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A short evaluation of the S::can Spectro::lyser

A portable, water proof UV/Vis spectrophotometer

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Preface

The work described in this report was performed within the BTO project "On-line Monitoring of Water Quality using a Portable UV-probe" (project number 111508.030), which is a part of the larger project "Integrated research on Sensors and *E*arly *W*arning *S*ystems for Managing and Safeguarding Drinking Water Supply Systems". The project described herein was set-up to evaluate a commercially available instrument in which considerable interest existed, but with which no experience was available amongst the BTO participants.

Summary

A S::can Spectro::lyser UV-probe was evaluated both under laboratory as well as field conditions. The instrument was tested in off-line and on-line modes in the laboratory at Kiwa Water Research in Nieuwegein, and at the water treatment plant WRK in Nieuwegein. The instrument was found to be simple to operate and robust.

In the laboratory, the limit of detection for a number of aromatic compounds and alifatic compounds was determined, and the lowest detection limit was achieved with phenylurea herbicides. In drinking water these could be measured down to the µg/L level without using a concentration procedure. When using a more complex matrix, such as surface water, detection limits were in the order of the mg/L.

When using the instrument in a flow through set-up, drinking water was monitored on-line using the UV-probe. Small, gradual changes in quality could be observed using the instrument. Furthermore, when spiking ascorbic acid and benzoic acid, the presence of these compounds could be detected down to the 0.1 mg/L level. A similar test was performed with the system connected to pre-treated water of the treatment plant WRK. The results were identical to those achieved in the laboratory.

Finally the instrument was installed at the intake of the treatment plant, where surface water was monitored. In this set-up fouling of the flow through cell was a problem, and the orientation of the probe within the flow through cell, as well as flow velocity determined the rate of sediment build-up. Despite fouling problems, the turbidity readings obtained from the UV-probe proved fairly accurate. Furthermore, a contamination event could be detected in the surface water using the software alarm tool of the instrument.

The overall conclusion on the S::can UV-probe is that the instrument is a useful tool for the monitoring of natural fluctuations in the composition of drinking and surface water and for monitoring sudden changes in overall quality.

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1 Introduction

Since 1999 a portable and waterproof UV/Vis spectrophotometer has been marketed by the company S::can Messtechnik from Vienna, Austria. This instrument has since been put into operation in a broad range of applications, such as influent monitoring and process control at waste water treatment plants, monitoring of groundwater, effluent control in industrial applications and monitoring of river water. The instrument utilises the UV/Vis range of the spectrum (200 – 750 nm) for simultaneous measurement of organic matter, suspended solids and nitrate. The instrument is a probe that can be installed directly in the process stream, requiring no sampling, no sample preparation and no additional reagents.

Despite the fact that a substantial number of these instruments have been operational all over the world and in various types of applications, experience with the system for monitoring drinking water (raw water, process control, product monitoring) remains limited. Furthermore, no experience exists within the Dutch drinking water community with this instrument. As the instrument could be a useful and relatively low cost addition to the monitoring tools already operated, a BTO project (On-line Monitoring of Water Quality using a Portable UV-probe, project number 11.1508.030) was set up to gain first hand experience with the instrument and to evaluate its usefulness for the Dutch drinking water companies. The results of this evaluation are presented in this report.

2 The UV/Vis spectrophotometer

All information in this chapter on long term stability and calibration has been taken from documentation supplied by the manufacturer as the evaluation period in this project was insufficient to thoroughly test these properties.

2.1 General Information

The submersible UV/Vis spectrophotometer (Figure 2.1 and 2.2) is a probe 44 mm in diameter and about 0.6 metres in length. It records light attenuation in the wavelength region between 200 nm and 750, or between 200 nm and 400 nm, depending on the version of the probe. The results of the measurements are recorded and displayed in real-time, with a single measurement typically taking 45 seconds. The instrument can be equipped with an auto-cleaning system, which uses pressurised air to rinse the optical windows.[1]

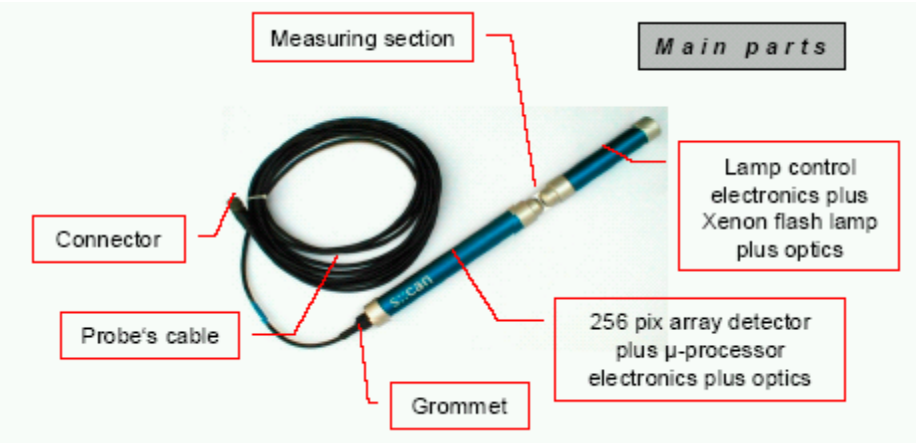

Figure 2.1: The Spectro::lyser probe.

The instrument is a 2-beam, 256 pixel, UV/Vis spectrophotometer, with a Xenon lamp as a light source. On-board electronics control the entire measurement procedure. All of the controller electronics are included in the probe, and include a data logger and a water level meter. Communication is via RS232 or RS485 interfaces. Power can be supplied either by means of a 220 V (AC) connection (requiring a power supply pack) or a 12 – 24 V (DC) connection. The low power consumption means the instrument can also run on a battery or on a solar power supply.

The use of dual light beams, one passes through the sample and one is used as a reference beam (Figure 2), guarantees long term stability of the signal produced due to the internal referencing made possible through this design.

[1] The probe used during the evaluation described in this report was not equipped with the autocleaning system.

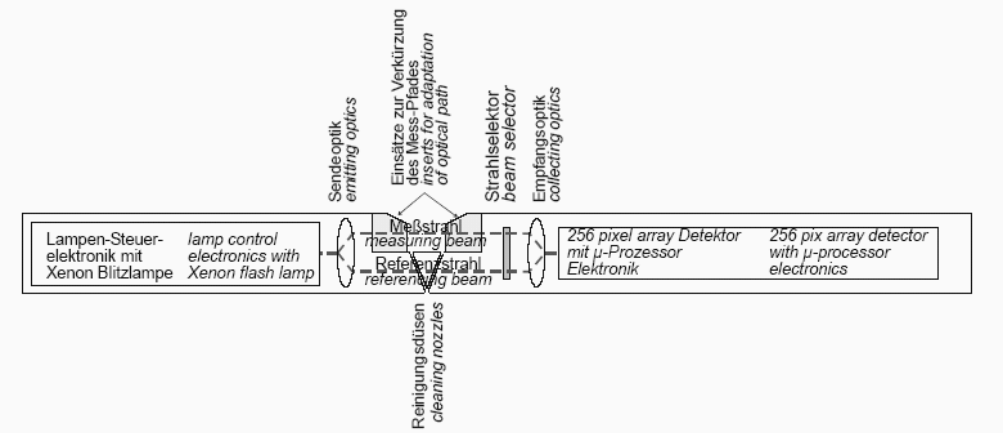

Figure 2.2: Schematic representation of the spectrophotometer.

