Observing the observer: Monitoring pH sensors by means of step response experiments

Kris Villez[1,*], Christian M. Thürlimann[1,2], Marco Kipf[1]

[1]Eawag, Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf, Switzerland

[2]ETH Zürich, Institute of Environmental Engineering, 8093 Zürich, Switzerland

*Corresponding author: *kris.villez@eawag.ch*

Abstract: While a lacking data quality is widely regarding as one of the major pitfalls for advanced automation strategies in wastewater treatment plants, there is limited information available regarding the performance of sensors in real-world conditions. This is true even for sensors based on measurement principles that have been in use since decades, such as the pH sensors studied in this work. To accommodate for this lack of information regarding sensor quality, we subject 8 pH sensors to the same reactor conditions over long periods of time. At regular intervals, dedicated step-response experiments are used to register the sensors' performance under standardized conditions. This is expected to reveal detailed information regarding the effect of ageing on the important features of the sensors such as their offset, sensitivity, and response time.

INTRODUCTION

The need for standardized assessment of online sensor data quality. On-line sensors are the most critical component in the control loops governing wastewater treatment processes. Despite decades of development in on-line instrumentation, sensing equipment is widely reported as a major source of measurement errors, next to calibration errors and errors caused wrongful installation. Slow changes in the provided data quality remain hard to detect without significant efforts. A promising approach is however given by Zambrano and Carlsson (2015). In this approach, changes in the sensor response time are detected by frequency analysis and analysis of the measurement variance of the signal. So far, this approach has not been tested under standardized conditions. Whether or not the changes in the sensors are detected timely with this method remains therefore difficult to assess.

Our approach. To evaluate whether on-line signals are sufficient to determine whether the data quality provided by a given sensor has deteriorated over time beyond acceptable levels, we propose that one ideally executes experiments which combine several ideas already proposed in the context of automated data quality evaluation: (i) measure the same variable multiple times with the same sensor, (ii) measure the same variable multiple times, possibly based on different measurement principles (as in Thomann *et al.,* 2002), (iii) execute dedicated experiments in standardized yet realistic conditions that mimic the actual application conditions (as in Villez *et al.,* 2017), and (iv) apply advanced data analysis to determine whether significant deviations from normal conditions have occurred (Zambrano and Carlsson, 2015).

Case study. In the present study, the urine nitrification process developed and studied at Eawag is taken as a motivating case. Measurements of dissolved oxygen and pH may suffice to determine whether an imbalanced activity of ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB) can lead to toxic nitrite accumulation events (Masic *et al.,* 2014). So far, noisy but high

quality measurements have been assumed (Villez *et al.,* Submitted). For this reason, we determine what kind of data quality can be expected from pH sensors and how it changes over time.

MATERIALS AND METHODS

Selected sensors. 4 pairs of the same type of ion-selective electrode (ISE) pH sensor were newly bought from Endress+Hauser and connected to a single transformer and data logging-computer (measuring interval: 1s).

Exposure to reactor contents. All pH sensors were placed in a horizontal pipe at a 45 angle to the horizontal plane. The inlet and outlet of the pipe are both connected to a urine nitrification reactor operated with suspended biomass. The pipe contents are continuously recycled by means of a peristaltic pump. The main objective of this operation is to subject the pH sensors to normal wear-and-tear. In addition, the collected data may be informative about the sensors' conditions.

Standardized experiments. At regular intervals, the sensor are removed from their normal placement, cleaned according to manufacturer's recommendations, and exposed to five different mixed media. The media are tap water (TW), nitrified urine with pH set to 4 (U4), nitrified urine with pH set to 7 (U7), calibration solution with pH=4 (C4), calibration solution with pH=7 (C7). Each sensor is exposed to the following sequence of media: TW-U4-U7-U4-TW-C4-C7-C4-TW in intervals of at least 5 minutes. In this particular contribution, we focus on the response time (as defined in ISO15839 (2003)). The data collected during the U4-U7-U4 sequence to compute response times in nitrified urine and the data collected during the C4-C7-C4 media sequence is used to evaluate response times with the sensor calibration solutions.

