Automated Titration in a Recirculating Water System

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Abstract—**Titration is a quantitative method for determining an unknown property (typically concentration) of an analyte. In a recirculating water system, the reagent is returned to the system, and in many circumstances it is desirable to ensure that the quantity of reagent is minimized. We describe an automated instrument for executing titrations in flowing streams that is well suited to recirculating water systems.**

I. Introduction

Titration is a process to assess chemical properties of aqueous solutions. Our interest is in designing an automated instrument (meter) that performs titration on flowing water. In particular, we are focused on the particular needs of a recirculating water system, such that any reagent used during a titration will necessarily be returned to the body of water.

The use case is to connect the meter to a water chemistry controller, which is responsible for monitoring and maintaining a body of water within an acceptable range of parameter values, such as pH, free chlorine concentration, temperature, conductivity. Examples of these systems include pools, water parks, animal habitats in zoos, drinking water treatment facilities, waste water treatment facilities, fountains, cooling towers, etc. In many circumstances, the alkalinity of the water must be maintained, and titration is the preferred method for assessing total alkalinity [7].

We describe several approaches to the control of an automated titration, most of which seek to diminish reagent usage. For each approach, we describe how it works, give examples of empirical data that support (or don't support) its adoption, and list techniques that are included in our instrument.

II. Background and Related Work

In a regular titration, we start with a known quantity of the analyte (sample) in a mixing vessel and add reagent (e.g., via a calibrated burette) until we reach the balance point. Frequently this is determined by a color change due to an indicator, added to the analyte prior to the titration. With knowledge of the quantity of analyte, quantity of reagent, and reagent concentration, we can determine the analyte concentration.

Consider the reaction

$$n_S\text{S} + n_R\text{R} \rightarrow \text{P},$$

where S is the analyte, R is the reagent, P is the product, and n_S and n_R are the stoichiometric coefficients of S and R, respectively. Blaedel and Laessig [2] demonstrated a flow titration by mixing the reagent at flow rate f_R with the analyte at flow rate f_S. The equivalence condition is given by

$$C^S \cdot \frac{f_S}{n_S} = C^R \cdot \frac{f_R}{n_R} \qquad (1)$$

where C^S is the concentration of S and C^R is the concentration of R. By controlling the reagent flow rate, f_R, to reach equivalence, the knowledge of reagent concentration, C^R, sample flow rate, f_S, reagent flow rate, f_R, and coefficients n_S and n_R allows one to determine C^S, the unknown sample concentration.

Ashworth et al. [1] described a similar system, however, they varied the sample flow rate, f_S, to reach equivalence. In our system, we have the additional complication that the output flow will be returned to the larger body of water, which motivates us to minimize the quantity of reagent used.

BECS Technology, Inc., is a firm that provides water chemistry monitoring and control equipment to the aquatics market. Its BECSys™ line of controllers measure a number of aspects of water chemistry (e.g., temperature, pH, oxidation-reduction potential (ORP), free chlorine, conductivity, etc.) and perform various control operations (e.g., feed chemical) to ensure that the water chemistry stays within desired parameters. EZConnect™ is the security infrastructure BECS has developed to provide remote access capability to equipment it manufactures [3], [5]. Its EZAnalytics™ system enables cloud-based data logging and analytics on water chemistry data from a collection of controllers [4].

III. Basic System Description

The titration instrument is shown in Figure 1. The sample water (at flow rate f_S) enters in the lower-left corner and flows up. Its flow rate is measured, the reagent flow (at flow rate f_R) is inserted, they are mixed, the pH is measured, and the resultant products exit in the lower-right corner. The reagent flow is pumped from a storage vessel via a precision peristaltic pump. The pump is controlled by a microprocessor (by establishing the step rate on the stepper motor driving the pump), which also reads the measured sample flow rate and product pH. The titration microprocessor communicates with the water treatment controller via an RS-485 interface.