The path length of the light beam in the water is a fixed distance. Probes with various path lengths are available (100 mm, 35 mm, 10 mm, 5 mm, 2mm and 1 mm) but a single probe has a fixed path length. It is possible to adjust the path length of a probe through the use of a separate insert, which is placed in the cell, thus reducing the length the light beam travels through the sample (Figure 3). However, the use of such an insert makes the automatic cleaning impossible, and thus is only suitable for short measurement periods or applications in water which induces little fouling.

2.2 Parameters

By recording the light absorption in a sample between 200 – 750 nm, the probe is capable of determining more than simply a fingerprint spectrum; besides this fingerprint, the values for a number of specific parameters are calculated from the data contained in the fingerprint, using algorithms provided by S::can. The parameters deduced from the fingerprint are: turbidity, TOC, DOC, nitrate and spectral absorbance at 254 nm (UV_{254}). Furthermore, specific compounds can be monitored once their fingerprint is known, and for this purpose the probe has been used, for example, to monitor benzene, toluene and xylene in groundwater. Applications in the monitoring of other organics, but also ozone, have been developed with various customers, but are not provided for in the standard software package.

2.3 Calibration

With the instrument a global calibration is provided. This global calibration is a *software tool* which allows the instrument to give relatively good values for the parameters mentioned above in any water type. This global calibration has been composed on the basis of hundreds of measurements performed during the development of the instrument. For implementation of the global calibration no samples need to be analysed, it is purely software controlled.

If the global calibration is not accurate enough, due to the composition of the water that is to be monitored, local calibration of the instrument is possible. For local calibration, samples with known concentrations have to be measured, and using the calibration tools in the software, the accuracy of the instrument can be enhanced.

As no separation takes place, a superposition of absorbance spectra is recorded. This can lead to cross sensitivity when a single compound is being monitored and other compounds are present (in high concentrations). Local calibration can then be used to solve the inaccuracy due to cross sensitivity.

Once calibrated, recalibration is not required frequently. The light source has a lifetime equivalent to 50 years of measuring time, with only slow dissipation of the brightness of the lamp. Therefore, a very constant signal is produced. Fouling of the optical windows can cause changes in the signal recorded, so cleaning is essential, the frequency of which will be dependent on the nature of the water. Finally, changes in the composition of the water can change the values obtained for the specific parameters. Therefore periodical calibration will be required, to verify the measurements have not become inaccurate. Recalibration every 3 to 6 months is recommended by the manufacturer.

2.4 Ease of use

Installation and use of the instrument is very straightforward. After installation of the software the instrument is connected to the computer and is ready for use. For process control applications, an industrial computer is available from S::can, which is waterproof and can be installed on-site and can be coupled to a SCADA control system. For application as a portable instrument and for laboratory or research applications, a standard laptop will suffice for control of the probe and for data management.

The instrument can be placed directly into the water at the site where measurements are to be performed. Operational limitations that apply are the following: water pressure should not exceed 2 bar (maximum water depth of 10 meters), the temperature range within which the probe can be used is 0 – 45^{o}C, and it can be operated at flow velocities between 0 – 3 m/s. Higher velocities can result in cavitation, which can lead to deterioration of the measuring results. Velocities below 0.5 m/s can lead to rapid sedimentation of particles on the probe, and thus also lead to a decrease in performance.

For operation at greater depths, special instruments that are proof up to 10 bars can be provided.

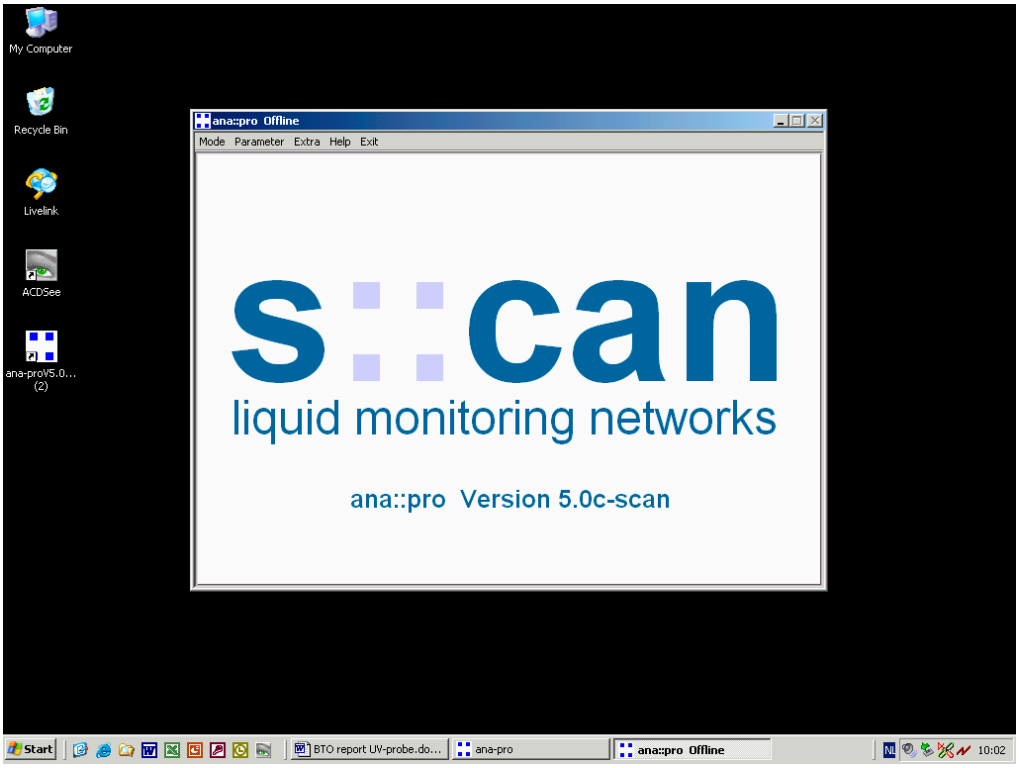

Figure 2.3: Opening screen of the control software for the UV-probe

The software for the control of the instrument (figure 2.3) is easy to use and allows control over the parameters calculated from the fingerprint (up to 8 different parameters, figure 2.4) as well as measuring frequencies, setting of different operational modes of the instrument (e.g. manual, automatic, data logger) and displaying and analysis of the results (figures 2.5 and 2.6). It can also be used to review old results. All data is saved automatically and can later be accessed either using the software from S::can or using a spreadsheet programme such as Microsoft Excel.

The software has built in tools for performing local calibrations and for measuring of background spectra. Furthermore, provisions are included to communicate with a control system (e.g. SCADA) using an analogue interface. Triggers for the communication with an external device can be set, for example the crossing of a certain level of turbidity can be used as a trigger.

A more advanced version of the software, which includes a special alarm option, was offered to Kiwa for evaluation. This module of the software is still under development, but was briefly tested during this project and will be described more extensively in chapter 3.

