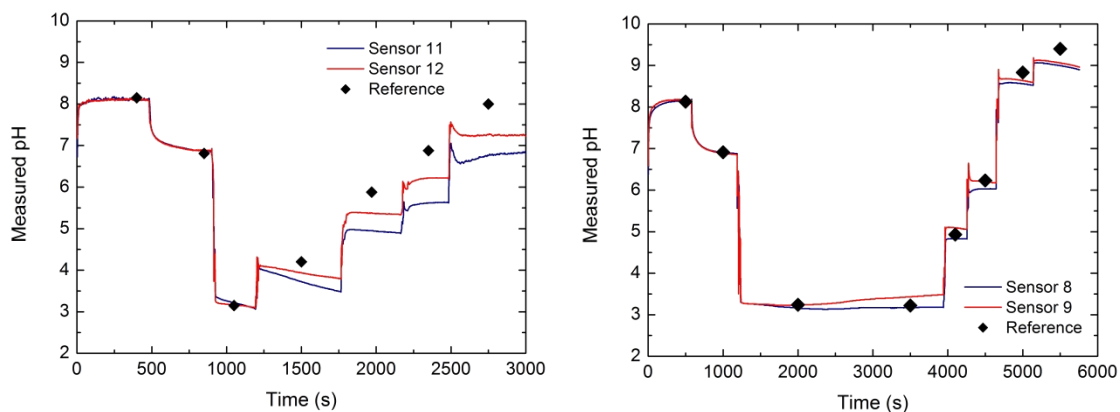
Table 2. sensor Calibration parameters from calibrations in buffer solutions and in drinking water (DW).

Sensor	Offset @ Holst (mV)	Offset @ KWR (mV)	Slope @ Holst (mV/pH)	Slope @ KWR (mV/pH)
#8 – Buffer	207.9	336.0	61.8	58.5
#8 – DW	-	99.9	-	59.0
#9 – Buffer	196.1	344.4	61.4	58.9
#9 – DW	-	141.9	-	59.2
#5 – Buffer	362.8	290.9	62.1	55.3
#5 – DW	-	556.0	-	57.9
#18 – Buffer	272.5	256.9	59.4	55.1
#18 – DW	-	168.2	-	54.4
#1 – Buffer	359.7	-	61.9	-
#1 – DW	-	526.9	-	58.9
#2 – Buffer	368.1	-	62.2	-
#2 – DW	-	325.4	-	52.7
#11 – Buffer	179.1	-	61.3	-
#11 – DW	-	256.8	-	61.3
#12 – Buffer	244.1	-	62.0	-
#12 – DW	-	148.3	-	59.1

3.1.5 Drinking Water Assessment after Drinking Water Calibration

With the calibration protocol in drinking water established, and identified as critical for successful operation, accompanying experiments were performed investigating the recovery of the correct pH level by the sensors after initial calibration. Figure 9 demonstrates results for sensors that had still been stored in buffer solution, as established protocol from the buffer solution experiments. The results shown are qualitatively similar compared to the drinking water experiments performed after calibration in buffer solutions. The spread in behavior between the different sensors is still noticeable with sensor #8 and #9 recovering the pH somewhat better than sensors #11 and #12. As observed in the latter parts of both experiments, stability of the readout signal / sensors is still an issue as well.

Figure 9: Calibration and pH recovery experiments in Drinking water. Sensors are calibrated using the initial pH levels. subsequently, pH is recalculated from the readout of the sensors using the calibration parameters. reference pH measurements performed manually.



As mentioned however, sensors were still stored in buffer solution. Therefore, with the knowledge of the previous experiments, pre-conditioning in drinking water was envisioned to improve equilibration of the sensors with the medium of interest. Effectively the equilibration time with the medium increases resulting in sustained longer term stability of the sensors. Results from sensors stored overnight in drinking water are shown in Figure 10.

Figure 10: Calibration and pH recovery experiments in Drinking water after pre-conditioning of the sensors in drinking water as well.

