HAS MICROFLUIDICS WITH NANODROPLETS FINALLY DELIVERED A SOLUTION FOR CONTINUOUS IN SITU MONITORING OF CRITICAL COMPONENTS FOR THE WATER USING AND PROCESSING INDUSTRIES?

SouthWestSensor Ltd has developed a nanodroplet microfluidics based platform technology that brings lab analysis to the water source. Perfectly suited for the continuous monitoring of nutrients and pollutants in fresh and sea water in applications ranging from environmental monitoring to waste water process control. The small sensor footprint and high-frequency lab quality data combined with low reagent and power consumption means long term autonomous deployment is possible in the field.

The monitoring of chemical quality has always been a critical part of the cycle of use for water from the abstraction point, through the processing and delivery of water to the end user and finally for the treatment and disposal of waste waters back into the environment.

Historically this has primarily been achieved by laboratory-based analysis on grab samples taken in the field which has many disadvantages. The logistics and costs of widespread sampling has historically limited the number of testing sites and frequency of testing, which in turn has limited the volume and time relevance of the data collected.

This process is also limited in terms of the time from sampling to result due to the time taken from sampling to laboratory and also on the sample throughput capacity of the laboratory which may be processing samples from a wide geographical area and many sources. The introduction of high throughput laboratory instrumentation, in-field autosamplers to collect multiple samples (or a time averaged composite sample) over a period of time and the use of passive samplers have all been employed to try and address some of these shortcomings. However, this has had limited success when it comes to using the analytical data for process monitoring and control or to detect and respond to transient excursions in the chemicals species of interest.

Advanced on-line process monitoring, and control has been adopted in many manufacturing industries and it begs the question why this technology has not yet been widely adopted in the water processing industries. Unfortunately many of the successful techniques for on-line analysis in the manufacturing industries measure bulk components in the percent range whereas many of the methods used in water analysis are for components in the trace analysis range (typically 1-100 mg/l) and are often based on traditional "wet chemistry" standard methods including titrimetric and colorimetric analysis.

The automation of these traditional methods to provide higher throughput lab-based analysis has been achieved using continuous flow analysis techniques including segmented flow analysis and later flow injection techniques. Segmented Flow Analysis was invented in 1957 by Leonard Skeggs and commercialized by Jack Whitehead's Technicon Corporation in the AutoAnalyzer instrument. The instrument is based on a continuous stream of liquid which is divided by air bubbles into discrete segments in which chemical reactions can be carried out. The continuous stream of liquid samples and reagents are combined and transported in tubing and mixing coils. The air bubbles segment each sample into discrete packets and act as a barrier between packets to prevent cross contamination as they travel down the length of the glass tubing. The air bubbles also assist mixing by creating turbulent flow. The presence of the bubbles creates an almost square wave profile and therefore bringing the reaction to steady state does not significantly decrease throughput but enables the lowest detection limits to be reached. The continuous segmented flow analyzer consists of different modules including a sampler, pump, mixing coils, optional sample treatments, a detector, and data generator. Standardized methods for segmented flow analysis have been published by ASTM, the US EPA and ISO for environmental analytes such as nitrite, nitrate, ammonia, cyanide, and phenol.

Although these lab based approaches can be highly automated and can help tackle the laboratory bottleneck they are not suitable for application as a field based analyser as they require a high degree of maintenance, require regular replenishment of significant volumes of reagents and removal of the resulting chemical waste. However, the development of the segmented flow principle to work in a microfluidic based platform by SouthWestSensor has created a paradigm shift in the applicability of conventional wet chemical based analysis for high frequency continuous monitoring in situ.

SouthWestSensor (https://southwestsensor.co.uk/) was founded in 2015 to commercialise the microfluidic technology developed by the research group of Dr Xize Niu at the University of Southampton in the UK. The company has been fully operational since May 2017 and is working on applying microfluidic based sensor technologies for rapid time-based monitoring of components with a focus on healthcare and water industry sectors. In Q4 2019 the company launched the SWS DropletSens™ probe for the simultaneous determination of Nitrate and Nitrite.

