Evaluation of online UV/Vis spectrometry based event detection systems at Bratislava waterworks

Martin Libovic[1], Alena Trancikova[1], Günter Langergraber[2,*], Franz Hofstädter[3] and Joep van den Broeke[3]

[1] Bratislava Water Company (BVS), Presovska 48, 826 46 Bratislava, Slovak Republic
[2] Institute of Sanitary Engineering and Water Pollution Control, University of Natural Resources and Applied Life Sciences, Vienna (BOKU), Muthgasse 18, A-1190 Vienna, Austria.
[3] s::can Messtechnik GmbH, Brigittagasse 22 - 24, A-1200 Vienna, Austria
* corresponding author: E-mail: *guenter.langergraber@boku.ac.at*

Abstract Online spectrometer probes are powerful tools for drinking water early warning systems. Bratislava Water Company (BVS) applied a multi stage procedure for evaluating this technology: 1) definition of the requirements, 2) evaluation of suitable instrumentation based on manufacturer specified performance, 3) field test of the short-listed monitoring technologies, and 4) evaluation of the event detection capability with real water samples. Two instruments were selected for evaluation in stage 3 and stage 4 and one of the two instruments was selected for application by BVS because the outcome of the evaluation confirmed the tool was useful and suitable as early warning system in their drinking water supply.

Keywords drinking water, early warning, event detection, online, spectrometry, UV/Vis.

Introduction

Bratislava Water Company (BVS) is responsible for the operation of water and waste water systems of Bratislava, the capital of the Slovak Republic. Furthermore, BVS is also responsible for performing of all physical-chemical, biological and microbiological analyses of surface water, drinking water and waste water in the west of the Slovak Republic.

The supply of safe and wholesome drinking water to its customers is one of the core responsibilities of BVS. BVS produces drinking water for and distributes it to the Bratislava agglomeration, which has a total population of well over 600.000 people. Distribution is done through a public water supply system of 2886 km length. The drinking water is produced in seven central water treatment facilities from 176 raw water sources with an overall capacity of over 6300 l/s. The main source is deep ground water of a very high natural quality. The only treatment performed is chlorination to prevent microbiological (re)growth during distribution. Despite this high quality, BVS decided an online water quality monitoring system is essential to ensure that this high quality is never compromised.

BVS is therefore looking to establish an early warning network that actually monitors all essential ground water sources used for its drinking water supply. This early warning system will monitor the raw water quality in real time, 24 hours a day. In the case that the actual ground water quality should be outside of the very strict quality limits specified, the water

from the source of concern will not be used for drinking water production. Only after a detailed laboratory analysis has confirmed the proper quality of this water source, the production of drinking water from this source will be reinstated. In this way the water used for the drinking water supply will be controlled continuously and only raw water of approved quality will be able to enter the treatment facilities. The key to the success of such a monitoring network is the selection of the appropriate monitoring equipment, both in terms of performance as well as operational aspects.

Materials and Methods

Driven by the requirement to establish an online quality monitoring and event detection system, BVS performed a multi stage evaluation of available technologies. This consisted of the following steps:

    (1) definition of requirements
    (2) evaluation of suitable instrumentation based on manufacturer specified performance
    (3) field test of short-listed monitoring technologies
    (4) event detection capability evaluation with real water samples