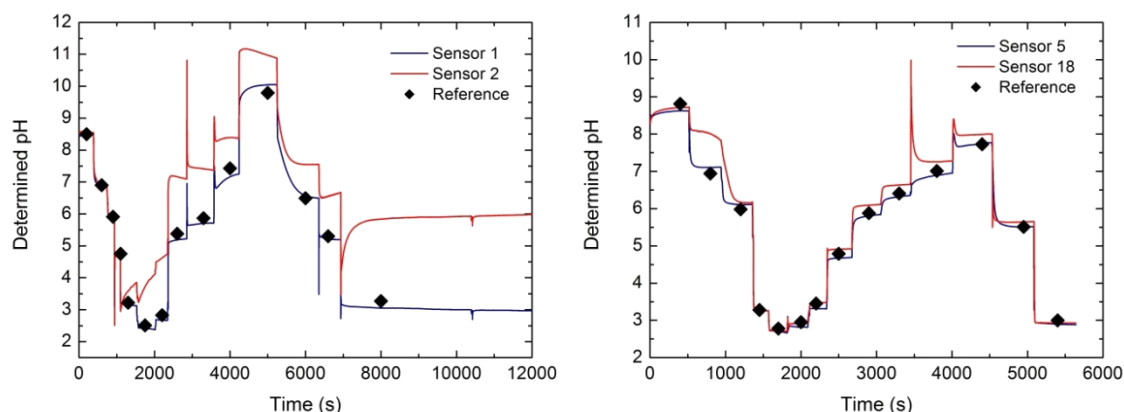
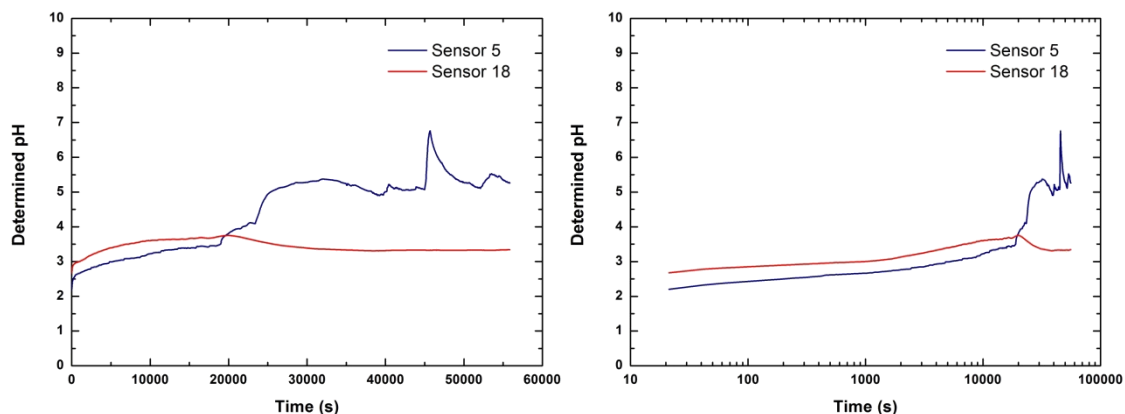


Figure 10 demonstrates that improved readings can be obtained using the pre-conditioning. However, also the inherent spread from sensor to sensor is still observed as *e.g.* sensor #2 drifts off. From the measurement of sensors #5 and #18 a rough estimate of the sensitivity of correctly working sensors can be obtained. The average difference (excluding the initial glitch of sensor #18 at pH = 6.94) between reference and the sensor readings is 0.25 pH point with a spread of 0.07 pH point. This yields an initial guess that pH reading using the sensors are to within 0.3 pH point accurate with the current calibration protocol.

Figure 11 shows the stability of the sensor readings of the batch measurement using sensors #5 and #18. The stability of the pH of the matrix was verified using the reference electrode (pH = 2.98 before and pH = 2.95 after the experiment). Excluding the first couple of data point for the re-stabilization of the readout at the beginning of the experiment, the pH reading in the more stable part still drifts ~0.75 pH in ~2.5 h before becoming unstable entirely. Clearly, for long term monitoring applications this is not nearly robust enough for implementation.