Our instrument uses a pH probe to assess the chemical properties of the effluent products. It is also possible to include an indicator with the reagent and use optical methods for sensing; however, in the context of the systems we work with, keeping the optical paths sufficiently clear can be problematic
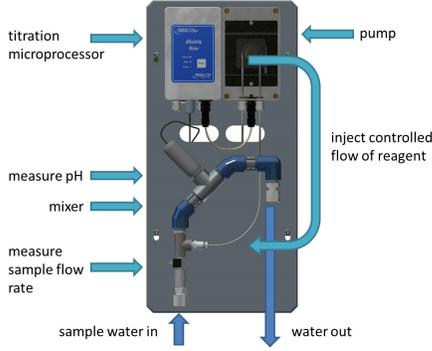
Fig. 1. Physical diagram of the instrument.

Fig. 2. Linear control of reagent feed.

over time, requiring higher maintenance overhead than a standard pH probe.

At its core, our control task is straightforward. We establish a reagent flow rate, f_R, that reaches equivalence (for our alkalinity use case, a measured pH of 4.5), then use equation (1) to determine the unknown sample concentration. In truth, it really does work like this; however, our initial experimental run of the system (with a 500 gallon test tank) inserted enough reagent into the water that the alkalinity of the tank crashed and the pH in the tank was falling rapidly.

In what follows, we will describe a number of approaches to diminishing reagent use, some of which were successful and are included in the commercial product, and some of which were discarded, for reasons that we will articulate.

IV. INSTRUMENT CONTROL

The most straightforward approach to controlling the reagent flow rate is a linear ramp, increasing the reagent flow rate until the measured pH falls below the target value. We approximate a ramp via stepwise changes in pump rate to accommodate delays in the pH probe's response.

Figure 2 shows the results of this experiment. First we will explain how to interpret the graph. The pH reading is shown in blue, with the scale on the left. The pump speed is shown in red, with its scale on the right. We have inverted the pump speed scale, since increased pump speed will drive pH down, in an attempt to make the cause and effect easier to follow when reading the graph(s). When observing graphs plotted in this style, the reader is cautioned to not try to infer too much by the relative positions of the two distinct curves. Since they have distinct scales, their relative positions are arbitrary. We superimpose them so as to make time comparisons easier.

The stepwise progression of pump speed is readily apparent, and the pH reading is tracking direction. At the 12 min mark, since the pH is below our target of 4.5, the measurement is terminated and the pump speed is returned to 0 rpm.

With knowledge of the pump rate required to achieve our target pH, we now have sufficient information to apply equation (1) to determine the concentration of the flow stream.

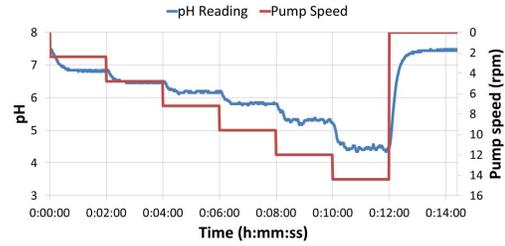$$C^S = C^R \cdot \frac{n_S}{n_R} \cdot \frac{f_R}{f_S} \qquad (2)$$

For an alkalinity measurement this is frequently reported as parts per million of equivalent calcium carbonate (ppm CaCO$_3$), since CaCO$_3$ dominates in many water systems. In what follows, we will abbreviate this to simply ppm, which is common practice in the industry.

Relabeling C^S as TA (for total alkalinity) and combining the terms that are constant in equation (2), alkalinity can be expressed in terms of the parameters that vary from one titration to the next, namely the sample flow rate and the reagent flow rate:

$$TA = K_{CAL} \cdot \frac{f_R}{f_S} \qquad (3)$$

where the calibration constant, K_{CAL}, not only encompasses the reagent concentration, C^R, and the stoichiometric coefficients, n_S and n_R, but also includes any unit conversions for the two flow rates. Because this analysis is linear in the ratio of the two flow rates, performing a calibration is as simple as inverting equation (3).