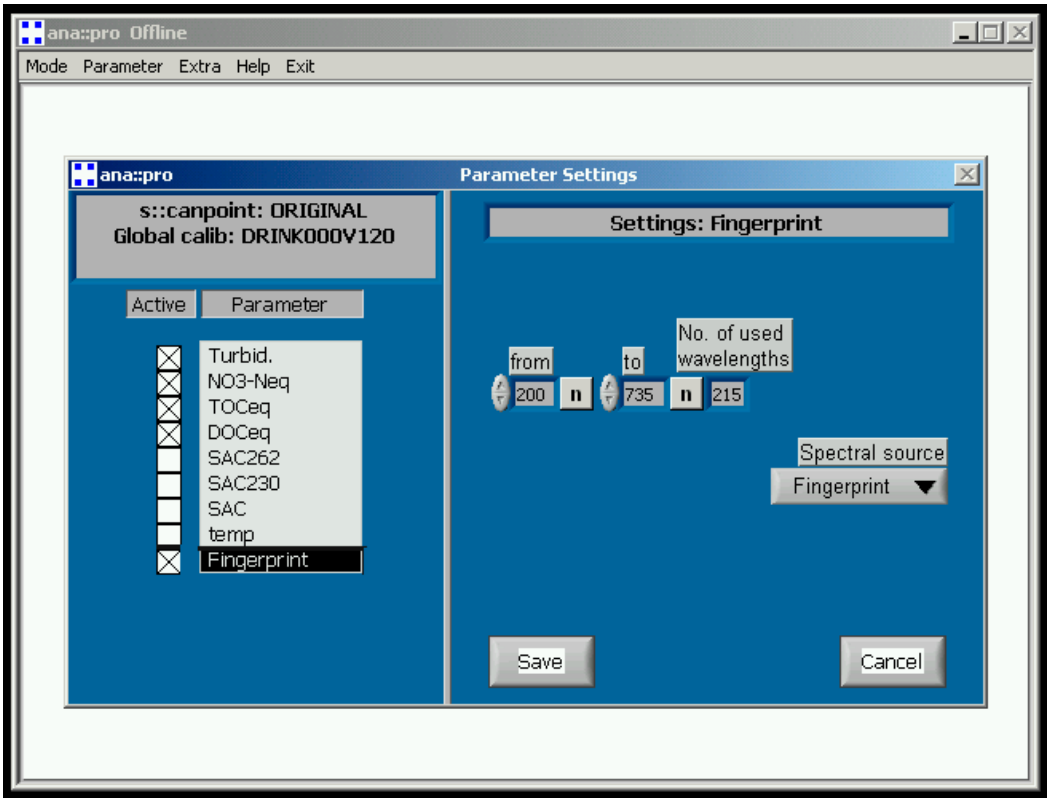

Figure 2.4: Screen used to set measurement parameters.

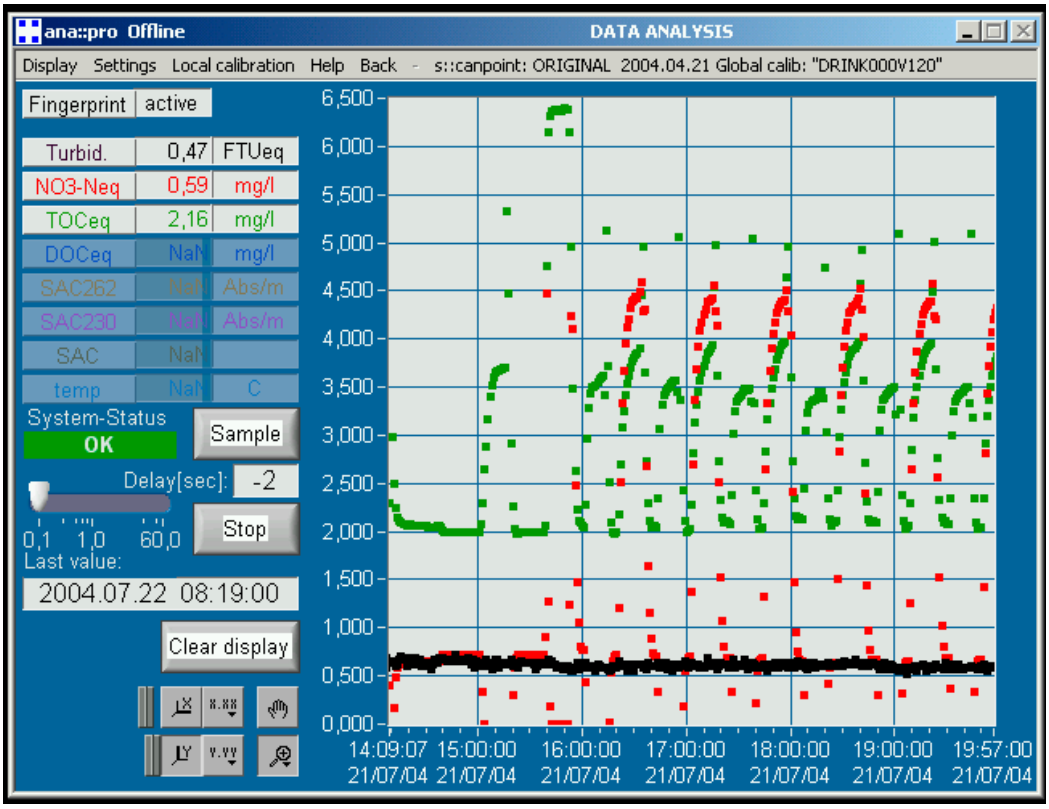

Figure 2.5: Display for viewing results of measured parameters.

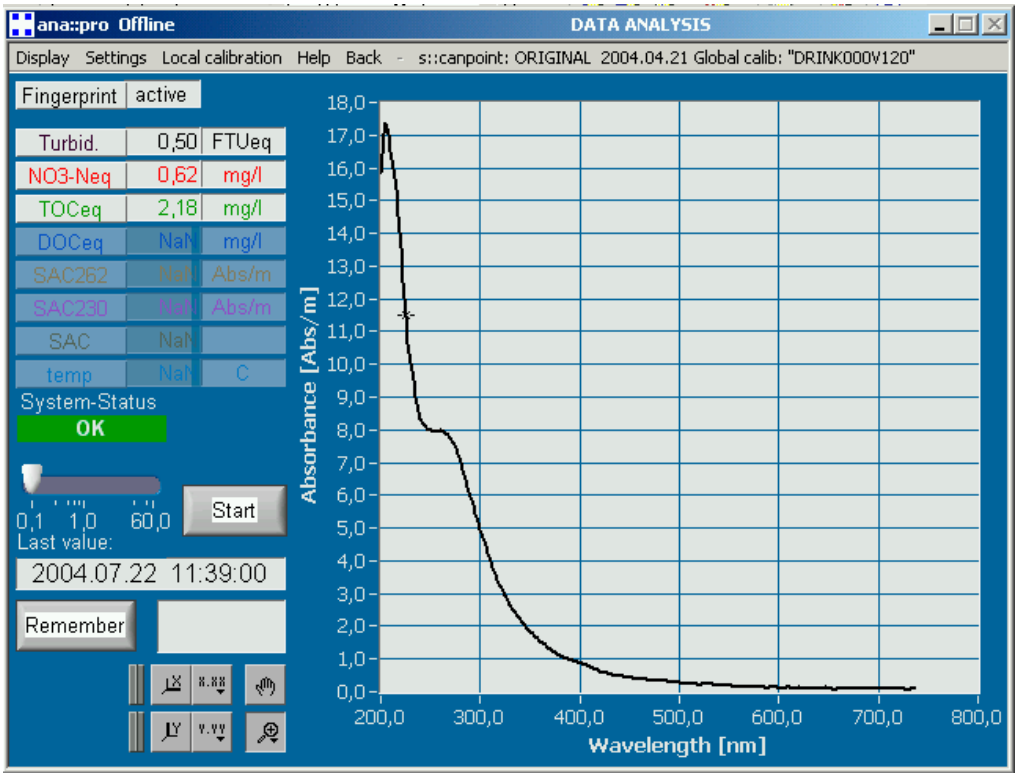

Figure 2.6: Display for viewing results of measured fingerprint spectra.