Response time computation. A response time is computed for each sensor and for each of the following media changes: C4-C7, C7-C4, U4-U7, U7-U4. A second-order linear dynamic model is fitted in the least-squares sense to the first 120 seconds of voltage measurements obtained after a medium change (e.g., Rosén *et al.,* 2008). Following this parameter estimation, the response time (as defined above) is evaluated with the fitted model.

RESULTS

A single standardized experiment. Fig. 1 displays the voltage signals obtained with four sensors during the first standardized experiment, executed 2 days after the sensors were exposed to the reactor contents for the first time. One observes that higher pH values (medium C7 and U7) lead to lower voltage signals and vice versa (medium C4 and U4). Interestingly, the steady-state voltage signals for urine media are not the same as those obtained with the calibration solutions (medium C4 vs U4 and C7 vs U7). This is explained by the fact that the urine media are not buffered. Still, the nitrified urine media cause voltage signal changes which are similar to those obtained with the calibration solutions. Another noteworthy observation is that the response following the U7→U4 media change is very slow. Furthermore, the signal does not seem to converge to final steady-state within the 411 seconds before the next media change. The fact that no steady-state value is obtained within 6 minutes suggests that this sensor is unlikely trustworthy for the considered process.

A comparison of the first set of collected response times. Table 1 summarizes the response times obtained with the first 4 pH sensors as well as for the second set of 4 pH sensors. In each row of the table, the ranking of the best-to-worst response times are indicated with colour. Interestingly, sensor type #3 is always the worst sensor type. Its response time ranges from 10.5 to 87.7 seconds. The response times for the other sensors range from 5.2 to 12.6 seconds. The ranking for sensor #1, #2 and #4 is subject to some variation. It is potentially interesting that sensor type #1 is ranked the best

3 times with the calibration media whereas sensor type #2 is ranked the best 3 times with the nitrified urine media. The response times for sensor types #1, #2, and #4 are generally in the same range so that a best sensor among these cannot be identified yet.
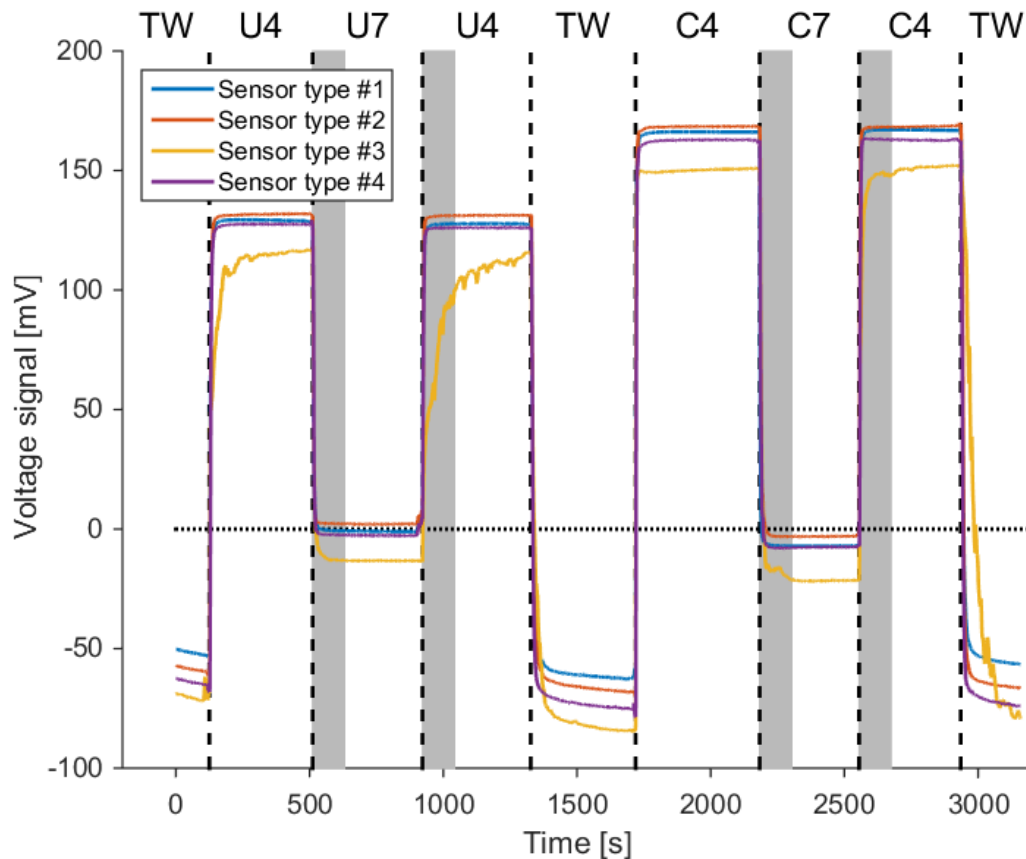