Figure 11: overnight stability of sensor readings in drinking water batch measurements after calibration in the identical drinking water sample and overnight pre-conditioning. Identical data is plotted on a linear (LEft) and logarithmic (right) timescale.



3.2 Flow Measurements

In order to characterize the pH sensors in a somewhat more realistic environment as in-line monitoring instruments, continuous flow measurements were performed. Because of the programmable and reproducible nature of the setup - close to identical amounts of solutions can be reproducibly added - repetitive dosing experiments were performed. Divergence of the sensor readings during the experiments was investigated judging the longer term stability of the measurements upon multiple additions or a (more) constant matrix. The sensors were initially calibrated with the protocol described above. A more averaged calibration was obtainable using the flow setup as more data points could be included in the linear fit since it was easier to perform multiple addition and recalculated readouts. Figure 12 shows calibration and recovery measurement results. It should be noted that a distribution in behavior was observed in the flow experiments as observed in the batch measurements. Nevertheless, linear calibrations were obtained from which other data was recalculated into pH. Table 3 summarizes the obtained calibration parameters.

Figure 12: Initial Calibration and recovery measurements using the continuous-flow setup. a subset of datapoints was used for calibration and subsequent pH levels calculated.

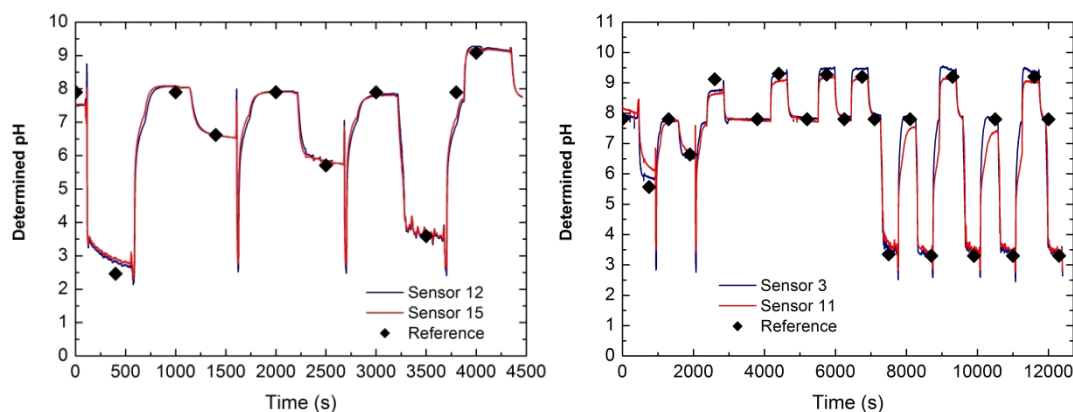


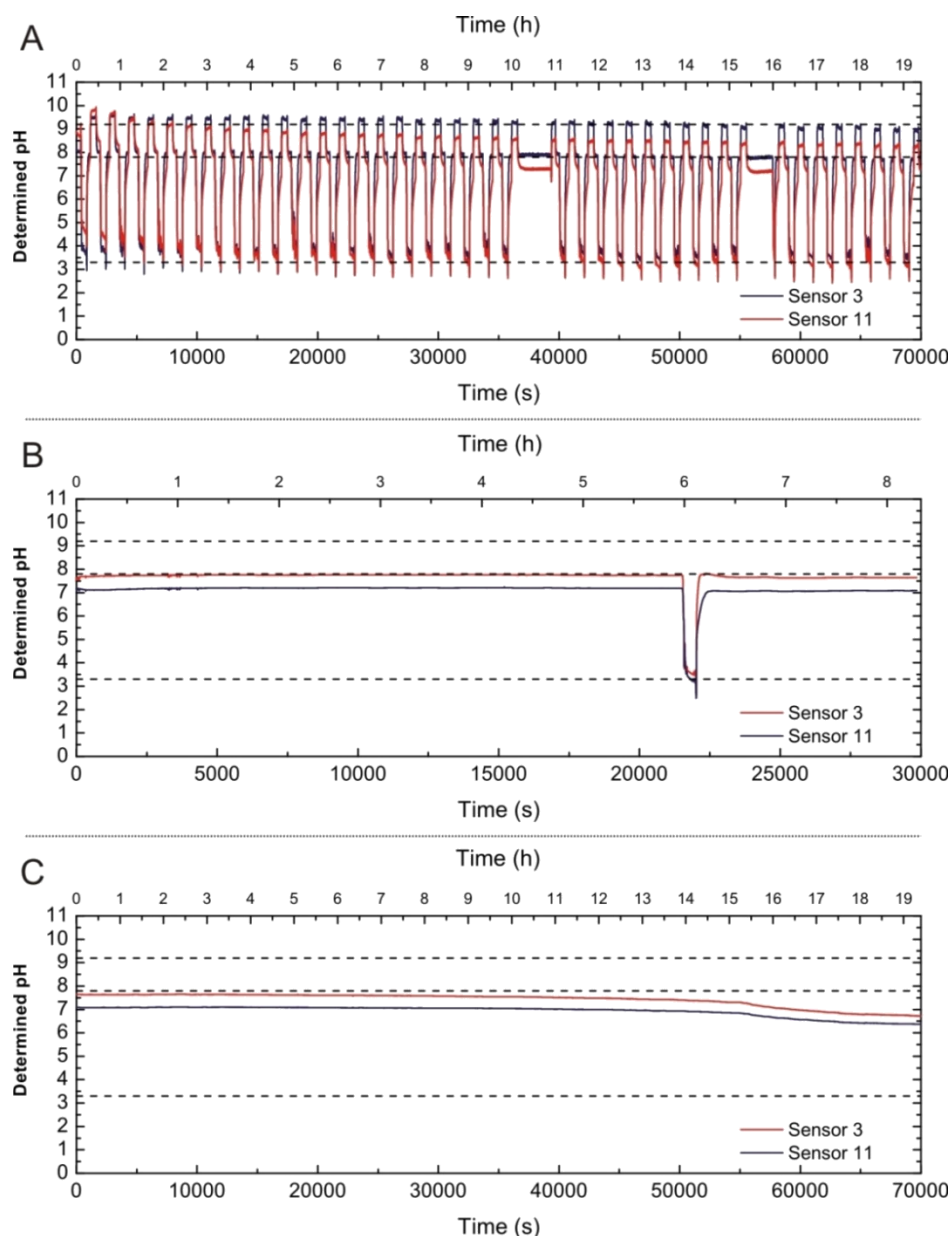
Table 3. sensor parameters from calibrations in continuous flow of drinking water compared with previous calibration parameters.

Sensor	Offset @ Holst (mV)	Offset @ KWR (mV)	Slope @ Holst (mV/pH)	Slope @ KWR (mV/pH)
#12 - Buffer	244.1	-	62.0	-
#12 - DW	-	148.3	-	59.1
#12 - DW Flow	-	214.4	-	44.3
#11 - Buffer	179.1	-	61.3	-
#11 - DW	-	256.8	-	61.3
#11 - DW Flow	-	516.3	-	53.7
#3 - Buffer	331.1	-	60.4	-
#3 - DW Flow	-	387.4	-	47.3
#15 - Buffer	267.2	-	61.9	-
#15 - DW Flow	-	271.8	-	44.8

The results from Figure 12 and Table 3 demonstrate that qualitatively similar results are obtained using the continuous flow setup compared to the results of the batch setup. In theory, probing an increased number of data points for the calibration fit could increase the quality of the calibration. However, it seems the intrinsic reproducibility of the measurements of the pH sensors leads to a spread in the pH levels that is larger than can be remediated with this procedure.