3 Results

The Spectro::lyser was tested under a number of conditions. It was tested as bench top instrument, during which its performance was compared with a spectrophotometer in the Kiwa laboratory. These bench top experiments were used to obtain a number of calibration curves and to determine the response of the probe to a number of (simulating agents of) organic contaminants. Furthermore, the probe was tested as an on-line instrument, both in drinking water, pre-treated water and surface water. For these on-line evaluations a flow through cell (available from S::can) in combination with the Kiwa designed and built SENSIBEL unit (Brandt, 2001) were used.

3.1 The instrument

A single Spectro::lyser was acquired from S::can. As the instrument was going to be evaluated under very diverse conditions, the most sensitive instrument (with an optical path length through the sample of 100 mm) was acquired. As this configuration is not suited for operation in water containing high concentrations of dissolved organics and/or suspended solids, two inserts, which can be used to shorten the path length to 35 mm and 10 mm respectively, were also acquired (figure 3.1, showing the 100 mm cuvette and the two inserts).

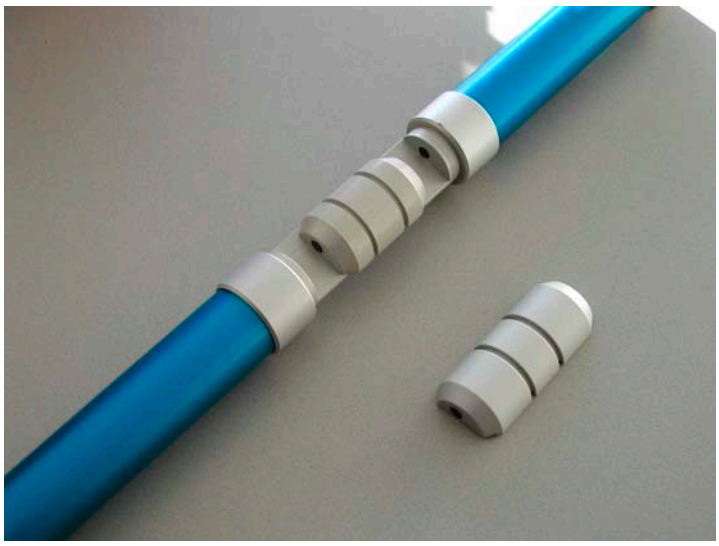

Figure 3.1: The 100 mm probe equipped with a 65 mm insert. A 90 mm is pictured besides the probe.

As described in Chapter 2, the Spectro::lyser can be equipped with an automatic cleaning system. This cleaning system uses a stream of pressurised air or water to clean the optical windows of the probe. The instrument used in

this project was not equipped with such a cleaning system, as this is not compatible with the use of inserts.

3.2 Off-line tests with the Spectro::lyser

Although the Spectro::lyser has primarily been designed for in-situ operations, it is also suited for use as a bench top instrument. Using it as such, a number of short tests was performed to become familiar with its operation and to obtain a first impression of the performance of the instrument.

3.2.1 Comparison of UV-probe with bench top UV/Vis spectrophotometer

Using the S::can Spectro::lyser with 100 mm and 35 mm path lengths the absorbance spectrum of Nieuwegein drinking water and milliQ water was measured. The same samples were analysed with the Thermo Spectronic Unicam UV 500 bench top spectrophotometer equipped with a 10 mm cuvette. Using the S::can probe, the spectrum was recorded between 200 and 735 mm, and with the Unicam UV 500 the spectrum was recorded between 200 and 300 nm. The spectral shapes obtained with both instruments were identical above 210 nm. Below this wavelength a small difference was observed, with the Spectro::lyser recording a lower absorption, by as much as 25%.

The absorbance given by Ana::pro, the software used to control the UV-probe, is a factor 100 higher than that given by the software of the Unicam. This difference it caused by the fact that the Unicam software simply gives the absorbance measured over 10 mm, whereas Ana::pro recalculates the absorbance to a value that would be measured when a path length of 1 meter would be used. Hence the factor 100 difference in the absorbance. To indicate the different approach Ana::pro uses the indication [Abs/m] instead of [Abs] which is more commonly used. When comparing values from different instruments, this difference must be taken into account.

The unit [Abs/m] is used for the Spectro::lyser because the instrument is available with different optical path lengths. Transformation of the results to [Abs/m] allows direct comparison of the data of all the different instruments without the need for recalculation of the data.

3.2.2 Calibration curves with sodium nitrate

Using sodium nitrate, calibration curves were made in both Nieuwegein drinking water and milliQ water. These calibration curves were made with the instrument in the 10 mm (with drinking water and milliQ) and 100 mm (milliQ only) path length configurations.

The calibration curves were determined using the local calibration tool provided by Ana::pro. When using this tool it is important to collect data for use in the local calibration by pressing the “sample” button (figure 2.5) during the measurement series. This must be done for each sample that is to

be included in the calibration curve. The use of the sample button will result in the information of that measurement being collected in a special data set that can be applied in local calibrations. The use of data collected using the "measure" or "start" button (figure 2.6) instead of the sample "button" can be used for calibrations after the measurement has been completed, but only with great difficulty.

The measurements for all three sets of calibration samples could be fitted very well with a linear curve fit. The mean error of the curves, which indicates the mean deviation between the laboratory measurements and the ideal curve, was less than 2.5 % for all three sample sets.

When using the global calibration for drinking water as a reference a significant discrepancy between the values given by ana::pro and the actual concentrations of the sample was observed. This global calibration is provided by S::can and is an average calibration, composed on the basis of measurements in various types of drinking water. The global calibration is intended as a starting point for measurements and not for highly accurate determinations. For truly accurate measurements local calibration is recommended by S::can, and this necessity was also shown by these results.

All samples used for the calibration curves contained nitrate concentrations within the detection limits provided by the manufacturer (0.1 – 10 NO_3-N_{eq} for 100 mm path length and 0.5 – 500 NO_3-N_{eq} for 0.5 mm path length. Although the linearity of the calibration curves was high, the measurement of samples with nitrate concentrations close to the upper detection limit showed a deviation in the order of 5% from the calibration curve.

The upper level of nitrate allowed in drinking water under European law is 50 mg/L, which corresponds with 11.29 NO_3-N_{ew}. Quantification is possible with the Spectro::lyser. However, this concentration is just above the upper detection limit of the 100 mm probe, but does fall within the measuring range of the 35 mm and 10 mm instruments.