Figure 1. Voltage signals collected with one row of pH sensors during the first standardized experiment. The vertical dashed lines indicate the exact time of the media changes. The data used for time response characterization are indicated with grey zoning.

Table 1. Obtained response times for each sensor type, sensor row, and imposed medium change. In each row the ranking of the response times is indicated in colour – from best to worst: green – yellow – orange – red. Value that are likely too low because steady-state was not reached are indicated in black. Incidentally, these are the highest values recorded.

Sequence change	Medium Type	pH change	Sensor row	Sensor type			
				#1	#2	#3	#4
C4-C7	Calibration solution	4→7	1	5.2	10.2	13.9	9.2
C4-C7	Calibration solution	4→7	2	6.2	10.6	19.0	11.8
C7-C4	Calibration solution	7→4	1	7.6	7.9	10.5	8.6
C7-C4	Calibration solution	7→4	2	12.6	10.3	14.9	8.0
U4-U7	Nitrified urine	4→7	1	6.4	6.1	15.9	7.9
U4-U7	Nitrified urine	4→7	2	7.2	10.3	19.0	12.4
U7-U4	Nitrified urine	7→4	1	8.0	6.9	**87.7**	7.0
U7-U4	Nitrified urine	7→4	2	8.9	7.7	**37.1**	9.1

CONCLUSIONS

With this contribution, the first results obtained with a dedicated study of several pH sensors are presented. An initial experiment has been presented within which 8 pH sensors are exposed to media changes which emulate an abrupt change of the pH value. This experiment was executed after prior exposure to the reactor liquor within which the pH ought to be measured accurately. By means of this first experiment and an analysis of the sensors' response times, one sensor type could already be excluded as a sensible sensor choice for the considered process, particularly in view of the development of an accurate model-based soft-sensor. Additional experiments have been executed and await detailed analysis to determine whether the response times of the considered sensor types change over time and whether the evaluation of additional properties (intercept value, sensitivity, precision) deliver important information. These sets of experiments are the first of their kind and will reveal so far little known details regarding the proper interpretation of data quality obtained with on-line ion-selective electrodes.

REFERENCES

ISO15839 (2003). Water quality – On-line sensors/ Analysing equipment for water – Specifications and performance tests, ISO15839, ISO, Geneva, Switzerland.

Masic, A., Villez, K. (2014). Model-based observers for monitoring of a biological nitrification process for decentralized wastewater treatment - Initial results. 2nd IWA Specialized International Conference "Ecotechnologies for Wastewater Treatment" (EcoSTP2014), Verona, Italy, June 23-25, 2014, 402-405.

Rosén, C., Rieger, L., Jeppsson, U., & Vanrolleghem, P. A. (2008). Adding realism to simulated sensors and actuators. Water Science and Technology, 57(3), 337-344.

Thomann, M., Rieger, L., Frommhold, S., Siegrist, H., & Gujer, W. (2002). An efficient monitoring concept with control charts for on-line sensors. Water science and technology, 46(4-5), 107-116.

Villez, K., Rieger, L., Keser, B., Venkatasubramanian, V. (2012). Probabilistic qualitative analysis for fault detection and identification of an on-line phosphate analyzer. International Journal of Advances in Engineering Sciences and Applied Mathematics, 4, 67-77.

Villez, K., Thürlimann, C. T., Brouckaert, C., Masic, A. (Submitted). Soft-sensing of nitrite concentrations in a urine nitrification system by means of the unscented Kalman filter. 12th IWA Specialized Conference on Instrumentation, Control and Automation, 11-14 June 2017 in Québec City, Québec, Canada.

Zambrano, J., & Carlsson, B. (2015). Fault detection of DO sensors subject to possible clogging. In WATERMATEX 2015, June 14–17, Gold Coast, Queensland, Australia.