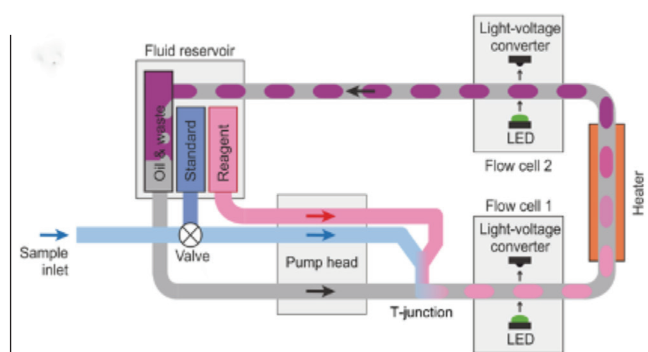

Figure 1: Schematic of the SWS DropletSens™ Monitor for Nitrate and Nitrite

The SWS DropletSens™ Monitor for Nitrate and Nitrite

In this article we will give a brief overview of the principles employed but a more detailed description of the technology and how it is applied has been published in the journal Environmental Science and Technology (1).

Microfluidic-based chemical sensors take laboratory analytical protocols and miniaturize them into field deployable systems for in situ monitoring of water chemistry to deliver highly efficient water sampling and analysis in a small, compact format with a significantly lower cost of ownership than conventional wet chemical approaches. In this application the sample is mixed with on-device reagents and injected into a stream of oil to form discrete nanodroplet zones in which the reagents mix and react with the species to be measured in the sample. The resulting coloured reaction product is then quantified photometrically using custom designed detectors. A schematic of the microfluidic analysis process is shown in Figure 1.

The SWS DropletSens™ Monitor for Nitrate and Nitrite employs the long established Griess Test where nitrite is detected first, based on the chemical diazotization reaction with sulphanilamide and N-1-napthylethylenediamine dihydrochloride (NEDD) under acidic conditions to form the coloured product. Following the detection and quantification of nitrite the flow of sample nanodroplets is heated, with vanadium (III) chloride to reduce any nitrate to nitrite which then further reacts with sulphanilamide and NEDD and the combined nitrate/nitrite concentration is measured photometrically by a second detector cell and the nitrate concentration is then calculated by difference. The sensor also includes automated internal standard checks using an in device nitrate standard solution.

The use of microfluidic discrete nanodroplet technology in this device has many advantages including:

- Rapid mixing and subsequent reaction of reagents and sample in each droplet aiding result consistency and giving reliable & accurate data (error < 10%)
- High sampling frequency – one nanodroplet is generated every 10 seconds giving autonomous high frequency data with a capacity of over 8000 analyses per day allowing the monitoring and capture of transient events.
- Low reagent and power consumption with a small instrumental footprint means long term autonomous deployment is possible in the field
- Low maintenance with user replaceable reagent cartridge (1 month for continuous use), simplifying reagent replenishment and reducing the risk of chemical exposure during routine maintenance
- Periodic internal standard checks
- Real-time data logging with on-board and Cloud data storage options
- Supports remote monitoring and control

Deployment in a Tidal River

The first test deployment of the DropletSens™ Monitor for Nitrate and Nitrite was in the River Itchen, which is a chalk river on the south coast of the UK and feeds ultimately into the English Channel via the Southampton Water estuary. The sensor was deployed in the river 250m downstream of tidal barriers and was subject to several meters of tidal variation. It was suspended from a pontoon with the water sample intake 50 cm under the surface throughout the deployment. A logging conductivity and temperature sensor was also deployed alongside the sensor, and grab samples were taken twice daily during weekdays for comparison lab analysis. Automated standard checks were performed every 6 hrs via the onboard standard solution. A blank of deionized water was run through immediately before deployment to establish the systems background readings. The sensor was operated continuously for 25 days and autonomously generated sensor data with a measurement frequency of 10 seconds. The less frequent lab data tracked the sensor results but in addition the high frequency data generated unique insight into the water system as the sensor picked up variations with tidal patterns, rainfall events and discharges from local water treatment plants. A more detailed discussion of the results from this deployment can be found in the Environmental Science and Technology publication (1).

