Automatic buffer capacity model building for the purpose of water quality monitoring

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Abstract In this paper, buffer capacity profiles are used in the framework of automatic monitoring of water quality. The aim of the proposed methodology is to automatically and stepwise build buffer capacity models for each particular titrated sample, and to quantify the individual buffer systems that constitute the total buffer capacity. An automatic and robust model building algorithm has been developed and applied to many titration curves of effluent and river water samples. It is illustrated that the application of automatically built buffer capacity models mostly results in similar or better estimations of ammonium and ortho-phosphate in the samples compared to *a priori* fixed buffer capacity models. The automatic modelling approach is also advantageous for alarm generating purposes on e.g. river waters, because unexpected buffers are easily detected.

Keywords Buffer capacity; mathematical modelling; model selection; on-line monitoring; pH titration; water quality

Water Science and Technology **Vol 43 No 7 pp 105–113** © 2001 IWA Publishing and the authors

Introduction

Methods and applications based on pH titrations are used in a wide variety of fields (aerobic, anaerobic and physico-chemical wastewater treatment, food and feed applications, soil science, microbiology, aquatic chemistry, etc.) (Gibs *et al.*, 1982; Hill *et al.*, 1985; Husted *et al.*, 1991; Sawyers and Dentel, 1992). However, these applications mostly rely on the off-line interpretation of titration curves, and can thus not be considered 'sensors'. Sensors making use of pH titration curves are often referred to as titrimetric sensors. These sensors mostly work with only a few titration points and a simplified and robust data interpretation method. One of the main application fields in this area is the control of anaerobic digestion where bicarbonate and/or volatile fatty acids (VFA's) can be monitored on-line with a titrimetric sensor (Rozzi *et al.*, 1985; Anderson and Yang, 1992; Moosbrugger *et al.*, 1993; Buchauer, 1998; Bisogni *et al.*, 1998). The buffer capacity based sensor used in this paper differentiates itself from the other sensors by the fact that the whole and detailed titration profile is used for model-based interpretation (software sensing).

In a previous paper (Van Vooren *et al.*, 1996), the use of an automatic on-line titration unit for monitoring the effluent quality of wastewater plants was presented. Ammonium and ortho-phosphate monitoring were established by using a simple titration device, connected to a data-interpretation unit. However, a limitation of the illustrated approach in Van Vooren *et al.* (1996) is that the applied mathematical buffer capacity model contained a fixed number of buffers. As a consequence, all titrated effluent samples were assumed to contain the same buffer systems. However, in reality, this assumption may not be true. In this paper, the aim is to automatically and stepwise build buffer capacity models for each particular titrated sample. The benefits of this approach compared to the fixed model approach will be highlighted and discussed.

Materials and methods

General linear buffer capacity model

In case one only considers acid-base chemical equilibria, a linear buffer capacity model can always be used (Van Vooren, 2000). Non-linearities are the result of considering, among

others, complexation or precipitation reactions, e.g. reactions between Ca^{2+} and OH^-, or between Ca^{2+} and HPO_4^{2-}. These more complicated reactions are outside the scope of this paper, but examples have been studied (Van Vooren, 2000). In a water sample containing several buffering components, one can write that the total buffer capacity β is equal to the sum (hence, the linearity) of the buffer capacities of the different components in the sample. The H_2O buffer is considered in the same way as any other monoprotic weak acid HA. Based on this additive property of β, one can write a general equation for the buffer capacity of a sample containing l monoprotic, *m* diprotic and *n* triprotic weak acids:

$$\beta = 2.303[H^+] \left\langle 1 + \sum_{i=1}^{l} C_i \left(K_a \frac{1}{([H^+] + K_a)^2} \right)_i + \sum_{i=1}^{m} C_j \left(K_{a1} \frac{[H^+]^2 + 4K_{a2}[H^+] + K_{a1}K_{a2}}{([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})^2} \right)_j + \sum_{i=1}^{n} C_k \left(K_{a1} \frac{[H^+]^4 + 4K_{a2}[H^+]^3 + (K_{a1} + 9K_{a3})K_{a2}[H^+]^2 + (4[H^+] + K_{a2})K_{a1}K_{a2}K_{a3}}{([H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3})^2} \right)_k \right\rangle \quad (1)$$

where

β = buffer capacity (eq l^{-1} pH^{-1})

$[H^+]$ = hydrogen ion concentration (mol l^{-1}), equals 10^{-pH}

$C_{i,j,k}$ = concentration of respectively a monoprotic, diprotic or triprotic weak acid (mol l^{-1})

K_a = acidity constant

Equation (1) reflects the linearity in the concentrations *C*, and non-linearities in the acidity constants and pH. More details about this model can be found in Van Vooren *et al.* (1999) and Van Vooren (2000).