From a detailed comparison of calibration parameters once more it is observed that they change as a function of the application setting. In the continuous flow experiments, it appears that the mV/pH slope is significantly lower than observed before (Table 2). The average for the current subset amounts to 47.5 mV/pH, compared to 57.8 mV/pH for the previous subset used in the drinking water calibrations. The difference is noteworthy and would have substantial impact on the calculated pH. No clear explanation of this phenomenon can be conceived at the moment.

Figure 13: (A) Continuous flow experiment with 87 acidic and basic additions (B) Constant-ph Stability experiment in continuous flow with a single addition experiment performed. (C) subsequent stability experiment without any additions.



Calibrated sensors (#3 and #11) were subsequently examined for a longer period in a continuous flow of drinking water. Figure 13a shows the results of automated overnight addition experiments on the plain drinking water stream. The reference pH levels were determined intermittently at the beginning of the experiment and at the end, with stable reference electrode readings of pH = 7.8 for the drinking water inflow, pH = 3.3 after addition of HNO_3 and pH = 9.2 after NaOH addition. The figure shows that sensor #3 is reproducing the pH of the plain drinking water and the basic additions within a window of ~ 0.5 pH points. The acidic pH is less properly reproduced but maintains relatively stable readings. The other sensor in the experiment, sensor #11, is seen to drift more. The readout of the more basic pH-values is continuously decreasing. The initial drift is large and decreases during the experiment. It is observed that the acidic pH levels exhibit more noise, as observed with sensor #3 as well, potentially because the change in pH is larger upon these additions. Nevertheless, the observed characteristics are an improvement over the observed stability in the long(er) term batch experiments.

While the experiment described above probes the stability of the readout upon multiple additions, the stability of the sensors in a continuous drinking water stream of constant pH was assessed afterwards as well. Figure 13b shows that under constant pH conditions the stability of the current sensors (#3 and #11) in continuous flow is superior to the batch measurements performed before. The pH levels remained within a window of 0.1 pH points for a period of 6 hours. The absolute value is slightly off because of the drift of the sensor readings during the addition experiment performed before. After the 6 hours, a single dosing experiment to pH = 3.3 was performed. This addition resulted afterwards in a shift of the pH signal of the drinking water flow. The difference between the pH determined before and after the addition amounts to ~ 0.1 - 0.15 pH points, remaining stable within a 0.1 pH window afterwards again. The experiments seem to demonstrate that the drift of the sensor signal observed in Figure 13a is the result of the pH shocks that the sensors experience instead of an underlying ageing effect drifting the average response of the sensors.

Because of the observed stability of the sensor readings, a second overnight experiment was performed. Figure 13c shows the results of the measurement. During this experiment however, the sensor reading at some moment in time started to drift, remarkably in a similar fashion for the two different sensors. A crucial difference between the two overnight experiments shown in Figure 13a and 13c is, in retrospect, the temperature stabilization of the laboratory environment. During the dosing experiments (Figure 13a) the laboratory (air) conditioning system was left running while during the second stability experiment the system has shut down as energy-saving measure overnight. In contrast, during daytime experiments the conditioning systems are always working. Although no specific moment can be correlated with the runaway of the signal, temperature is envisioned as a potential reason. We have involved temperature to explain the difference between the Holst/Imec and KWR buffer experiments and are aware that other pH instruments (including the reference pH electrode used) measure temperature to correct the sensor readings. Two effects will need to be discerned here. The intrinsic pH of the matrix will change, albeit faintly, with temperature and the sensor characteristics and readout change with temperature. The first is an intrinsic effect while for the latter temperature correction of the sensor readings should be applied.

Comparison of the stability in continuous flow with the batch experiments shows that in flow the stability appears to be increased. A hypothesis is that this is influenced by accumulation of contaminants in stagnant water on the sensor surface, deriving from potential chemical reactions instigated by leakage currents, which are in effect flushed away by the stream over the surface in the flow experiments.

