



## AUTOMATIC BUFFER CAPACITY BASED SENSOR FOR EFFLUENT QUALITY MONITORING

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### ABSTRACT

The use of an automatic on-line titration unit for monitoring the effluent quality of wastewater plants is presented. Buffer capacity curves of different effluent types were studied and validation results are presented for both domestic and industrial full-scale wastewater treatment plants. Ammonium and ortho-phosphate monitoring of the effluent were established by using a simple titration device, connected to a data-interpretation unit. The use of this sensor as the activator of an effluent quality proportional sampler is discussed. Copyright © 1996. Published by Elsevier Science Ltd.

### KEYWORDS

Buffer capacity; effluent quality; mathematical modeling; on-line monitoring; pH titration; quality dependent sampling.

### INTRODUCTION

Titration is a technique which by its nature is discontinuous, but accurate and precise. It is mostly used for pure or purified samples containing moderate concentrations. However, titration can also be used to analyze several species in more complex matrices, e.g., ferrous hydroxide, ammonia, organic acids, ...in landfill leachate (Sawyers and Dentel, 1992; Gibs *et al.*, 1982), volatile fatty acids in anaerobic digestors (Powell and Archer, 1989; Anderson and Yang, 1992), ammonia and carbonate in cattle slurry (Husted *et al.*, 1991), protein degradation products and organic acids in silage press-juice (Moisio and Heikonen, 1989).

There are actually two ways to interpret pH titration curves. The first one is the classical end-point titration used to determine one component in a well defined matrix. Many examples of this type of titration can be found in APHA (1992). The second type is based on more advanced data interpretation techniques. This can be based on simple calculations using a limited number of characteristic points of the titration curve (typical 3 to 5 points) (Moosbrugger *et al.*, 1993), or can be based on the modeling of the complete titration or the corresponding buffer capacity curve (Gordon, 1982).

In this paper, the possibilities of a titration based sensor for purified wastewater are investigated. First the principle of the measurement is presented, followed by the presentation of two validation experiments, one on domestic wastewater effluents and a second one on an industrial effluent. The purpose of the validation experiments was twofold. First, the accuracy and precision were evaluated by comparing the concentrations of ammonium and ortho-phosphate in the effluent as found with the titration sensor with the results of the off-line analysis. Second, the relationship was investigated between classical effluent parameters like the COD and the buffering components not related to the ammonium or phosphate buffer.

### PRINCIPLE OF THE DEVICE

The elementary measurement used in this sensor is a pH measurement. Successive measurements of pH as a function of stepwise acid or base addition (with known concentration) to the sample is called a titration curve. In this work only stepwise base addition is used. From this measured titration curve (typically around 30 to 50 points), the buffer capacity at each point is calculated as the derivative of the amount of base needed (in meq/l) for a pH increase of one pH unit. The function obtained as the buffer capacity (meq/l.pH) in function of the pH is called the buffer capacity profile. The pH(s) at which a certain component gives its maximum buffer capacity is (are) called the  $pK_a$ (s) of that component. For samples containing several pH buffering components, the buffer capacity curve consists of the sum of the buffer capacities of each individual component. From the buffer capacity curve, estimates of the different buffering components can be computed using a mathematical model. The principle of the decomposition of a complex buffer capacity curve into its components is illustrated in Figure 1.

