Buffer Capacity Based Multipurpose Hard- and Software Sensor For Environmental Applications

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Introduction

During the last decades the demand for on-line (field) measuring techniques (process control, alarm generation,…) has increased significantly. An on-line multipurpose titrimetric sensor was developed. The hardware part of the sensor consists of a robust titrator unit to perform acid-base titrations. The software part of the sensor can be seen as the complete data interpretation of the recorded titration curves. This sensor allows the measuring of several buffering components in one sample using only one (relatively simple) set-up.

Principle of the titrimetric sensor

(1) Sampling
(2) Sample preparation (pH adjustment and CO_2 stripping)
(3) Recording of complete titration curve with own developed titration software
(4) Advanced data interpretation

- Calculation of buffer capacity profile
- Fit mathematical models with automatic buffer capacity model building algorithm
- Report buffer concentration and pKa

Automatic buffer capacity model building algorithm

Starting from a model using a priori knowledge on the sample, blind buffers (unknown monoprotic buffering componounts) are sequentially added to the model (based on detailed residuals analysis) in order to obtain a better description of the buffer capacity profile. The criterium used to define the pKa for the blind buffer is the maximum sum of residuals, as illustrated in Figure 1.

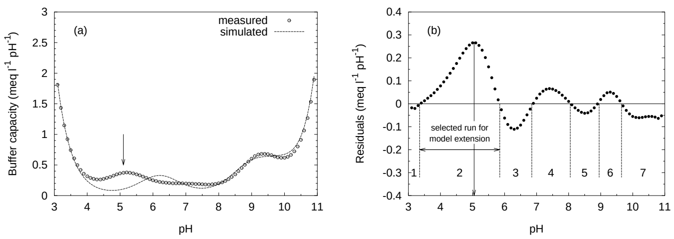

Figure 1. Experimental and simulated buffer capacity curves (a) and calculated residuals (b), with indication of the runs, the best candidate run for model extension and the best candidate pH within that run

To select the most appropriate model from the resulting set of automatically built models for each individual sample, 6 different model selection criteria were evaluated (run-test, F-test, AIC, AIC_C, FPE and SIC). No best general model selection criterium was found. The AIC, AIC_C, FPE and SIC mostly select the same model. The Run-test criterium performed best for the simplest types of buffer capacity curves whereas the F-test was better for the more complicated type of curves.

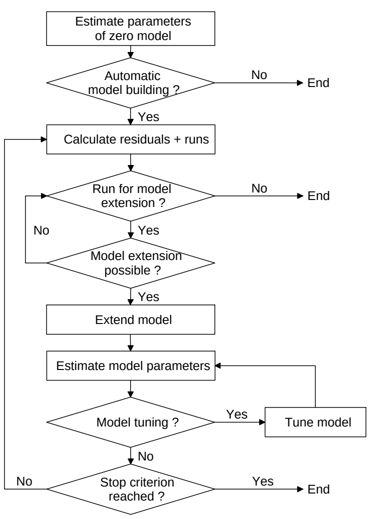

Figure 2. Flowchart of the automatic model building algorithm

Illustrating example

Figure 3 shows experimental and simulated buffer capacity curves of a well-kown sample containing a monoprotic and triprotic buffer (Table 1). The different curves in the figure show the sequentially built models for this test case. Table 2 gives the estimated pK_a and concentrations for the different buffers found through the automatic model building algorithm.

Table 1. Chemicals for the preparation of the well-known sample (Test case)

Chemical	Code	Protonicity	pK_{a1}	pK_{a2}	pK_{a3}	Concentration ($mmol l^{-1}$)
Sodium acetate	ace	1	4.75			0.5
Citric acid	cit	3	3.14	4.77	6.39	0.33

Model 5.0 was selected by most of the model selecion criteria (Except for the run-test which selected Model 4.0). The algorithm introduced two unexpected buffers in the third and fifth modelling step. Further investigation showed that it is a fair assumption that the buffer introduced in the third modelling step originates from interfering silicates. The buffer introduced in the fifth modelling step is not considered very important, however, the concentration is still significantly different from 0 (t-test, α=0.01).