Buffer capacity optimal model builder

The C++ program *bomb* is an acronym for "Buffer capacity optimal model builder" (Van Vooren, 2000). The three main objectives for this software are to:

- calculate buffer capacity curves from raw titration curve data;
- fit mathematical models to experimental buffer capacity curves with a non-linear least squares optimization routine. The implemented algorithm is PRAXIS (Gegenfurtner, 1992), which is an algorithm for minimization of multi-dimensional functions. The estimated parameters are concentrations and/or pK_a values of selected buffer systems included in the mathematical buffer capacity model;
- stepwisely and automatically construct an optimal buffer capacity model for samples with a lack of *a priori* knowledge about the buffer systems that are expected in the sample.

A literature research on advanced buffer capacity modelling software yielded little. The majority of available software programs were developed for one specific application, e.g. the determination of VFA and HCO_3^- in anaerobic digesters. Such programs are not portable to other application areas for other types of buffer systems. One exception is the software described by Gordon (1982). Gordon analyzes titration data for an unknown solution. However, no references more recent than 1982 about this program, its applications, or similar programs were found.

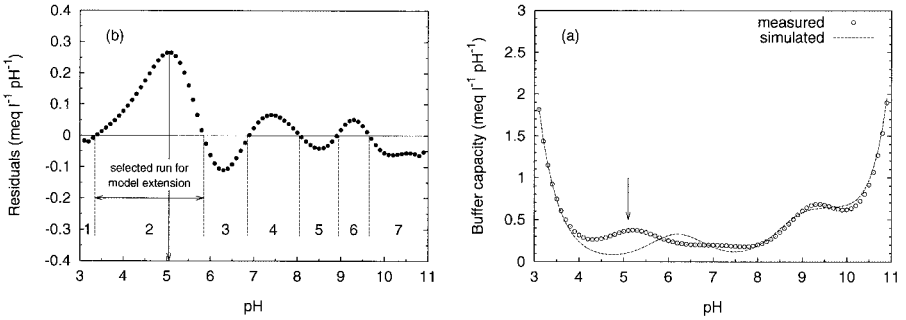

Figure 1 Experimental and simulated buffer capacity curves (a) and calculated residuals (b), with indication of the runs, the best candidate run for model extension, and the candidate pK_a of a new buffer within that run

The *bomb* model building software is designed for an automatic, stepwise and robust buffer capacity model development. Unknown buffers that are added automatically in the model are also termed "blind" buffers. The algorithm starts with the fitting of an initial model (= zero model). The residuals and runs (a run is a sequence of consecutive positive or negative residuals) obtained with the initial model are calculated. The best candidate pH (and corresponding pK_a) for model extension was obtained when the run with the highest positive sum of residuals was selected, and within that run the pH with the maximum residual value. This is illustrated in Figure 1.

A number of additional rules for model extension are reported in Van Vooren (2000). When an extended model is fitted, the algorithm proceeds, if necessary, with one or several model tuning cycles. Model tuning is defined as the process in which the boundaries for acidity constants (pK_a's) of blind buffers that have been estimated, are moved if the estimated value is too close to the allowed boundaries of the pK_a values. The zero model is coded as model 0.0, and the first model extension results in model 1.0. If model tuning cycles are performed, this will result in model 1.1, 1.2, etc. The next model extension will result in model 2.0, etc. Finally, after each tuning session, the model building stop criteria are calculated and evaluated.

Optimal buffer capacity model selection

When the automatic model building algorithm described in the previous paragraph is applied, one ends up with a set of mathematical models that have all been fitted to the experimental data. The next logical step is a selection of the model most appropriate for the purpose it will be used for. Model structure selection techniques are widely available from literature (Vanrolleghem and Dochain, 1998).