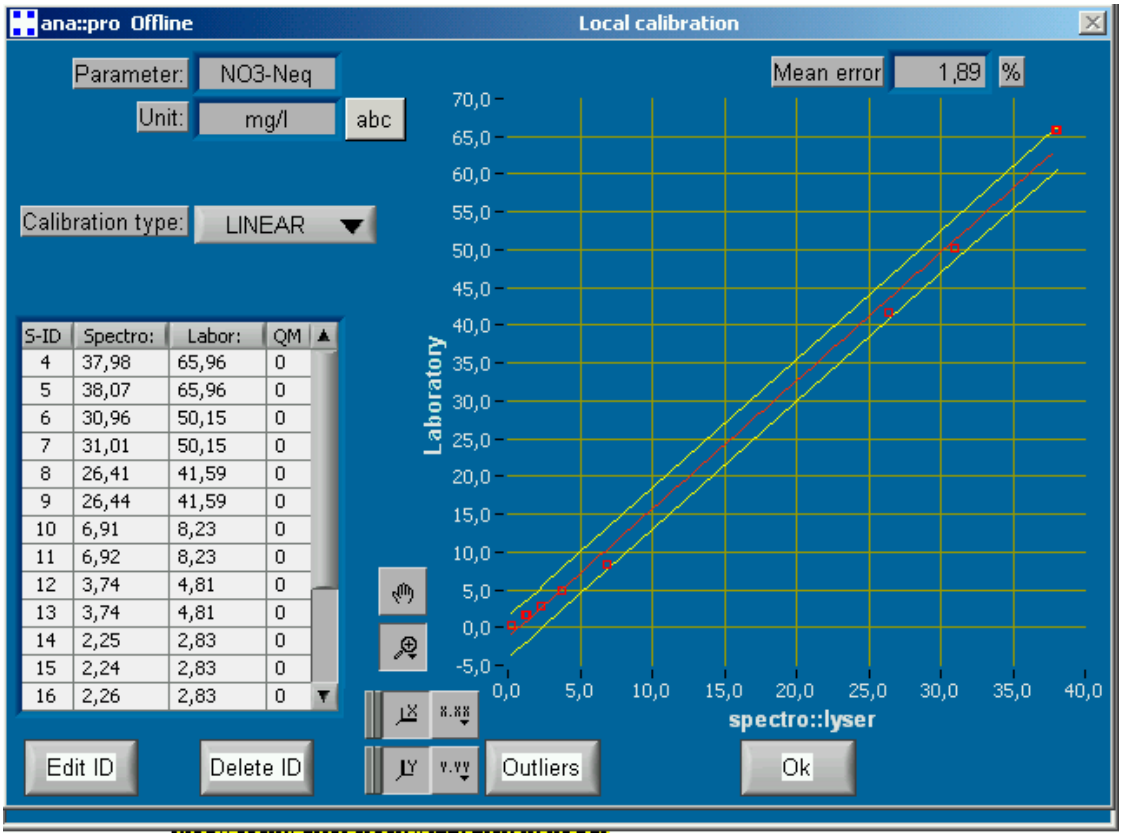

Figure 3.2: calibration curve obtained for nitrate in milliQ using a 10 mm path length.

3.2.3 *Differences in drinking water fingerprints*

The fingerprint of three drinking water samples was recorded (figure 3.3). These drinking water samples were collected in Utrecht, Nieuwegein and Driebergen. A clear difference was observed between the three samples: the Nieuwegein sample has by far the highest absorption in the 200 – 400 nm range. This high absorption is caused by a higher content of organics, and the Spectro::lyser indicates the following TOC_{eq} levels: 0.53 mg/L (Driebergen), 0.63 mg/L (Utrecht) and 1.97 mg/L (Nieuwegein). The high level of organics in Nieuwegein drinking water corresponds with laboratory measurements, which show a relatively high level of humic acids.

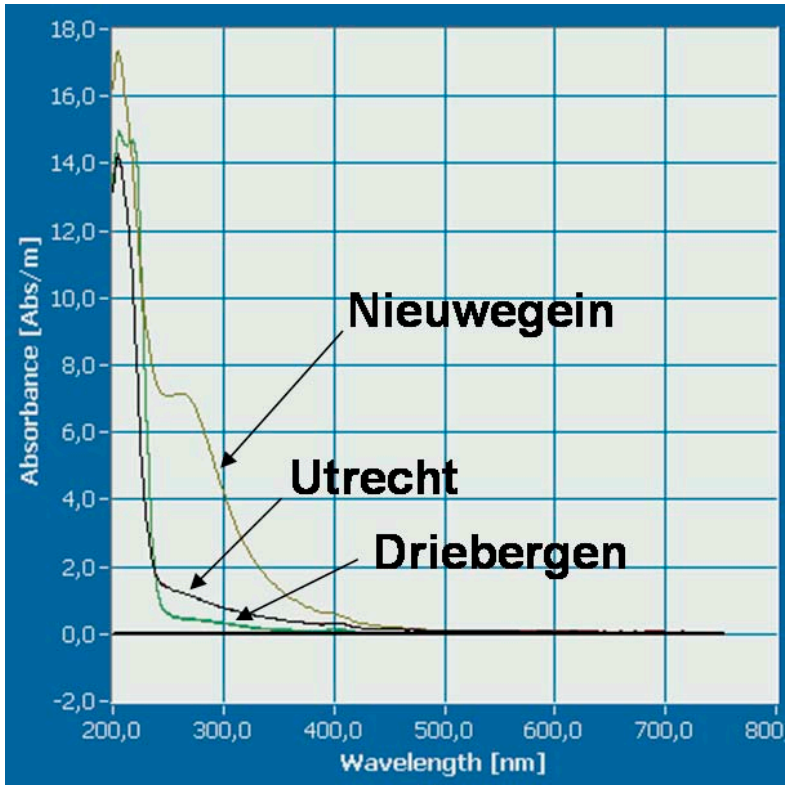

Figure 3.3: The fingerprints of drinking water samples collected from Nieuwegein, Utrecht and Driebergen.

3.2.4 *Analysis of specific organic contaminants*

The sensitivity of the Spectro::lyser towards a selection of organic compounds was determined. This was done to get an idea for the capabilities of the instrument in the detection of organic contaminants, as well as in the identification of those contaminants.

Benzene

Benzene is a commonly encountered contaminant (e.g. in surface water) and has a strong UV absorption. Therefore, the detection limit that can be achieved with benzene is a good indicator for the lowest detection limits that can be achieved for other compounds as well.

It was shown that benzene could be detected in drinking water down to 0.05 mg/L when using the 100 mm path length of the Spectro::lyser. Below this concentration the deviation from the background spectrum (drinking water) becomes too small for unambiguous detection.

When measuring in water with a higher background signal such as surface water (high turbidity, high levels of humic acids), the detection limit is higher. In combination with the necessity to use a shorter path length instrument with such a water type, this results in an increase in the detection limit up to high mg/L levels.

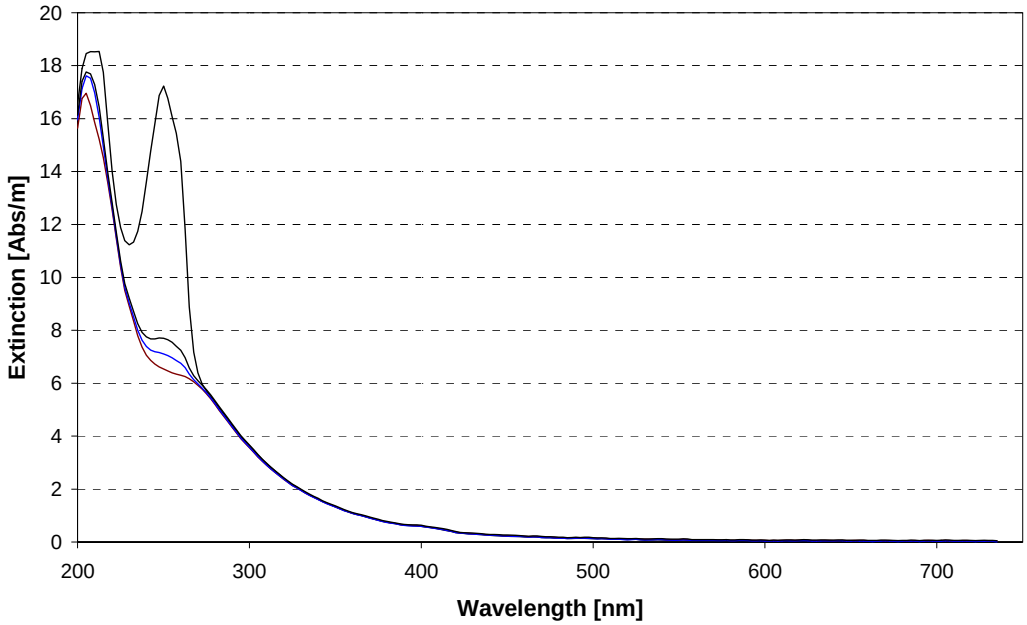

Figure 3.4: Absorption spectra of drinking water contaminated with benzene. From top to bottom benzene concentrations are 1 mg/L, 0.1 mg/L, 0.05 mg/L and 0 mg/L.