As is apparent from the expressions above, the formal theory is straightforward, and measurements are independent of the size (volume) of the recirculating water system. The issues we face are all on the practical side, and we will now turn our attention in that direction.

The first few things we will consider are fairly independent of how the instrument actively controls the reagent flow rate, they relate to the sample flow rate and the measurement frequency. To minimize reagent usage, it is beneficial to keep both as low as is reasonable.

Minimizing flow rate and measurement frequency: The lowest reasonable sample flow rate is determined by a pair of factors. One, variability in this flow rate seen in the field can be caused by a number of factors (e.g., filters clogging/getting cleaned) and we need to keep the variability below the nominal flow rate. Two, peristaltic pumps result in uneven (pulsed) flow at sufficiently low pumping rates. The instrument's nominal sample flow rate is 10 gal/hr (gph); however, it can make readings over a range of 5 gph to 15 gph.

Lowering measurement frequency is straightforward in practice. The tradeoff here is twofold. One, regulatory requirements often specify a limit in the time between readings that get logged for compliance purposes. Two, if we are ultimately interested in providing automatic alkalinity control based on the readings, the needs of proper control will determine the necessary measurement frequency.

The next set of things to consider are issues with the stepwise linear ramp approach to reagent pump rate control. A few of those issues are listed here:

1) The inherent resolution of a reading is limited by the step size. Decreasing it, however, runs completely counter to our goal of minimizing reagent usage.
2) Long (fixed) step durations contribute to reagent flow well above the minimum required. Even an informal observation of the pH reading's response to each step in Figure 2 makes it clear that this could be improved.
3) The linear ramp is not resilient to changes in the sample flow rate during the run.

Binary search and step early termination: We start by pointing out that in the manual titration process one cannot reduce the quantity of reagent, once inserted it is always present. Flowing water titrations have no such limitation. We will exploit this fact and move away from what is essentially a linear search for the equilibrium point to a binary search, as proposed by Martelli et al. [6]. At the same time, instead of a fixed step time, we will actively monitor the pH reading during a step and terminate it early when possible.

Figure 3 shows an experiment that encompasses both binary search and early step termination. At the beginning of the run, the reagent pump rate is set to the midpoint of its range (12 rpm, out of a range of 0 to 24 rpm supported by the pump). As the pH falls below 4, the step is terminated and the pump rate is set to 6 rpm. At time 3:36, the pH has climbed back above our target, so the pump rate is set to 9 rpm, which results in a pH right at 4.5. In general, we test to see if the pH is within a settable error, ϵ, of the target, i.e., we consider the pH to be on target when $4.5 - \epsilon \leq \text{pH} \leq 4.5 + \epsilon$.
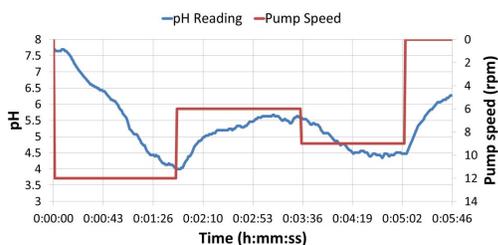

Fig. 3. Binary search control of reagent feed.

Early termination of a step is determined by the following. If it is a step that increases the pump rate, pH falling well below the target indicates that the pump rate can be decreased. Similarly, if it is a step that decreases the pump rate, pH rising well above the target gives us sufficient information to terminate the step. Finally, we detect a stable pH reading by first passing the reading through a low-pass, finite impulse response filter whose coefficients are scaled so that the arithmetic can be performed using integer math (recall that our instrument is being driven using a microcontroller). Taking a numerical derivative of this filtered pH signal results in what we call an *instability index*. This index is compared to a threshold, which

is used to indicate that the pH reading is sufficiently stable to terminate the step.

While the binary search technique with early termination helps address the first two issues identified with the stepwise linear ramp, it does nothing to address the third issue. The sample flow rate can range from 5 gph to 15 gph and the instrument is expected to still function properly.