The Run-test or testing changes of sign. Let R be the number of changes of sign in the residual sequence $\varepsilon(1) \ldots \varepsilon(N)$, with N the number of data points. For example, for the illustrated example in Figure 1, R=6 and N=79.

$$u = \frac{R - N/2}{\sqrt{N/2}}. \qquad (2)$$

If the residual sequence is a zero mean white noise, the test statistic u is standard normal distributed. Hence, a 95% confidence interval for u is given by $|u| \leq 1.96$ for $\alpha = 0.05$. If several models have to be compared, the model with the lowest number of parameters for which $|u|$ is lower than u_α is selected.

F-test for comparison of model structures. Let M_1 and M_2 be two model structures, such that $M_1 \subset M_2$ (for example M_1 corresponds to a lower-order model than M_2) Further, let SSEi denote the sum of squared errors (or residuals) in the structure M_i (i=1, 2) and let M_i have p_i parameters. The test statistic

$$F_w = \frac{(SSE_1 - SSE_2)/(p_2 - p_1)}{SSE_2/(N - p_2)} \tag{3}$$

is used to compare the model structures M_1 and M_2. If $F_w > F_{\alpha;p_2-p_1;N-p_2}$, the decrease in loss function from SSE_1 to SSE_2 is significant and, hence, that the model structure M_2 is significantly better than M_1.

Akaike's information criterion (AIC). Another approach to model structure selection consists of using a criterion that in some way penalizes the decrease of the loss function with increasing model complexity.

$$\mathrm{AIC} = N \log\left(\frac{SSE}{N}\right) + 2p \tag{4}$$

with *SSE* the sum of squared errors, and *N* and *p* as defined before. The first term in equation (4) decreases with increasing *p* (increasing complexity) while the second term penalizes overparametrized models.

Experimental data collection and data processing

The experiments to evaluate the performance of the buffer capacity sensor were first performed on the effluents of 26 different domestic wastewater treatment plants. Two to eleven different samples were analyzed per plant. The samples were collected in October 1993 and June 1994. Second, the effluent of an industrial activated sludge wastewater treatment plant of a food company was monitored for 3 months (February to May 1994), with a sampling frequency of 3 to 5 samples per week. This plant was in a start-up phase, so that the effluent concentrations, especially of ammonium, showed a large variation (200 to 500 mg NH_4^+–N l^{-1} in the beginning and between 10 and 20 mg NH_4^+–N l^{-1} at the end of the measurement period). Third, 118 different surface waters in Flanders were sampled in September 1993. From each sample, two or more titration curves were recorded. The off-line laboratory analyses of ammonium, ortho-phosphate and COD were performed by two independent, certified laboratories, respectively referred to as lab A and B.

All titration curves were obtained with a laboratory construction of the titration sensor. This experimental set-up consisted of a pH adjustment unit to lower the pH of the sample to pH 2–3; an aeration unit, to strip off the carbonate buffer; and an automatic titration unit (Metrohm Titrino 716). The titration algorithm used was DET (dynamic equivalence-point titration), but in order to obtain the complete titration curve, no end-points were defined in the algorithm. The data processing was performed off-line.

Fixed buffer capacity model

A mathematical buffer capacity model containing the following components was used to fit the experimental buffer capacity data of river water and effluent samples: water, inorganic carbon (IC), ortho-phosphate, ammonium and an undefined component (called soap) with a pK_a between 4.0 and 6.0. The latter component stands for a range of substances (e.g. organic acids) that all have a buffer capacity in the range around pH 5. The detailed model specifications of the buffer capacity model are given in Table 1.