Pesticides

A small selection of pesticides was analysed using the Spectro::lyser. The pesticides were selected from two groups commonly encountered in surface water, namely phenyl urea compounds and organophosphorus compounds. Drinking water spiked with aldicarb, mevinphos, oxamyl, azinphos-methyl, methamidophos, isoproturon and linuron was analysed using the Spectro::lyser in 100 mm path length configuration. Drinking water in combination with the 100 mm path length was used in order to determine the maximum sensitivity of the instrument in a realistic matrix.

All compounds were measured in the concentration range 1 g/L – 1 µg/L. All seven substances were clearly detected at 1 g/L, even to such an extent that absorption exceeded the maximum that could be analysed. The lower detection limits are shown in table 3.1. This clearly shows that the instrument is capable of detecting some single pesticides in drinking water down to sub-µg/L concentrations. The information contained in the fingerprint proved insufficient for indentification of the pesticdes. When measuring in a matrix with higher background absorption, an instrument with a shorter path length will required which will reduce the sensitivity.

Table 3.1: lower detection limit of the Spectro::lyser towards a selection of pesticides

Compound	Detection limit[a]
Aldicarb	0.1 mg/L
Mevinphos	0.1 mg/L
Oxamyl	0.1 mg/L
Azinphos-methyl	10 mg/L
Methamidophos	1 mg/L
Isoproturon	0.05 mg/L
Linuron	0.001 mg/L

[a] Lower detection limit: the maximum absorbance in the differential spectrum (Abs/m) should be larger than 0.5 (see figure 3.8). At this value the change in absorbance is higher that caused by short term changes in the water itself.

Simulating compounds for nerve gasses

A group of compounds that is perceived as a possible threat to the drinking water supply are nerve gasses. As it would be interesting to have a detection technique that could monitor the presence of such compounds in water, the Spectro::lyser was evaluated for such an application. However, as the facilities to work with the actual toxic compounds were not available, compounds with a lower toxicity but with a similar chemical makeup were used (Steiner et. al., 2003). The compounds are shown in figure 3.5. Although it can be deduced from these structures that strong UV-absorption can not be expected for these compounds, the usefulness of UV-spectroscopy in the detection of these compounds was investigated. As the known nerve gasses all have highly related chemical structures, the test with the selected compounds should give a good indication on the capabilities of the Spectro::lyser to detect such compounds in drinking water.

DMMP and PMP

DMMP, which was used as a simulant for Sarin, could be detected down to 0.05 g/L (figure 3.6). PMP, which was used as a simulant for Soman, could also be detected down to 0.05 g/L. This shows that although the compounds display a weak UV-absorption, they can be detected with the Spectro::lyser, albeit only at high concentrations. Noteworthy is the fact that a decrease in UV absorption was observed when PMP was added to drinking water.

2-(Butylamino)-ethanethiol

2-(Butylamino)-ethanethiol was visible down to 80 µg/L. However, this can not be explained when the structure of this compound is considered. This high absorbance must be due to an unknown contaminant present, but the supplier of the chemical was not able to provide any further information.

These results indicate that UV-spectroscopy is a suitable tool for the detection of compounds with a structure similar to nerve gases only at high concentrations.

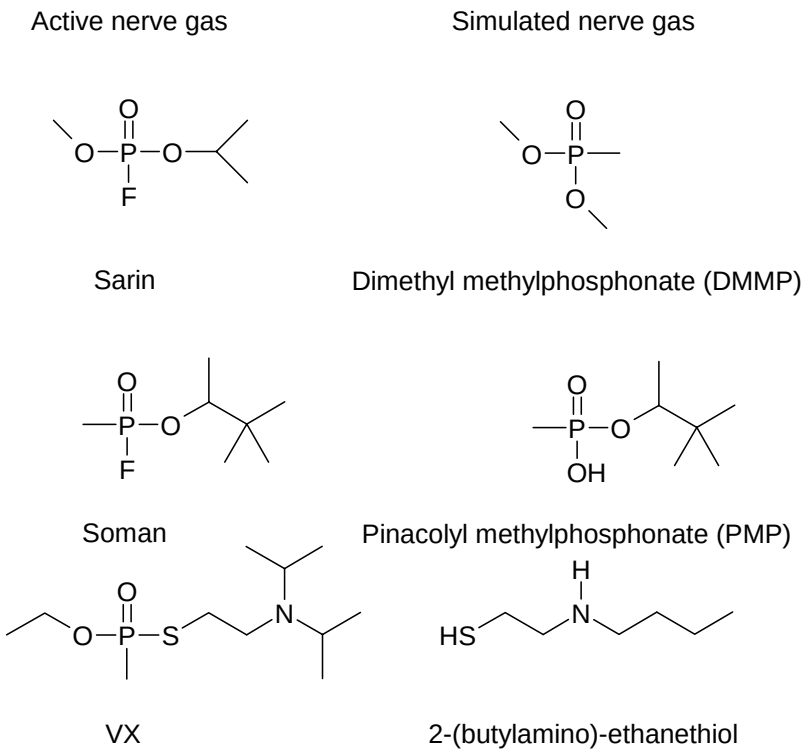

Figure 3.5: Overview of the nerve gas simulants measured with the Spectro::lyser.