Back-off algorithm: In practice, the sample flow rate doesn't change rapidly over its entire range. The two most common behaviors observed are: (1) the flow rate changes a small amount during a reading, or (2) there is some external event which causes a significant flow rate change, but the flow is fairly stable after the change.

We address this behavior in the binary search algorithm by incorporating a conditional back-off capability. If the maximum number of search steps have been executed, and the pH value is still not within ϵ of our target, we back up several steps in the search algorithm and re-engage the binary search with a wider scope. This back-off is repeated several times before the instrument reports an error that it is unable to complete a valid titration.

Exploring exponential response: An additional observation one can make about the system is that it might not be necessary to wait until the pH reading stabilizes before we know the final value. First principles (supported by observation) say that when the reagent feed rate is changed, the response of the pH reading is exponential. With this knowledge, it is quite reasonable to take sufficient readings as to understand the exponential curve, extrapolate the final value, and move on to the next step immediately.

Figure 4 illustrates this effect, showing the time series of pH readings for just over one minute after a step change in the reagent feed rate. The pH value is read once per second. The solid curve represents an exponential curve fit to the first 60 seconds of the series, which results in the following expression for pH as a function of time:

$$\text{pH} = 1.4e^{-t/18} + 6.2. \tag{4}$$

Clearly, the final pH value of 6.2, at $t = \infty$ in equation (4), matches well with the actual value over 4 time constants out.
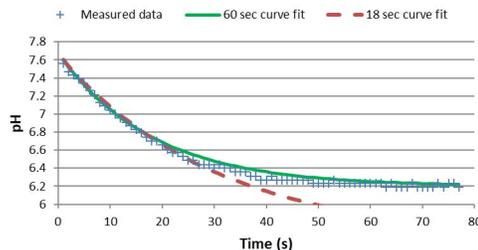

Fig. 4. Exponential response of the pH measurement.

We note, however, that the alignment between the data and curve is not particularly good especially at the beginning of the transition. If we perform an exponential curve fit just over the

points in the first 18 seconds (essentially one time constant), the result is the following expression:

$$\text{pH} = 2.0e^{-t/30} + 5.6. \tag{5}$$

This curve is shown as the dashed line in Figure 4. In this case, the final pH value of 5.6, at $t = \infty$ in equation (5), deviates significantly from the empirical data. The above is a particularly well behaved step response. Many are much more noisy. As such, the current instrument does not attempt to exploit this property to further decrease reagent usage.

Addressing tubing compression: One of the techniques to reduce reagent usage is to decrease the meaurement frequency. This has implications well beyond the obvious, however, as we discovered when we tried it. The tubing used to feed the reagent is a PVC material that has a fairly small inside diameter (2 mm) so as to support very low flow rates. The operation of the peristaltic pump pinches the tubing as part of its normal operation; however, the pinch point moves along the tube when reagent is flowing. When the pump is stopped, the pinch point is stationary, and the tubing stays pinched at this location until the subsequent titration run.

Unfortunately, when the pump is stopped for most of a day the tubing takes time to rebound to its original shape, and until that happens the actual flow rate through the pump is reduced. We can see evidence of this in the experimental data presented in Figure 3. Note that in the first step, the response of the pH reading looks much more linear than it does exponential. This is due to the recovery time required for the tubing to return to its normal shape and function.

We addressed this issue by not allowing the pump to actually ever completely idle. When our desired flow rate is zero, we rock the rollers back and forth along the tubing so that no one position is pinched for an extended duration.

V. Field Experience

While the initial testing took place in our wet lab, an instrument has been installed since March 2017 in a high school natatorium. This is a significantly larger body of water than was used in the lab. It is common in systems of this type to have two distinct mechanisms for pH control, a muriatic acid feed and a CO_2 feed. Feeding either muriatic acid or CO_2 has the effect of lowering pH. One of the benefits of this dual feed system is that the acid feed also pushes alkalinity lower, while the CO_2 feed allows the alkalinity to climb.