Table 1 Buffer capacity model specifications for a simulation interval between pH 4 and pH 10

Buffer	Variable	Initial guess or value	Estimated?	Lower limit	Upper limit
Water	pK_a	15.74	No		
	C_a	55.5 mol l^{-1}	No		
IC	$pK_{a\,1}$	6.37	No		
	$pK_{a\,2}$	10.25	No		
	C_a	2 mg CO_2 l^{-1}	Yes	0	5
o-PO_4	$pK_{a\,1}$	2.15	No		
	$pK_{a\,2}$	7.21	Yes	6.5	7.4
	$pK_{a\,3}$	12.35	No		
	C_a	5 mg P l^{-1}	Yes	0	200
NH_4^+	pK_a	9.25	Yes	9	9.75
	C_a	20 mg N l^{-1}	Yes	0	600
Soap	pK_a	5	Yes	4	6
	C_a	5×10^{-4} mol l^{-1}	Yes	0	0.02

Results and discussion

Fixed buffer capacity modelling results

A prototype titration sensor was used for the monitoring of pH buffering substances (Van Vooren *et al.*, 1996). The sensor was capable to give an indication of the ammonium and ortho-phosphate level in the tested effluents and surface waters. It was shown that the variability between the laboratory analyses and the titrimetric estimations is comparable to the variability between the two independent laboratory results. The proposed fixed buffer capacity model (see Table 1) has been shown to be useful for the detection of possible changes in the effluent composition (alarm generator function). However, it is suggested that a site-specific tuning of the mathematical model could offer some perspectives for better and more specific predictions. The *a priori* knowledge that holds for all titration curves is that an ortho-phosphate buffer, an ammonium buffer and an IC buffer are to be expected. It is considered important to use such *a priori* knowledge in the automatic buffer capacity model development. Therefore, the zero model or starting model is chosen in correspondence with the model specifications given in Table 1, except for the following modifications:

- The "soap" buffer is not included any more. The automatic modelling algorithm has now the flexibility to include no, one, two or more buffer systems that account for the previously used "soap" buffer.
- The simulation interval (previously between pH 4 and pH 10) is extended to an interval between pH 3.5 and pH 10.5. This offers the possibility to take into account more potentially present buffers.

Based on the above described zero model, the automatic model building algorithm may stepwise enter blind buffers in the model, but not with pK_a's in the 2 pH ranges 6.5–7.4 and 9-9.75, which are the lower and upper limits for the variable pK_a values of respectively ortho-phosphate and ammonium. Other important settings for the automatic model building algorithm in *bomb* are: $\alpha = 0.0001$ as the critical significance level for the Run-test and F-test, and 0.2 as the minimal range for a pK_a of a blind buffer.

In the following, these points will be investigated:

- What are the differences in the results when considering different model selection criteria?
- Is the automatic model building algorithm able to detect and quantify buffers other than ammonium and ortho-phosphate, and does this reveal extra information about the titrated sample?

- Is the automatic model building advantageous for ammonium and ortho-phosphate assessment, compared to the fixed model approach that was presented in the previous paragraph?

Evaluation of the model selection criteria

The ammonium and ortho-phosphate estimations resulting from automatically built buffer capacity models based on the three model selection criteria considered were compared with the laboratory determined concentrations. This was performed for the 118 Flemish surface waters. At the current stage, for samples of the type "surface water", it might be concluded that the AIC criterion is superior to the Run-test and F-test criterion. Although the AIC criterion sometimes tends to select high degree models, it does not suffer from the two major disadvantages of respectively the Run-test (i.e. that the criterion is sometimes never fulfilled) and the F-test (i.e. the selection of a too low degree model) (Van Vooren, 2000). Mostly, 2 or 3 blind buffers were sufficient to obtain the final or selected model. This information is useful for a more advanced monitoring of the water quality (represented by its buffer systems) compared to the fixed model approach.

Despite the significantly better results for many individual samples with the automatic modelling approach, the overall comparison between laboratory and titrimetric results via scatterplots was still comparable to the results obtained with the fixed model approach.

Effluents model building results

The automatic buffer capacity model building of effluent samples gives results similar to the surface waters. However, some new interesting phenomena were observed for the industrial effluent samples. One domestic wastewater effluent (Hofstade, sampled at October 19, 1993) and two industrial effluent samples (sampled respectively at April 20 and 27, 1994) are selected for more detailed analysis and discussion. The summarized results of the selected samples are given in Table 2.