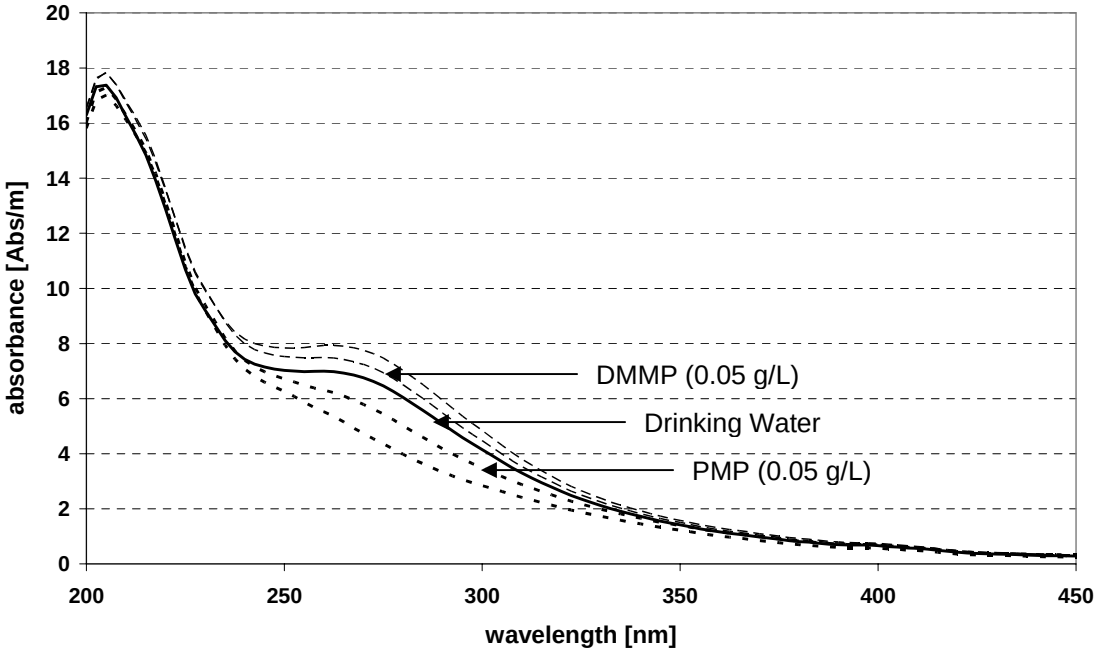

Figure 3.6: Detection of nerve gas simulants in drinking water. Fingerprints of water contaminated with simulants are shown for 0.05 and 0.1 g/L.

Conclusions on detection of organic compounds

The lowest limit for detection of specific compounds observed during the experiments performed was around 1 µg/L, (linuron, table 3.1). Similar sensitivity can be expected for other compounds with a high UV-absorbance in a matrix with a low background absorption, such as drinking water. However, the detection limit for most compounds of interest for drinking water applications will be higher, as phenylurea herbicides, the class to which linuron belongs, is known for their high UV absorption. Furthermore, detection limits in a more difficult matrix, such as surface water, will be significantly higher (mg/L). Such a limit of detection is too high for monitoring of trace contaminants, but is low enough for larger contaminations as they occur in surface water. The spectral information for most compounds will not be sufficient for positive identification. However, indicator parameters such as TOC, DOC and UV_{254} in combination with the spectral fingerprint can be used to detect water pollution. Furthermore, this should work well in the tracking natural fluctuations of water quality. However, monitoring specific compounds will not be possible, unless it is known exactly what to look for (e.g. benzene contamination in ground water at an industrial site).

3.3 Online-laboratory evaluation

To assess the reproducibility and stability of the data generated by the Spectro::lyser, the instrument was installed on a test bench, the SENSIBEL (Brandt, 2001), and connected to the drinking water supply using a flow through cell. One week of continuous measuring, with a sampling frequency of once per 15 minutes, showed a very stable signal with no significant noise. Small variations in turbidity and TOC in the drinking water were observed.

After establishing that the signal during online operation is stable and with little noise, the SENSIBEL was used to spike the water flow with pre-set concentrations of ascorbic acid (vitamin C) and benzoic acid. The goals of this test were to establish the reproducibility of the measurements and to establish the lower detection limit for these strongly UV-absorbing compounds in a continuous flow of drinking water. The SENSIBEL was used to automatically dilute 1 g/L stock solutions of the two acids down to concentrations of 2 - 0.1 mg/L in drinking water.

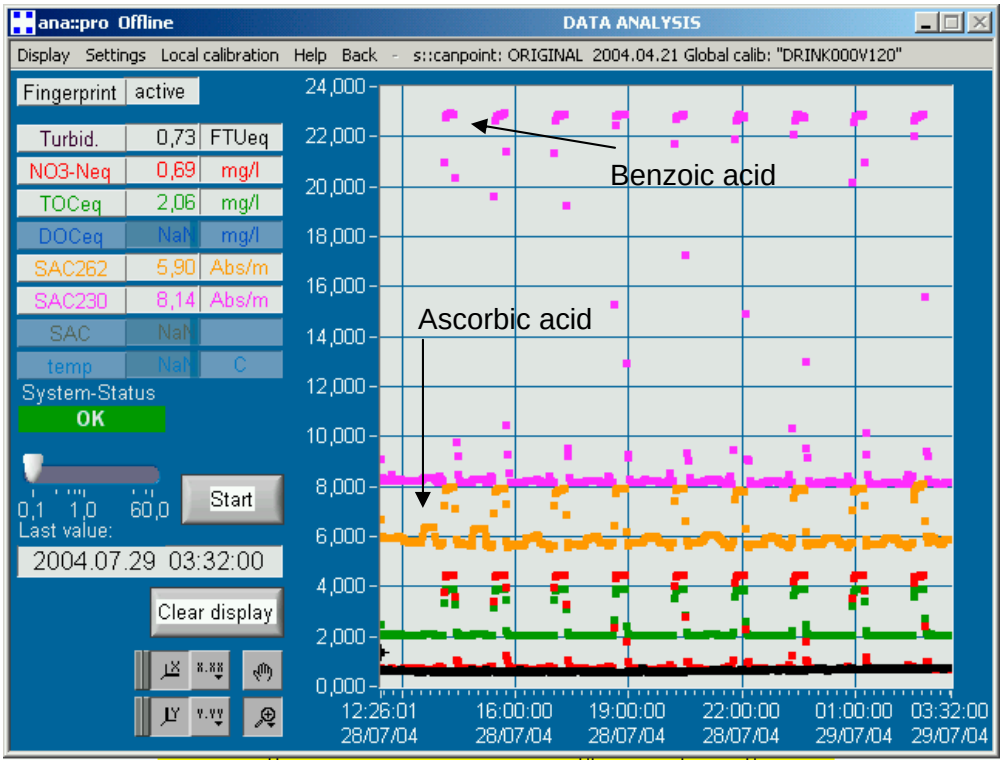

Figure 3.7: Monitoring drinking water with alternating additions of ascorbic and (0.2 mg/L) benzoic acid (5 mg/L).

Initially, ascorbic acid and benzoic acid were spiked at 2 mg/L and 5 mg/L respectively. At this concentration both substances can clearly be detected, the UV-absorption at 254 nm increasing by about 200% over that recorded for drinking water (up to 22 Abs/m from 8 Abs/m). The TOC levels recorded show a similar increase. It should be noted that the nitrate concentration recorded by the instrument is also influenced by the presence of benzoic acid and increases from around 0.7 mg/L (NO_3-eq) to 4.4 mg/L. The software delivered with the Spectro::lyser is not capable of automatically compensating for this disturbance, as the absorption maxima of benzoic acid (230 nm) and wavelength used by the Spectro::lyser for determing nitrate concentrations are close together.

During the entire test the spiked concentration benzoic acid was kept at 5 mg/L. The concentration of ascorbic acid was gradually lowered from 2 mg/L to 0.1 mg/L. The lowest concentration that could still be detected was 0.2 mg/L. Below this concentration no change in the fingerprint could be observed. This can either be caused by the fact that the change in the fingerprint is too small to be detected, or because the SENSIBEL was not able to dose the small amount of stock solution required to achieve the 0.1 mg/L concentration. This was not further investigated, as the 0.2 mg/L concentration yielded a change in the fingerprint which was hardly larger than the natural fluctuations observed in the background spectrum and therefore was already close to the limit of detection.