Figure 5 shows empirical data from the instrument for about 3 months starting on March 29. On May 24, May 26, May 31, June 1, and June 13, pH control output was switched. In addition to the data points, which represent individual measurements, the graph also contains linear curves fitted to each of the time ranges described above. It is clear that during periods of CO_2 feed the alkalinity of the pool is climbing and during periods of acid feed the alkalinity is falling.

Manual testing has a minimum resolution of 10 ppm, so we will use data from the beginning of the time period up to the change in pH control output that occurred on May 24 to assess the variability in the instrument's readings. Treating
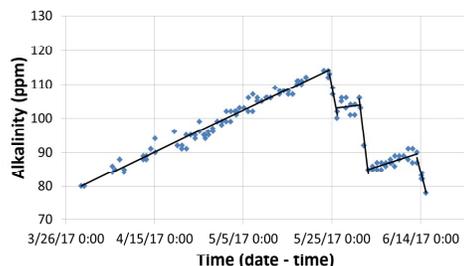

Fig. 5. Measured alkalinity from instrument.

the straight line curve fit to the data as the "true" values, the error is computed as the difference between this "true" value and the actual measurement. The mean error (absolute value) is 0.9 ppm with a std. dev. of 1.5 ppm.

VI. Conclusions

We have described the design of an instrument for automatic titration that has been developed with the particular needs of recirculating water systems in mind. Primarily, this implies minimizing the quantity of reagent utilized.

The reduction in reagent usage is accomplished by: (1) minimizing the sample flow rate; (2) minimizing the measurement frequency; (3) using a binary search algorithm to determine the reagent pump rate that matches the target pH reading; and (4) terminating individual steps when the pH reading is determined to be stable. In addition, the instrument must deal with the real effects of: (1) sample flow rates varying during a measurement and (2) the pump being idle for long durations having negative effects on the reagent tubing.

The result is an instrument that can repeatedly perform measurements in a recirculating water system that is only 500 gallons in capacity (the test tank in our facility), has been installed and running in the field for several months, and is currently available as a commercial product.

References

[1] M. R. F. Ashworth, W. Walisch, W. Becker, and F. Stutz, "Ein gesteuerter dynamischer titrierautomat mit konduktometrischer indizierung," *Fresenius' Zeitschrift für analytische Chemie*, vol. 273, no. 4, pp. 275–281, Jan 1975.
[2] W. Blaedel and R. Laessig, "Continuous automated, buretless titrator with direct readout," *Analytical Chemistry*, vol. 36, no. 8, pp. 1617–1623, 1964.
[3] R. D. Chamberlain, M. Chambers, D. Greenwalt, B. Steinbrueck, and T. Steinbrueck, "Layered security and ease of installation for devices on the Internet of Things," in *Proc. of IEEE Int'l Conf. on Internet-of-Things Design and Implementation*, Apr. 2016, pp. 297–300.
[4] ——, "Water in the Cloud: Remote Understanding of Water Chemistry: Poster Abstract," in *Proc. of ACM/IEEE Int'l Conf. on Internet-of-Things Design and Implementation*, Apr. 2017, pp. 353–354.
[5] ——, "Devices can be Secure and Easy to Install on the Internet of Things," in *Interconnection, Integration, and Interoperability of IoT Systems*, R. Gravina, C. Palau, M. Manso, A. Liotta, and G. Fortino, Eds. Springer, 2018, pp. 59–76.
[6] P. B. Martelli, B. F. Reis, M. Korn, and J. L. F. Costa Lima, "Automatic potentiometric titration in monosegmented flow system exploiting binary search," *Analytica Chimica Acta*, vol. 387, no. 2, pp. 165–173, Apr. 1999.
[7] T. R. Martz, A. G. Dickson, and M. D. DeGrandpre, "Tracer monitored titrations: Measurement of total alkalinity," *Analytical Chemistry*, vol. 78, no. 6, pp. 1817–1826, 2006.