For the 3rd and 4th stages two submersible UV spectrometer probes were selected: the s::can spectro::lyser™ (Figure 1), supplied and supported by s::can Messtechnik GmbH, and the Trios ProPS CW, supplied and supported by Hach-Lange. Both instruments are fully submersible UV spectrophotometer probes. The spectro::lyser™ was equipped with a 100 mm optical path length (OPL), the ProPS CW had 60mm OPL. Both the spectro::lyser™ (Langergraber et al., 2003; Rieger et al., 2004; van den Broeke et al., 2007; Sutherland-Stacey et al., 2007) and the ProPS CW (Winkler et al., 2008) can be used to measure multiple parameters simultaneously (e.g. turbidity, TOC, nitrate) from the spectral information. The spectro::lyser™ was additionally equipped with 4 spectral alarm parameters (Langergraber et al, 2004) that exploit the 1st derivative of the absorption spectrum to detect changes that indicate untypical, possibly harmful, water quality events. These parameters were trained on the data from the online evaluation and their performance was then tested during the subsequent spike test.
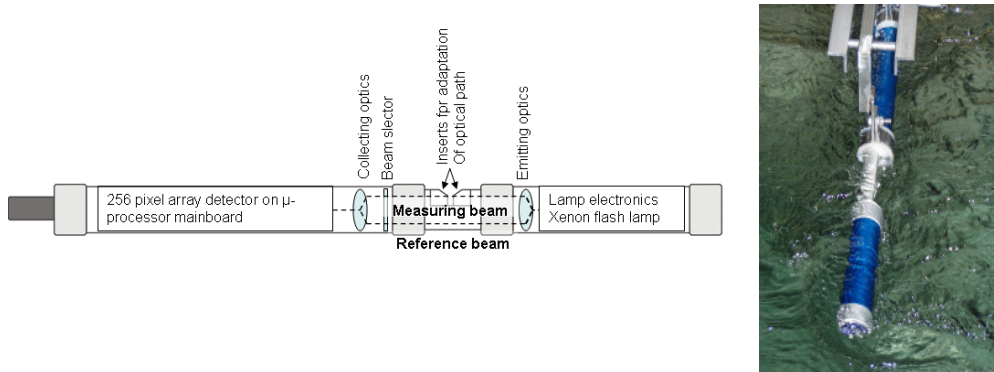

Figure 1: Schematic drawing of the main components of the spectro::lyser™ (left). Example of a submersed installation of the spectro::lyser™ (right).

During the test, water samples spiked with contaminants were prepared by the certified laboratory of BVS and consisted of untreated raw water taken from the source in which the

spectrometers were installed. Samples with following additives were prepared TOC standard solution, (equivalent to 1, 2 and 4 mg/L TOC, based on Potassium Phthalate), carbendazim (20, 50 and 100 µg/L) and benzene (10, 50, 100 and 500 µg/L). The concentrations of benzene in the prepared samples were analysed by GC/MS for confirmation.

Results and Discussion

Stage 1

The first step of the selection procedure consisted of the definition of the requirements. Besides the more general capabilities expected of early warning systems, e.g. quick response time, reproducibility and availability, operational aspects, e.g. easy installation, low maintenance, total costs of ownership, were taken into account. In the long run, only reliable technologies that can be installed, operated, maintained and validated with low effort and costs are practically applicable in widespread monitoring networks. Furthermore, it was deemed critical that the event detection system would not only monitor traditional parameters, but should also be able to detect a broad spectrum of possible contaminations. The conventional standard parameters (nitrate, TOC, SAC254, temperature, electrical conductivity) are foreseen to detect probable harmful natural events affecting the raw water quality, e.g. surface water inflow in water sources that could make it microbiologically unsafe. Innovative matrix parameters were considered to be a solution for the detection of dangerous contaminations of anthropogenic origin (Langergraber et al., 2004): Especially water soluble components of oil (mainly aromatic substances), pesticides and chemical warfare agents were identified to be potential contaminants of reasonable risk. The conclusion of this stage was that out of the available sensor technologies online UV/Vis spectrometry is the one that fulfils best the demands of an early warning system for drinking water protection.

Stage 2

The second step consisted of the comparison of the technical features of available UV/Vis spectrometers as provided by the suppliers. Both technical specifications and proven excellence in comparable applications were evaluated. Technical specifications included sensitivity, precision, availability and maintenance intervals. The instruments from two suppliers were selected for further evaluation (the spectro::lyser™ from s::can Messtechnik and the Trios ProPS CW from Hach-Lange), although proven excellence in terms of reference applications using advanced spectral alarm features and confirmed drinking water applications was available for the spectro::lyser™ only.

Stage 3

The third step was a field test with the selected spectrometer probes. Both instruments were evaluated under field conditions in one of BVS' reservoirs. The instruments were installed in-situ, and operated in the months of October and November 2008. The performance of the two instruments could subsequently be evaluated and compared. As performance criteria primarily the precision and availability of the standard parameters in process application were taken into account. Besides also operational aspects, e.g. pre-calibration accuracy and installation, as well as the response of the conventional parameters, e.g. linearity, were validated.