Deployment in a Water Treatment Plant Outflow

The DropletSens™ Monitor for Nitrate and Nitrite was deployed in the outflow of a main water treatment plant in Germany in an outbuilding comprising in-line instruments to measure outflow total carbon, total phosphate and ammonia. The DropletSens™ probe was placed in a reservoir which continuously received outflow water entering at the bottom and overflowing at the top as shown in Figure 2.

Figure 2. The DropletSens™ Monitor for Nitrate and Nitrite deployed in the outflow reservoir at the water treatment plant.

Nitrite and nitrate levels were not routinely measured online but samples were taken and sent to a remote central lab for analysis. Outflow nitrite and nitrate levels need to be below safe discharge level as mandated for instance by European Regulations for safe drinking water (1 mg/L NO2-N and 11 mg/L NO3- N, respectively). In Germany this can be a particular challenge given the intense livestock farming and fertilisation resulting in high nitrate loads in ground water.

The lab analysis sampling regime at the plant was to take a sample for every 100m^3 of outflow from the 24h outflow sampler and these discrete samples were then bulked once a day to provide a composite 24 hr average sample for lab analysis each day ('24h_NOx'; NOx = nitrite + nitrate). In addition, to gain a more meaningful comparison with the continuous DropletSens™ data, a second collection was introduced with spot samples taken out of the outflow multiple times a day ('Spot-NOx').

The sensor was successfully deployed for 41 days to monitor nitrite and nitrate levels in the outflow and the NOx sensor data broadly tracked reference lab based measurements as shown in Figure 3.

Out of all three data sets, the continuous sensor data provides the most detailed data trends including noticeable daily variations. This is illustrated for 24th December (Christmas Eve) and 31st December (New Year's Eve), see red boxes. On both days the typical daily patterns can be seen from the continuous sensor data: (i) NOx levels falling in the morning, (ii) minimum reached around mid-day, followed by (iii) steady increase to peak levels at around midnight. For 31st December this daily 'digital fingerprint' is also picked up by the spot sample measurements which were performed at mid-day, mid-night and 7:00 the next morning. In all other 40 deployment days this pattern is only observed by the continuous sensor, but not by the infrequent lab measurements.

The significantly higher data density, >320000 sensor measurements vs 100 lab based, provided a detailed digital fingerprint of NOx levels. This data always demonstrates compliance with outflow limits during the trial, which is in itself extremely valuable, but the real value of such data is that it could be employed for data-driven closed loop optimisation of water treatment processes. In addition such data allows trends to be monitored and can give advanced warning of transient events and alarms can be set to warn when the outflow regulatory limits may be breached. The sensor ran autonomously for 6 weeks with frequent automated internal standard checks and required no maintenance apart from one simple filter change which was performed by on-site untrained staff. The unique combination of high performance, low cost and low maintenance demonstrates the potential of this sensor as a unique tool for the high frequency pseudo real time analysis of water treatment.