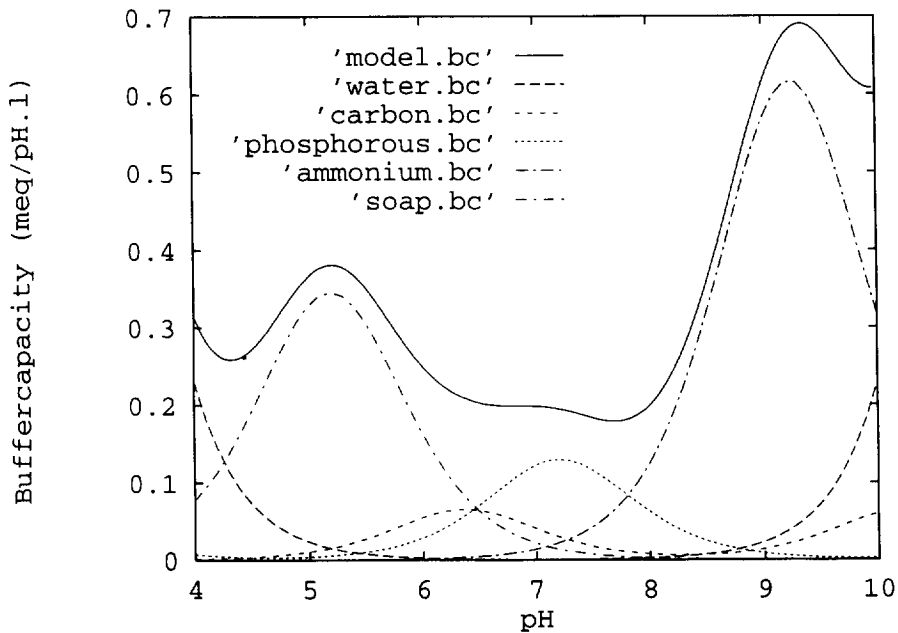


Figure 1. Buffer capacity curve of an aqueous model system ('model.bc') containing water ('water.bc'), 5 mg  $CO_2/l$  ('carbon.bc'), 7 mg  $oPO_4-P/l$  ('phosphorus.bc'), 15 mg  $NH_4-N/l$  ('ammonium.bc') and 6 mmol/l of a soap ('soap.bc')

An example of three different Flemish surface waters with various loads of ammonium and ortho-phosphate is given in Figure 2. Ortho-phosphate buffers around pH 7, while the ammonium buffer can be seen around pH 9.25.

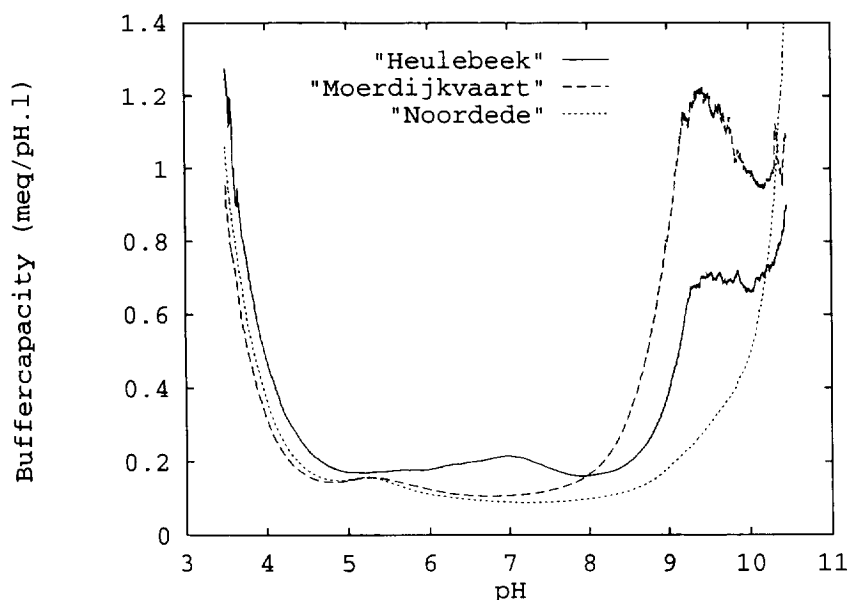


Figure 2. Buffer capacity curves from 3 different surface waters: Heulebeek (10.6 mg  $oPO_4 - P/l$ ; 3.5 mg  $NH_4 - N/l$ ), Moerdijkvaart (1.0 mg  $oPO_4 - P/l$ ; 9.6 mg  $NH_4 - N/l$ ) and Noordede (0.5 mg  $oPO_4 - P/l$ ; 1.0 mg  $NH_4 - N/l$ ).

The principle of the sensor is illustrated in Figure 3. In the wet part, the first step is the sampling (typically 100-200 ml) and a pH adjustment to pH 2, followed by a short aeration of 5 minutes to strip the dissolved  $CO_2$ . In the second step a dynamic titration is effected from pH 2 to 11. The data processing part is performed in a computer connected to the titration apparatus. First, the titration data are filtered (smoothed, outliers removed) if necessary. Second, the buffer capacity at each point of the titration curve is calculated as the derivative of the amount of base needed for a pH increase of one pH unit. The next step is the mathematical model selection followed by a parameter estimation. The candidate models differ in the number of buffering components they include. After the parameter estimation, the concentrations and eventually corresponding  $pK_a$  values for the buffering components defined in the model are obtained. Eventually a different model can be selected if the fit is not satisfying.

The mathematical models used describe the chemical equilibria taking place in the reaction vessel during titration. Models were built using different chemical reaction equilibria described by Stumm and Morgan (1981).

In the final output of the sensor, a list of concentrations of buffering components is given. If certain preset values are exceeded an alarm is given and/or an automatic sampler is activated to take a sample for further laboratory analysis. The time for 1 complete run is approximately 30 minutes.