Stage 4

In the final step of the evaluation an event detection competition on site was performed. Several samples of realistic water compositions were produced to represent the potential contamination events that could realistically occur. Samples of Bratislava's ground water spiked with TOC standard, benzene and carbendazim were presented to the two monitoring systems (Figure 2). This test series was executed on site to assess the sensitivity of the automatic spectral event detection features of the instruments under evaluation. Furthermore, a theoretical sensitivity analysis for a number of extremely toxic substances (e.g. saxitoxin), which could not be used under the available field conditions, was also performed. Also this theoretical sensitivity analysis did consider the actual raw water matrix of the ground water sourced by Bratislava BVS.
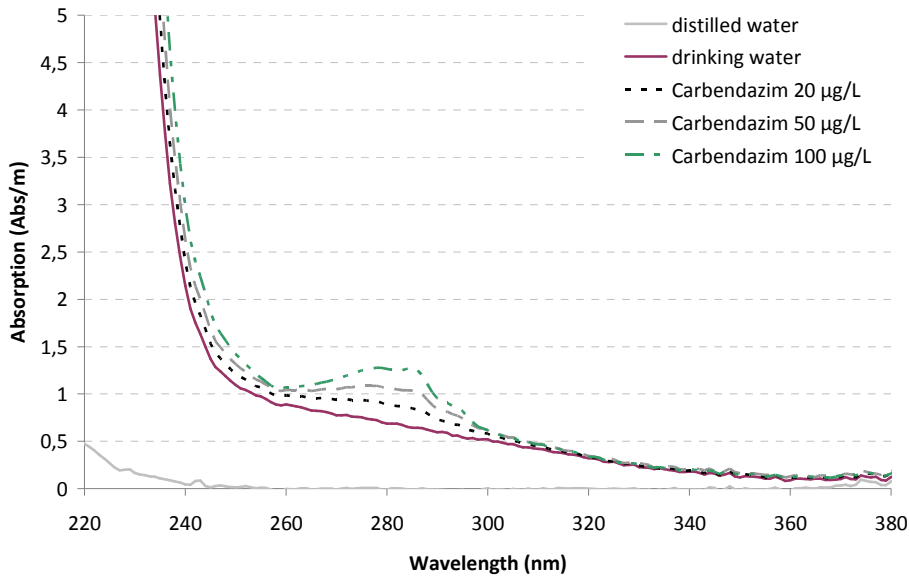

Figure 2: Absorption spectra of Bratislava ground water spiked with carbendazim, recorded with the spectro::lyser™.

The evaluation with the specific substances showed that both tested spectrometer probes were able to detect potassium phthalate at all concentrations presented as well as carbendazim at all concentrations tested, i.e. as low as 20 µg/L. Whereas the trained spectral alarm parameters of the spectro::lyser™ reproducably triggered alarms fully automatically as a result of water composition changes, the spectral absorbance readings of the ProPS CW had to be visually analysed to verify the presence of contaminants.The latter procedure is of questionable value for application in widespread early warning systems where near real-time response is required.

In the samples spiked with benzene the accurate concentration of the added substance was uncertain. Although the samples had been analysed using GC the day before the spike tests, it is known that benzene in water solutions are not stable and benzene disappears from the aqueous phase through adsorption and evaporation. Based on the manufacturers' specifications both instruments should have been able to detect the absorption signal due to the presence of 500 µg/L benzene. In this test, however, only the s::can spectro::lyser™ responded to the benzene. Through By comparison of the absorption observed signal with

literature data (Perkampus, 1992) it can be concluded that the actual benzene concentration remaining was only 150 µg/L. Finally, the presence of saxitoxin, and the response of the spectro::lyser™ to it, was simulated using a spectrum from a previous publication (Tangena et al., 2006). Using the online data collected during the month long trial a reliable assessment of the system in detection of saxitoxin could be made, without the need for actually working with this higly toxic substance. The method of such a theoretical evaluation is described in van den Broeke et al.

The trained spectral alarm system on the spectro::lyser™ showed an unambiguous alarm in the ground water at the following concentration levels: 1 mg/L TOC standard, 50 µg/L carbendazim, 150 µg/L benzene (Figure 3). Using the signal strength to determine the lowest concentrations that would trigger an alarm yield the following results: 0.1 mg/L TOC, 25 µg/L carbendazim, 100 µg/L benzene and 50 µg/L Saxitoxin.