The example in Figure 2(a) is a typical case of buffers interfering with the ammonium estimation. Without automatic model building, the estimated ammonium concentration was about three times higher than the measured laboratory concentration. With automatic model building, two interfering buffers at pH 9 and 10.5 of respectively 0.1 and 0.6 mmol l^{-1} are recognized. As a consequence, the ammonium estimation becomes lower than before, but the estimation is still almost two times higher than the laboratory concentration. This indicates that other interferences could be present at the same pK_a as ammonium. No interfering buffers around the ortho-phosphate pK_{a2} are found, and thus the estimated ortho-phosphate concentration is not significantly different compared to the previously obtained results. The standard deviations on the estimates of ortho-phosphate are rather high, indicating a high uncertainty of the estimated values.

The second and third example (in Figure 2(b) and 2(c), respectively) represent industrial effluent samples that were both taken in the third month of the measurement period. As mentioned earlier, the wastewater treatment plant was in a start-up phase, with very high ammonium concentrations (>200 mg N l^{-1}) in the first two months and lower concentrations (<20 mg N l^{-1}) in the last month of the measurement period. For the samples taken in the first two months, the fixed model approach resulted already in an acceptable agreement between the experimental and simulated data, and the automatic modelling approach produced similar results (results not shown). However, in the third month, extra buffer systems on top of the expected buffers appeared in the buffer capacity profiles, resulting in a bad fixed model fit. It is in the latter period that the automatically built models are found superior compared to the previously used fixed model. The extra added blind buffers were not always found at the same pK_a positions for the different samples, as illustrated in Figure

Table 2 Ammonium and ortho-phosphate results for three samples, compared with prior obtained results. Concentrations are expressed as mg N l^{-1} or mg P l^{-1} and the table entries are estimate ± standard deviation

		Automatic model building results	Previously obtained results (Van Vooren *et al.*, 1996)	
Buffer	**Figure**	**AIC**	**Laboratory[a]**	**Fixed model**
NH_4^+	2(a)	10.8 ± 0.42	5.89 ± 0.02	14.9 ± 0.19
NH_4^+	2(b)	17.0 ± 0.82	16.4 ± 3.68	23.1 ± 0.60
NH_4^+	2(c)	4.87 ± 0.94	2.03[b]	8.03 ± 0.33
o-PO_4	2(a)	2.89 ± 2.38	1.79 ± 0.02	2.36 ± 0.30
o-PO_4	2(b)	5.95 ± 7.07	5.75 ± 2.62	9.43 ± 1.41
o-PO_4	2(c)	6.43 ± 4.79	6.55 ± 1.06	14.7 ± 0.87

[a] Mean and standard deviation of the laboratory A and B results.
[b] There is only 1 laboratory result