## MATERIALS AND METHODS

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 installation. Secondly, the effluent of an industrial activated sludge wastewater treatment plant of a food company was monitored for 4 months, with a sampling frequency of 3 to 5 samples per week. This installation was in a start-up phase, so that the effluent concentrations, especially of ammonium, showed a large variation (200 to 500 mg  $NH_4 - N/l$  in the beginning and between 10 and 20 mg  $NH_4 - N/l$  at the end of the measurement period).

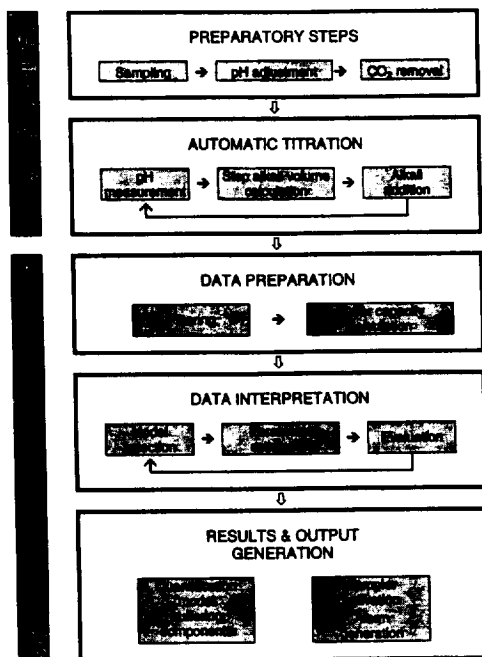


Figure 3. Principle of the buffer capacity based effluent monitor.

All titration curves were obtained with a prototype of the titration sensor. This experiment set-up consists 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 716 DMS Titrimo, Metrohm Ltd., Switzerland). The titration algorithm used was DET (dynamic end-point titration), but in order to obtain the complete titration curve, no end-points were defined in the algorithm. A PC-XT was coupled to the titrator via RS-232 for data capturing.

The off-line laboratory analysis of ammonium, ortho-phosphate and COD was performed by two independent certified laboratories, respectively referred to as laboratory A and B.

The data processing of the collected titration data was performed off-line, using a workstation (Apollo 425e, Hewlett Packard). The software developed was written in C++ and parameter optimization was performed using routines from M++ release 4.0 (Dyad Software Corp., USA).

A mathematical buffer capacity model containing the following components was used for the validation: an undefined component (called soap, expressed in mol/l) with a  $pK_a$ -value between 4.0 and 5.0; a bicarbonate component (expressed in mg  $CO_2/l$ ) with  $pK_{a1} = 6.37$  and  $pK_{a2} = 10.25$ ; an ortho-phosphate component (expressed in mg  $P/l$ ) with  $pK_{a1} = 2.12$ ,  $pK_{a2} = 7.21$  and  $pK_{a3} = 12.67$ ; and an ammonium component (expressed in mg  $NH_4-N/l$ ) with a  $pK_a$ -value between 9.0 and 9.5.

## RESULTS AND DISCUSSION

The average ammonium concentration in the domestic wastewater effluents was  $11.8 \pm 9.1$  mg  $NH_4-N/l$  for laboratory A;  $11.2 \pm 7.8$  mg  $NH_4-N/l$  for laboratory B and  $26.0 \pm 11.0$  mg  $NH_4-N/l$  with the titration based sensor. The average concentration for ortho-phosphate in the domestic wastewater effluents was  $2.1 \pm 1.6$  mg  $P/l$  for laboratory A;  $2.3 \pm 1.6$  mg  $P/l$  for laboratory B and  $6.6 \pm 5.2$  mg  $P/l$  with the titration based sensor. Hence, for both ammonium and ortho-phosphate, the titration based sensor overestimates the concentration with a factor 2 to 3 in comparison with the laboratory results. This can be explained by the fact that buffering components other than ammonium and phosphate are present in the effluents, and they are

modelled as ammonium or phosphate in the buffer capacity model. However there is a different interpretation of the regression equations for ammonium and phosphate: for ammonium the overestimation was mainly due to the negative intercept of the regression equation, meaning that there is a constant interfering buffer component, independent of the concentration of ammonium; and for ortho-phosphate the overestimation was mainly due to the slope of the regression equation which is lower than 1, meaning that the interfering buffer components are increasing when the ortho-phosphate concentration is increasing.