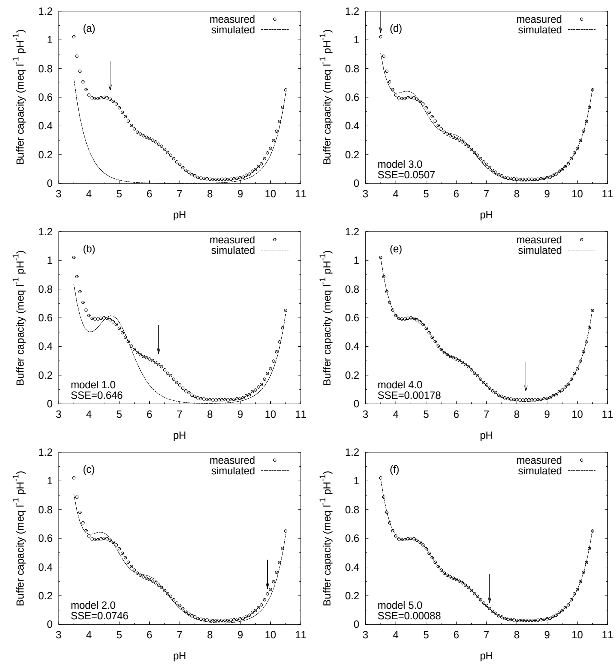

Figure 3. Experimental and simulated buffer capacity curves af a well-known sample. The stepwise model building starts with plot (a) and ends with plot (f) (the final model). The arrows indicate the proposed pK_a positions for model extension

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Table 1. Simulation results of a well-known samle for the automatic built buffer capacity models illustrated in Figure 3, plots (b) until (f). The concentrations are expressed in $mmol\ l^{-1}$ and the table entries are estimate ± standard deviation

	Model 1.0 Plot (b)	Model 2.0 Plot (c)	Model 3.0 Plot (d)	Model 4.0 Plot (e)	Model 5.0 Plot (f)	A posteriori interpretation
pK_a blind1	4.78 ± 0.06	4.51 ± 0.03	4.50 ± 0.02	4.74 ± 0.01	4.74 ± 0.007	cit + ace
pK_a blind2		6.08 ± 0.06	6.08 ± 0.05	6.24 ± 0.01	6.22 ± 0.008	cit
pK_a blind3			9.88 ± 0.21	9.90 ± 0.04	9.99 ± 0.03	?
pK_a blind4				3.50 ± 0.05	3.50 ± 0.03	cit
pK_a blind5					8.21 ± 0.13	?
C_{blind1}	1.00 ± 0.05	0.93 ± 0.02	0.93 ± 0.02	0.83 ± 0.008	0.83 ± 0.006	cit + ace
C_{blind2}		0.47 ± 0.02	0.47 ± 0.02	0.40 ± 0.004	0.40 ± 0.003	cit
C_{blind3}			0.08 ± 0.02	0.08 ± 0.003	0.08 ± 0.002	?
C_{blind4}				0.32 ± 0.007	0.32 ± 0.005	cit
C_{blind5}					0.02 ± 0.002	?

Some developed applications

- Automated on-line monitoring of pH buffering substances of wastewater treatment effluent and river water (alarm generation)
- Monitoring of tertiary algal wastewater treatment (influent, effluent and reactor content)
- On-line simultaneaous measurement of nutrients N and P in destructed and diluted manure samples

Conclusions

The automatic buffer capacity building algorithm:
- Is used to develop tailor-made models
- Is robust and fail safe
- Uses advanced model selection criteria
- Is useful to obtain supplementary in formation compared to a fixed model approach

Rerefences

L. Van Vooren. *Multi purpose hard- and software sensor for environmental applications*. PhD thesis, Universiteit Gent, Coupure links 653, B-9000 Gent, 2000