UNIVERSITEIT
GENT

Faculteit Landbouwkundige en
Toegepaste Biologische
Wetenschappen

Academiejaar 1999 – 2000

Buffer capacity based multipurpose hard- and software sensor for environmental applications

Een op buffercapaciteit gebaseerde multifunctionele hard- en softwaresensor voor milieutoepassingen

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Thesis submitted in fulfillment of the requirements for the degree
of Doctor (Ph.D.) in Applied Biological Sciences

Proefschrift voorgedragen tot het bekomen van de graad van
Doctor in de Toegepaste Biologische Wetenschappen

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Summary

In this work, a multipurpose titrimetric sensor was developed. The hardware part of the sensor developed in this work consists of a titrator unit, capable to perform acid-base titrations of aquatic samples. A titration curve has a typical S-shape, and can be transformed into a buffer capacity profile with an appropriate mathematical algorithm. The software sensor part of this work can be seen as the complete data interpretation of the recorded titration curves. The developed hard- and software sensor differentiates itself from most existing sensors by the fact that the whole and detailed titration profile is used for model-based interpretation. It is a multipurpose sensor because, on the one hand, it is useful for the quantification of buffering components (e.g. ammonium and ortho-phosphate in effluents or in destructed animal manure samples), and, on the other hand, it can be used as an alarm generator or early warning system (e.g. the detection of accidental pollutant discharges in rivers). An important part of the research described in this thesis was performed in the framework of research projects in which industrial partners were involved. Therefore, the research described in this thesis is interdisciplinary and practically oriented.

The first part of the thesis describes the fundamentals and the background of the research work. The constructive approach, illustrated with didactic examples should allow the reader to obtain a solid introduction and a consistent overview of pH buffer capacity modelling. This overview was partially based on literature research, however, major parts were adapted or further developed to fit the requirements of this work. Furthermore, in the literature a number of pitfalls and serious confusions related to this subject were pointed out. An interesting aspect is that not only buffer capacity models were developed for the simplest type of chemical reactions (acid-base equilibria), but that also more complicated buffer systems (i.e. where complexation and/or precipitation reactions occur) could be considered in the same framework. Appropriate simulation software was developed for each of the presented approaches. Further, a literature review on field technologies for on-line measurement in wastewater treatment systems, rivers and other aquatic streams is presented.

The second part of the thesis summarizes the main software developments. A commercial automatic titrator with a built-in dynamic titration algorithm was used to collect the experimental titration curves. Using this algorithm, some disadvantages were encountered, and therefore a combined data- and model-driven titration algorithm was developed, capable of performing the titration task as needed for the purpose of this work. A dosing system, coupled to a computer and using the developed algorithm also offers perspectives for use in the laboratory as an alternative for traditional end-point titrators. The complete data processing part of the titrimetric sensor is implemented in the software *bomb* (buffer capacity optimal model builder), with

strong emphasis on the robustness for field-use. From a particular titration curve, this software extracts information about individual buffer systems and estimates their concentrations. Further, the same software is capable to automatically build buffer capacity models.

The third part of this work is application oriented. Three on-line (field) application areas for the developed sensor were investigated in detail: effluent and river water monitoring, algal wastewater treatment monitoring and animal manure nutrient measurements. The minimum amount of ammonium and ortho-phosphate that can be successfully recovered with the buffer capacity based sensor is around 0.5 $mg\,\mathrm{N}\,l^{-1}$ and 0.5 $mg\,\mathrm{P}\,l^{-1}$ respectively. These values are only indicative, because they are case dependent. The results obtained show that the buffer capacity based sensor is an useful measurement system for on-line monitoring of ammonium and ortho-phosphate in effluents, river waters and algal wastewater treatment systems. Because the titrimetric measurement methodology is undoubtedly sensitive to interferences, the sensor application should in the first place be seen in the context of alarm generation. In an algal wastewater treatment plant, the inorganic carbon buffer could accurately be assessed with the developed sensor, and this measurement was interpreted as an useful control input. The simultaneous measurement of ammonium, ortho-phosphate and inorganic carbon with one single device was experienced as an important advantage of the developed methodology.

The on-line measurement of nitrogen and phosphorus in animal manure is a new application area, for which the developed sensor was evaluated. In Flanders, a taxation system on the production and surplus of nitrogen and phosphorus has been approved (Mestdecreet, May 11th, 1999). In this framework, increasing demands for analyses of N and P in animal manure and other organic streams are to be expected in the coming years. The most important difference compared to the other applications is that the titrated sample is now free of organic interferences because of a destruction step with H_2SO_4 and H_2O_2 prior to titration. Complexation reactions with Ca^{2+} and Fe^{3+} were modelled and pointed to be responsible for extra buffer capacities around pH 5, pH 8 and pH 10. It was also found that the buffer capacities of o-PO_4 and NH_4^+ (the buffers of main interest) are only influenced to a limited extent by the complex formation reactions. Taking into account some further optimizations discussed in this work, the analysis results with this titrimetric sensor are expected to be comparable with the laboratory results. The strongest points of the titrimetric method are: Simultaneous N and P measurement with one method, minor sample manipulations, N and P results within 30 minutes, low and inexpensive chemical consumption, consumption of only one and non-hazardous reagent (NaOH).

The fourth part of this work describes the automation of buffer capacity model building, of which the purpose is to efficiently find an useful and adequate buffer capacity model, tailormade for each individual sample. This methodology supports a new idea developed in this work, being 'quality proportional sampling' in effluents and river waters. This is proposed as an alternative to time or flow proportional sampling. It is suggested that the buffer capacity profile is used as a fingerprint for the water composition. When the fingerprint is changing, an alarm is triggered and a sample is automatically taken for further laboratory analysis. For a number of selected samples (e.g. industrial effluent samples), the estimations with automatically built models were highly superior to the fixed model approach, because the buffer composition was drastically changing during the measurement period. Other benefits of the automatic modelling approach are its usefulness for titrator problem detection and its application as a support tool for the characterization of unknown buffer capacity profiles.