4 Conclusions

4.1 Results of the Study

The results of the current study have demonstrated that mainly the sensor-to-sensor reproducibility and the individual stability of the sensors from Holst/Imec are in need of improvement for foreseen implementation in the (Dutch) water sector for real-time monitoring purposes. Encouraging results that demonstrated the potential of the technology have been obtained with a subset of sensors recovering proper pH levels after calibration in the medium of interest and exhibiting stable characteristics over multiple hours, especially in continuous flow. However, a different set of identical have not reproduced pH levels to a satisfactorily extent and sensor readings, though initially with correct values, have drifted off significantly within a couple of hours yielding unrepresentative readings for the matrix of interest. This variation in the characteristics not only limits intended applications but has hindered, to a certain extent, a structured investigation and generic conclusions from the performed experiments as well.

The storage of sensors in between experiments in buffer solution or drinking water, *i.e.* the medium of interest, appears to improve the stability of the sensors. With the quasi-reference electrode based on AgCl the composition of the medium is known to be of importance, specifically the Cl^- concentration. Equilibration between the electrodes, boundary layers and the environment seems to be necessary, which potentially is a slow process. Subsequent calibration in the medium of interest is important because of identical reasons.

The influence of temperature has been shortly touched upon in the difference in calibration parameters of the sensors between Holst/Imec and KWR and, more importantly, the stability of sensor signals in the continuous flow experiments. It is critical to have an independent determination of temperature in order to correct for changes herein.

4.2 Implications for the Water Sector

The current status of the technology is not mature enough for implementation in the (Dutch) water sector. However, from a study as described above, clear areas for improvement can be identified and new research initiatives can be streamlined. The pH sensor technology of Holst/Imec needs improvement regarding sensor-to-sensor reproducibility and general stability of the sensors in aqueous environments as addressed above. This study has nevertheless identified the potential of the pH technology and, as the pH example was initiated as a benchmark of the generic underlying technology, the ion-sensitive technology developed by Holst/Imec. The (Dutch) water sector should remain closely involved to monitor and assist in development and characterization of new prototypes in order to further streamline (Dutch) water sector *sensing*-needs into applied research and development.

4.3 Recommendations

With the above identified technological points of interest, directions can be identified to move the technology forward. Below a number of issues are suggested where development could be focused on:

- **Reproducibility**

The reproducibility between the characteristics of the sensors needs attention. The largest influence on this is the detailed fabrication process that is involved to create the sensor chips. However, based on detailed chemical composition measurements of the sensor surfaces, before and after prolonged exposure to aqueous environments, lessons can be learned what transformation potentially occur on the surface and what remediation procedures can be used to gain progress. Holst/Imec has started the abovementioned analysis.

- **Stability**

The stability of sensor readings has been shown to be a major point of concern. Stability details can be investigated concurrently with the surface analysis measurements proposed above. Additionally however, on the technological implementation side of the spectrum, changes in the measurement protocols might increase the final stability of the readout. Currently, the (prototype) software controlling the readout electronics results in a continuous measurement, and therefore, continuous leakage current through the measurement circuit. This leakage current can cause chemical reactions at the electrode surfaces and can cause deterioration of the readout signal. Therefore, this duty cycle of measurements can potentially be shortened by disrupting the circuit. Furthermore, countermeasures to intermittently change the direction of current can cause small amounts of compounds formed by electrochemical reactions that occurred on the interface of the electrode to be reversed, potentially resulting in a regenerated electrode. The process might even be used to create an internal standard reference measurement protocol by applying appropriate current flow sequences before performing the actual pH measurement.

- **Temperature – Calibration & Correction**

An understanding of the temperature-dependent response of the sensors seems critical for further implementation. If understood, a thermometer might be implemented in the technology – on chip or separately – in order to correct for changes in temperature and the accompanying readout response of the pH sensors.

- **Towards Implementation II**

Concurrently with renewed development, additional validation experiments in the continuous flow setup can be performed to assess the different technological solutions. After further development of the technology has resulted in improved sensors deemed ready for implementation, a pilot study with a number of pH sensors in a sensor-network could be performed.