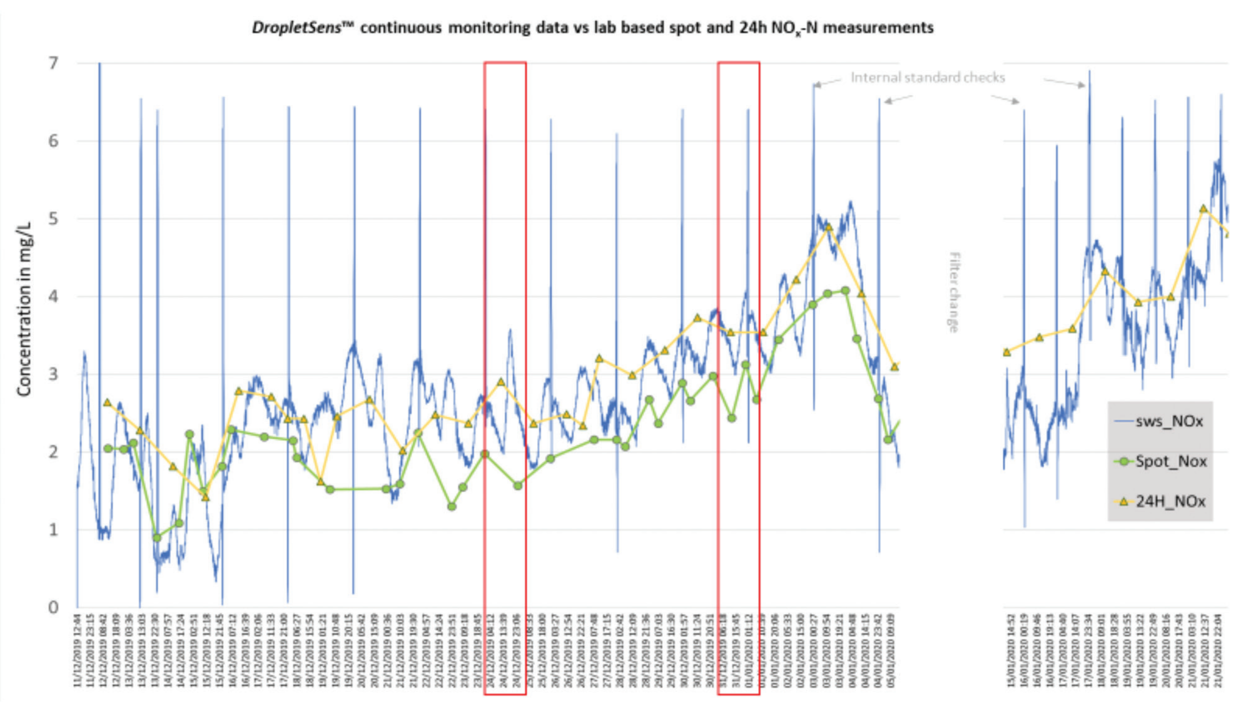

Figure 3: Result comparison of data collected during the waste water plant evaluation.

Closing Observations

In the mid-1990s there was a lot of hype that microfluidics and lab on a chip devices were going to revolutionise the way we performed chemistry in all aspects of our lives and it is fair to say that too often, apart from a few exceptions, the research devices supporting such claims never really transitioned into commercial products. The SWS DropletSens™ Monitor for Nitrate and Nitrite bucks that trend and with the price quoted on the website look extremely good value for such a powerful in situ analyser.

This now proven technology leads the way to the further development of high data frequency sensors utilising the many industry standard wet chemical analysis which have been in routine use in laboratories for many decades. Indeed the SouthWestSensor team already have sensors for Phosphate and Ammonia in water in their development pipeline.

In addition to water analysis methods there are many other industries which routinely employ proven analytical methods based on colorimetric analysis. These methods often have many benefits including specificity and sensitivity and this technology could be applied to many of these industries too provide a new chemical sensor approach to autonomous on line analysis for both process control and final product monitoring for direct release. I am sure the SouthWestSensor team would welcome discussions on potential future applications of their innovative approach to wet chemical analysis **(contact email: admin@southwestsensor.co.uk).**

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Reference

(1) A Droplet Microfluidic-Based Sensor for Simultaneous in Situ Monitoring of Nitrate and Nitrite in Natural Waters : Adrian M. Nightingale, Sammer-ul Hassan, Brett M. Warren, Kyriacos Makris, Gareth W. H. Evans, Evanthia Papadopoulou, Sharon Coleman, and Xize Niu: Environ. Sci. Technol. 2019, 53, 9677–9685

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