Nevertheless, a useful correlation between the laboratory results and the titration sensor was obtained, as illustrated in Figures 4 and 5. These two figures show the results of a linear regression analysis with the 95% confidence and prediction intervals between the titration sensor result and the analysis of laboratory A for ammonium and ortho-phosphate respectively. For ortho-phosphate, only concentrations found by the titration sensor lower than 8 mg P/l are considered, because on a few installations the interferences of buffering components around pH 7 to 8 were too high to be useful for ortho-phosphate estimation.

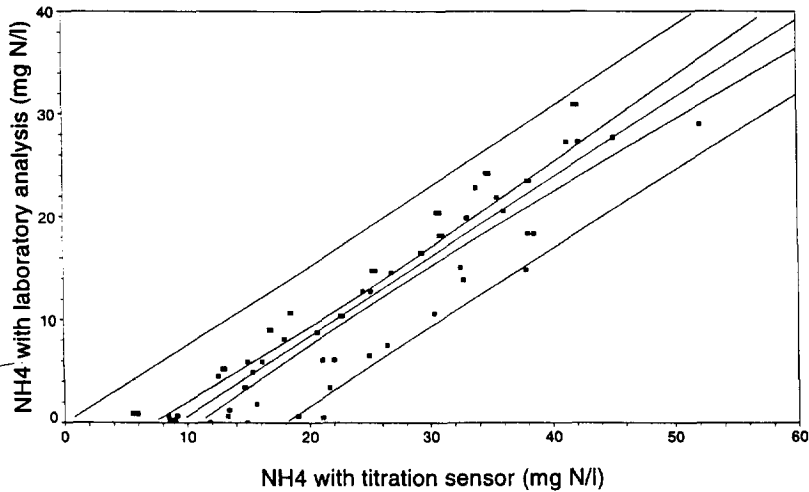


Figure 4. Regression line and 95% confidence and prediction intervals between the results obtained with the titration sensor and the analysis of laboratory A for ammonium on 26 domestic wastewater effluents.

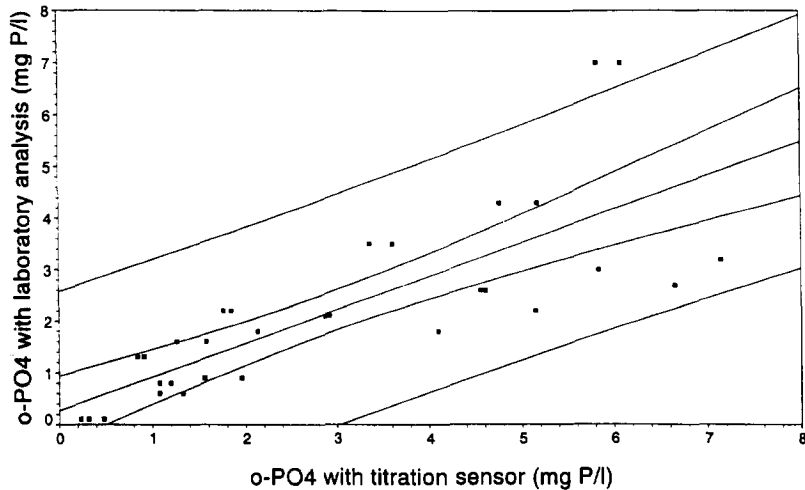


Figure 5. Regression line and 95% confidence and prediction intervals between the results obtained with the titration sensor and the analysis of laboratory A for ortho-phosphate on 26 domestic wastewater effluents.

The average ammonium concentration in the effluent of the industrial wastewater treatment plant was  $115 \pm 92$  mg  $NH_4-N/l$  for laboratory A;  $108 \pm 117$  mg  $NH_4-N/l$  for laboratory B and  $141 \pm 109$  mg  $NH_4-N/l$  with the titration sensor. The average concentration for ortho-phosphate in the industrial effluent was  $3.1 \pm 2.0$  mg  $P/l$  for laboratory A;  $3.6 \pm 2.4$  mg  $P/l$  for laboratory B and  $8.1 \pm 5.5$  mg  $P/l$  with the titration based sensor. A comparison of the three independent ammonium analyses during the measurement period is shown in Figure 6. In the beginning of the measurement period the ammonium concentrations were very high because of the start-up phase of the plant. At the end of the measurement period, the ammonium concentration decreased below 10 mg  $NH_4-N/l$ . Over the whole period the titration sensor was able to estimate the ammonium concentration in the effluent. The Pearson correlation coefficient between the titration sensor and the laboratory measurements was  $r = 0.96$ , almost the same value as the correlation between the ammonium concentration measured in the two independent laboratories ( $r = 0.97$ ).

