Submersible probe with in-line calibration and symmetrical reference element for long-term continuous measurements

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Nitrogen plays an essential role in plant and crop growth, promoting photosynthesis, which is essential for a healthy ecosystem. Although nitrogen is naturally present in the atmosphere, plants mostly absorb it through the soil. To enhance plant growth and therefore productivity, nitrate fertilisers have been used routinely in agriculture all over the world. At the same time, due to leaching in the groundwater or surface runoff, nitrate pollution has become an increasing concern for water pollution. In 1991, the European Commission (EC) established a decree aiming to reduce nitrate pollution and prohibit further pollution.[1] Since this directive, the use of nitrate-based fertilisers has been more adequately regulated and systematic water quality monitoring has been implemented. Although recent trends show a decrease of nitrate levels and an increase of the general water quality, the monitoring process is not uniform and still rather tedious. The current strategy relies on fixed sampling stations and punctual sampling at strategic sites, which both require manpower and expensive measurement techniques making it impossible to ensure a constant monitoring of nitrate levels.

Submersible potentiometric probes have been used previously in environmental studies,[2] but they require a pump to drive the sample towards the measuring site. To enable constant monitoring, the pump would have to run continually, which would lead to unreasonable power consumption.

We present here a new nitrate-selective submersible probe that can perform independent and continuous measurements over an extended period of time. In this case the sensing head is located directly in contact with the sample allowing for constant monitoring without any additional power. An in-built miniature low consumption peristaltic pump can be pre-programmed to perform a one-step calibration at a predetermined time interval to correct for underlying drifts that would bias the results. To reduce the temperature dependency on the sensor signal, a new reference element based on the principle of electrochemical symmetry has been tested and implemented into the probe. This probe has been successfully deployed in Lake Geneva and the Arve river during field campaigns and the nitrate levels that were measured on-site were comparable with those of traditional measurements methods. Due to its low power consumption and drift correction, it is estimated that this system can run maintenance-free for several months.

[1] *European Commission (EC). Official Journal L 375*, **31/12/1991**, 0001–0008.

[2] N. Pankratova, G.A. Crespo, M.G. Afshar, M. Coll Crespi, S. Jeanneret, T. Cherubini, M.-L. Tercier-Waeber, F. Pomati, E. Bakker, *Environ. Sci-Proc. Imp.* **2015**, 17 (5), 906-914