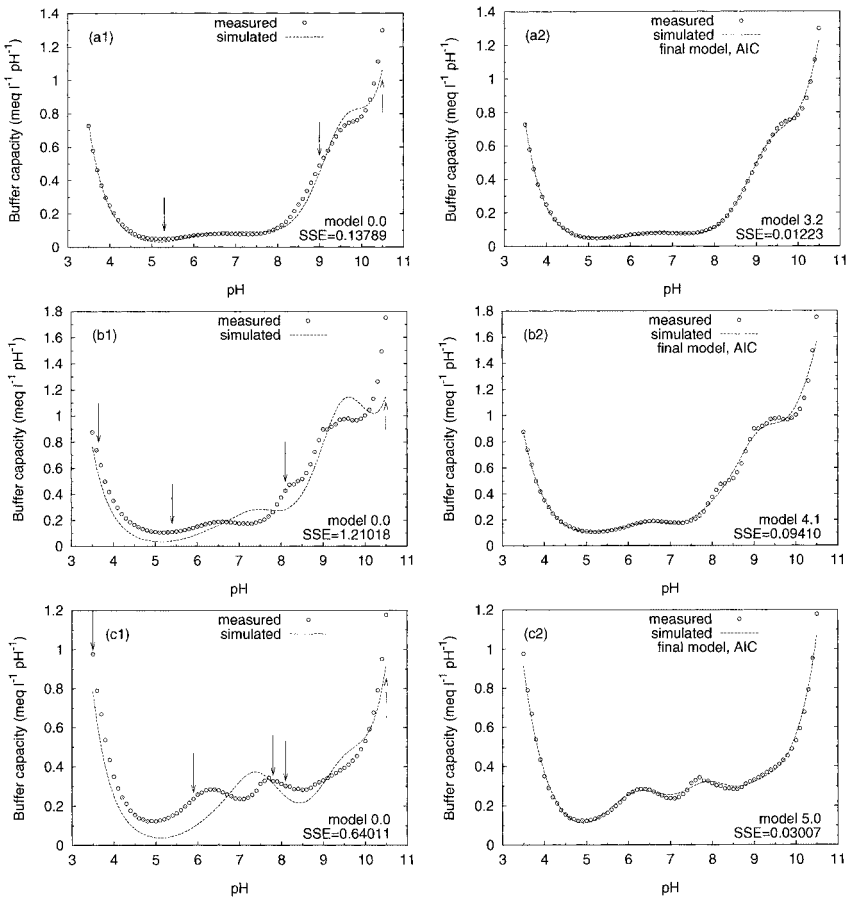

Figure 2 Experimental and simulated buffer capacity curves of a domestic wastewater effluent (a) and an industrial effluent (b) and (c). Two plots per sample show respectively the zero model (1) and the AIC selected final model (2). The arrows indicate the automatically proposed pK_a positions for model extension

2(b) and 2(c). Consequently, it was found that the ortho-phosphate and ammonium concentrations estimated with the automatically built models are much closer to the laboratory data compared to the previously obtained results (see Table 2). However, the standard

deviations (calculated from the variance-covariance matrix of the parameter estimates) on the estimated ortho-phosphate concentrations are high, indicating that a careful interpretation is necessary.

The benefits of the automatic buffer capacity model building can be summarized as follows:

- With the automatic modelling approach, it is possible to use a wider simulation pH range (e.g. between pH 3 and 11), whereas with the fixed model approach, one attempts to choose an as small as possible interval, to avoid problems of interfering buffers outside the strict pH range of interest. A larger simulation interval allows to detect more possibly interfering buffers.
- An automatic modelling approach allows to adapt the model quickly and efficiently to changing sample compositions. In the case of the industrial effluent, it has been shown that the most adequate buffer capacity model at the end of the measurement period was quite different from the best model at the beginning of the measurement period.
- If detailed *a priori* knowledge about the sample composition is available, one can define this buffer information in a "rich" zero model. If the automatic model building environment selects this zero model as the final model, it ensures that the zero model is still valid as an adequate model. If the final model is different from the zero model, it points to changing buffer compositions in the sample.
- Automatic buffer capacity modelling is useful for alarm generating purposes in case extra buffers are detected and quantified on top of the expected buffers defined in the zero model. Moreover, the model building algorithm will add blind buffers in order of importance. The corresponding standard deviations on the estimates can be used to statistically test whether the reported concentrations are significantly different from 0. The pK_a's of blind buffers can be used to identify the unknown pollutants.

Conclusions

The automatic model building algorithm that is implemented in the software *bomb* was applied to previously collected titration curves of effluent and river water samples, with the objective to develop tailor-made buffer capacity models. At present, the model building algorithm has been evaluated as robust and fail-safe.

There is no "best" model selection criterion for general purposes, because all criteria have advantages and disadvantages. On the one hand, the AIC sometimes selects overparametrized models, but on the other hand, it has the advantage of generally satisfying performance, and being independent of a user-defined critical significance level α. The Run-test suffers from the problem that its solution criterion is not fulfilled for any of all models built, whereas the F-test sometimes selects a model with a too low model degree.

It has been illustrated that the application of automatically built buffer capacity models mostly results in similar or better estimations of ammonium and ortho-phosphate compared to fixed buffer capacity models. For some applications (e.g. the industrial effluent), a fixed model approach is not useful because the buffer composition of the effluent stream can continuously change. For a number of selected samples (e.g. the industrial effluent samples in the last weeks of the measurement period), the estimations with automatically built models are highly superior to the fixed model approach.

The automatic buffer capacity model building approach offers a number of interesting perspectives compared to the use of fixed buffer capacity models. The approach can be applied as a support tool for characterization of unknown buffer capacity profiles or to develop an appropriate fixed model for a specific application. In retrospect, a lot of time could have been gained if the automatic modeller would have been available for the development of adequate models for the various applications investigated in this paper.

Acknowledgement

This research was part of the project 3G010297, which was financially supported by the fund for scientific research Flanders (FWO-VL).

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