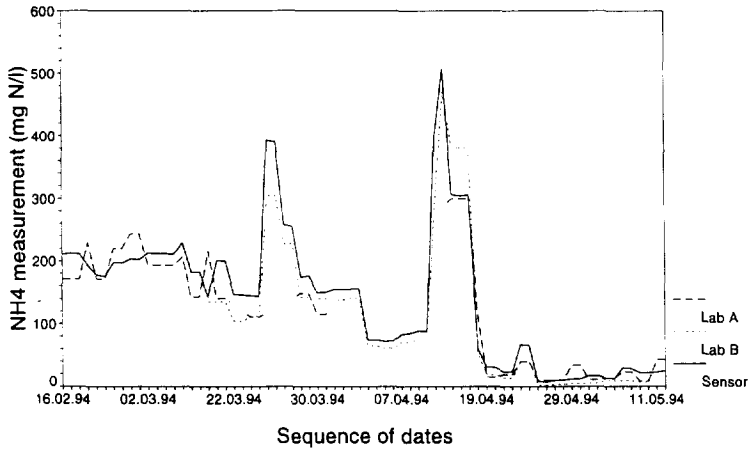


Figure 6. The ammonium concentration measured by two independent laboratories (Lab A and Lab B) and the titration sensor (Sensor) in the effluent of an industrial wastewater treatment plant.

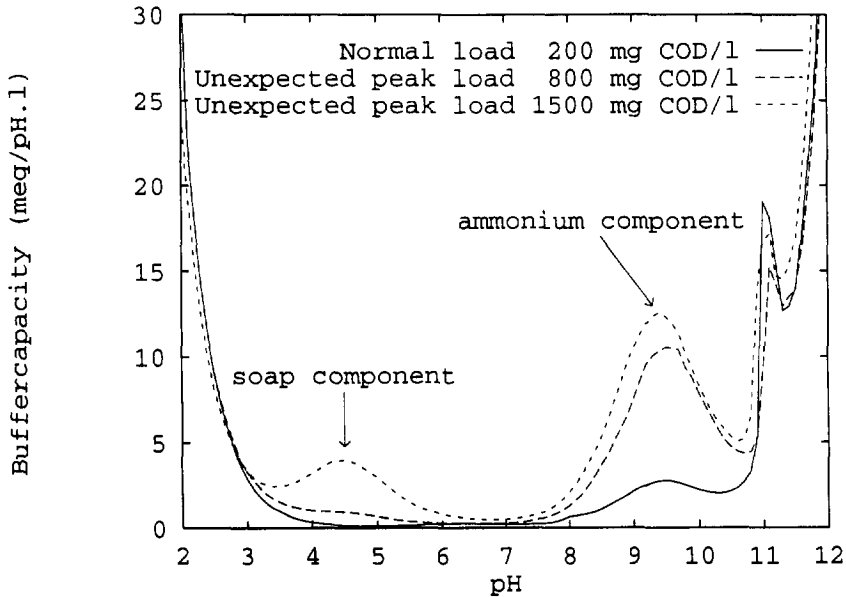


Figure 7. Buffer capacity curves of an industrial effluent with a normal COD load and containing 2 unknown peaks.

The Pearson correlation coefficient between the concentration of the undefined buffering component between pH 4 and 5 (assumed to be the soap component) and the COD in the effluent was 0.83. This buffering component was consequently used as an indicator of sudden organic loads in the effluent as illustrated in Figure 7. This figure shows the buffer capacity curves of the effluent during normal operation (200 mg COD/l), and two unexpected peak loadings (800 and 1500 mg COD/l respectively). The buffering components between pH 4 and 5 were not identified conclusively.

## CONCLUSIONS

The proposed titration sensor can be used for effluent monitoring of pH buffering substances. Experiences with different types of effluent have shown that the accuracy and precision is influenced by the composition of the effluent. The sensor is capable of giving an indication of the ammonium and ortho-phosphate level in the effluents tested. The sensor can be used for alarm triggering when the buffer capacity profile changes. The buffer capacity at certain  $pK_a$ s is suggested to give an indication of the organic load. Due to possible interferences of buffering components and the presence of unmodeled buffering components in the effluent, this titration sensor cannot be proposed for use as an analytical instrument. Rather it should be used as an effluent quality indicator and detector of possible changes in the effluent composition. The titration sensor is suitable for integration in a robust and reliable automated instrument. An important advantage of the sensor is that no filtration is required. The model database can be easily extended and fully adjusted to particular requirements. This sensor coupled to an automatic sampler can be used for quality dependent sampling. In this case the buffer capacity profile is used as a fingerprint for the water composition, and when the fingerprint is changing, a sample is taken for further laboratory analysis.

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