The spectro::lyser™ showed higher sensitivity than the ProPS CW, which is clearly exemplified by its ability to detect benzene. Because of its performance, its proven excellence in comparable applications and the availability of the easily trained and operated spectral alarm system, BVS selected the spectro::lyser™ for use in its event detection system.
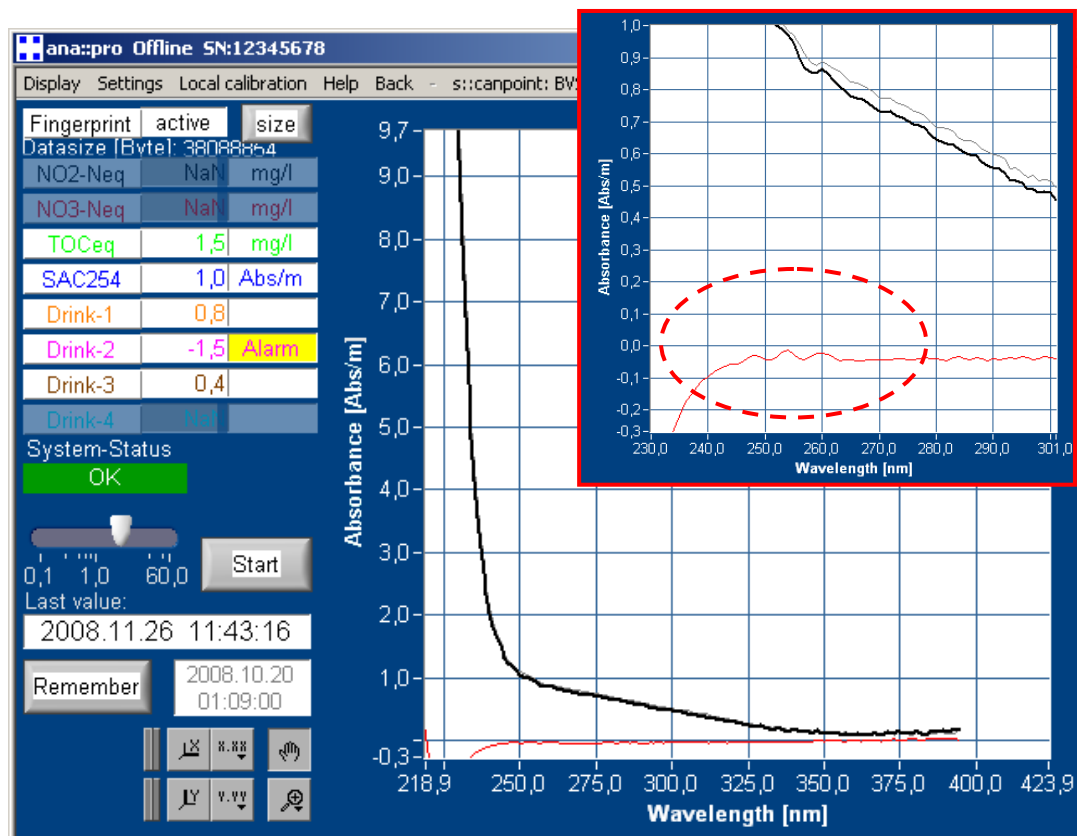

Figure 3: Screenshot of the response of the spectral alarm system to 150 µg/L benzene, with deviation in the spectrum as a result of the presence of benzene in the inset.

Conclusions

The results clearly show that online spectroscopy is a powerful tool for monitoring of drinking water quality and security. Online spectrometer probes are instruments that, in a small and easy to use package, combine a cost efficient monitoring capability both for standard water quality parameters as well as a powerful event detection system for unknown contaminants. Contaminants presented could be detected down to low µg/L concentrations and the spectral alarm system of the s::can spectro::lyser™ additionally generated unambiguous water quality alarms at these low concentrations. During the spike tests the spectro::lyser™ demonstrated a higher sensitivity than the Hach-Lange supported Trios ProPS CW instrument. This lead to BVS' selection of the spectro::lyser™ for use to protect the Bratislava drinking water.

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