The reproducibility of the signal was very good: the standard deviation in the absorbance for 5 mg/L benzoic acid was 0.3% (determined over 16 measurements). For ascorbic acid the standard deviation for the absorbance measured in a 2 mg/L solution was 0.9%. Furthermore, the standard deviation was 1% for a 0.2 mg/L solution, which corresponds with the lower detection limit. These standard deviations represent the errors in both the accuracy of the SENSIBEL in the spiking of the substances, the error in the measurement by the Spectro::lyser and the variance in the background spectrum of the drinking water over a period of approximately 1.5 days. It can thus be concluded that the reproducibility of the results obtained from the UV-probe are very high.

Assessment of the recorded data

For the evaluations described in sections 3.2 and 3.3 both the UV/Vis spectrum (the fingerprint) as well as time series of the derived parameters were used. Two further options that can be used to assess the data have not been discussed so far: the use of differential spectra and the use of the first derivative of the fingerprint. The use of differential spectra allows subtraction of a background spectrum (e.g. drinking water) from the spectrum of a sample. In this way the difference between the two spectra is directly visible (figure 3.8).

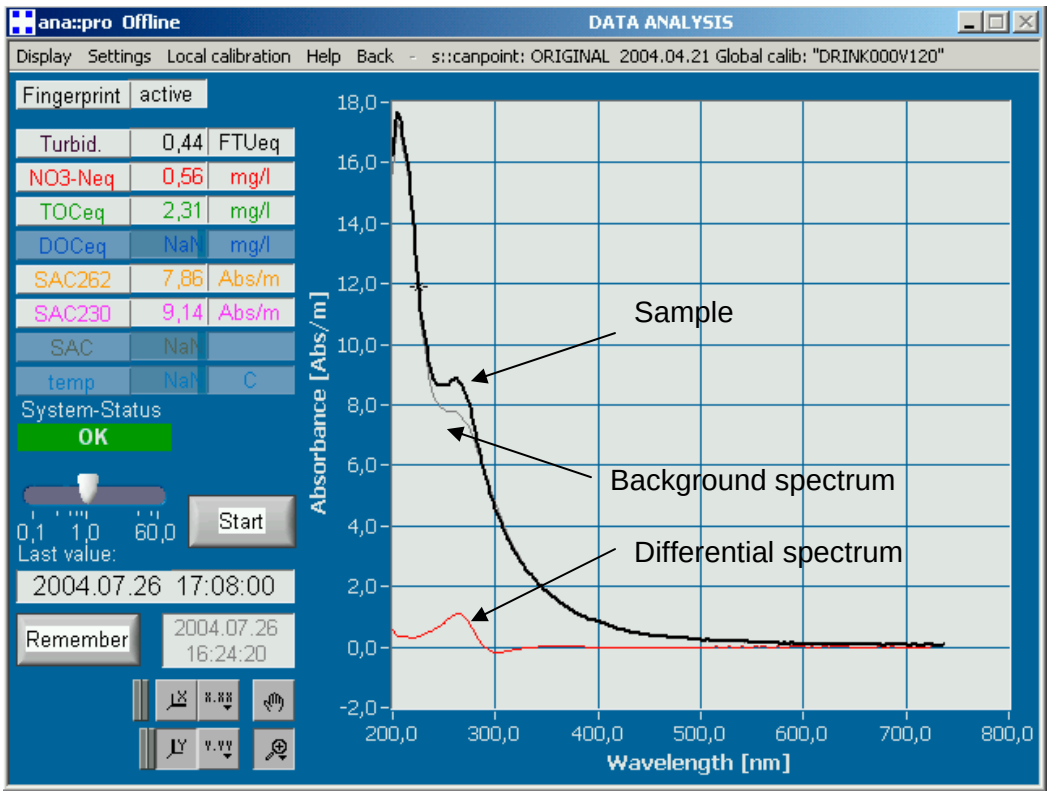

Figure 3.8: Differential spectroscopy.

The use of the first derivative of the fingerprint spectrum (figure 3.9) can in some cases lead to higher resolution. However, in the experiments described

above no difference in sensitivity was observed between using the normal fingerprint and using its first derivative.

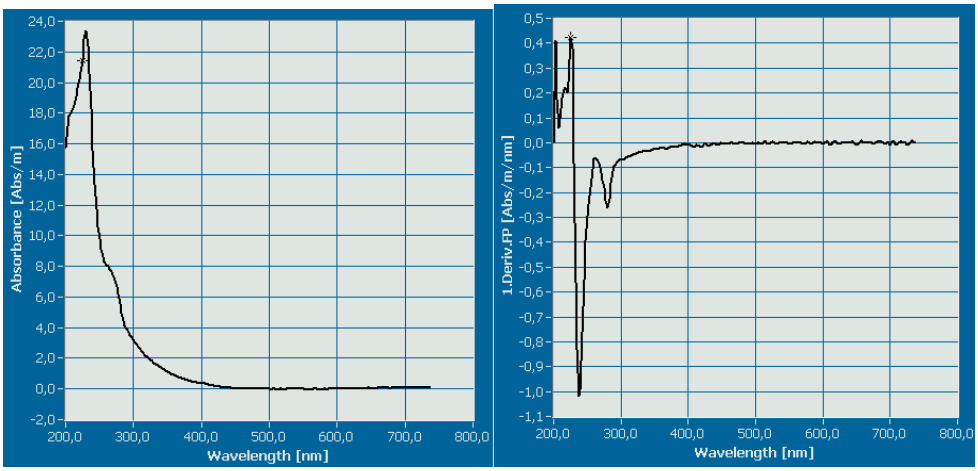

Figure 3.9: Fingerprint spectrum of 5 mg/L benzoic acid in drinking water (left) and the 1st derivative spectrum (right).

3.4 On-line and on-site evaluation

After the online evaluation in drinking water, the Spectro::lyser was installed at the WRK treatment plant in Nieuwegein. At this location, the probe was used to monitor the incoming surface water as well as the outgoing pre-treated water. The outgoing water was monitored for 2 months, while the probe was installed for over 1 month at the intake of the plant. For both the outgoing water and the surface water the use of an insert was required, as the absorption of the water was too high for measurement with the 100 mm path length configuration of the probe. For the surface water the path length had to be reduced to 10 mm, while the pre-treated water could be monitored using a 35 mm path length.

Surface Water
It was suspected before starting the test in surface water that the configuration of the UV-probe used was not suited for these conditions. Surface water, with turbidity in the range of 20 – 40 FTU will cause rapid fouling of the measuring area in the flow through set-up, especially since no automatic cleaning was possible. Nevertheless, the UV-probe was installed and evaluated for 1 month.

It quickly became evident that the sediments present in the water indeed resulted in rapid fouling. The orientation of the instrument had an important effect on the build-up of sediments; a horizontal orientation of the measuring cavity of the Spectro::lyser, with water flowing in from below, resulted in the settling of sediment in front of the optical windows and thus blocking the path of the light beam. This occurred within 7 days. A vertical orientation, again with water flowing upwards, prevented this extensive build-up. However, sediments still accumulated in the tubes, tap and measuring cavity, which resulted in clogging and strong fluctuations in the water flow through

the measuring cell. Increasing the flow rate did not totally prevent these variations. Because of this, strong jumps in the turbidity readings were observed (Figure 3.10).

The turbidity data collected was compared with those obtained from the turbidity meter which is used for regular monitoring at the WRK.[2] This showed that, despite the problems with the sediment build-up in the set up, the measured turbidity and fluctuations therein represent the actual changes as observed by the monitor of the WRK quite well. The background level of turbidity observed by the UV-probe is somewhat higher, at 30 – 40 FTU, than the 20 – 30 FTU observed at WRK. The height of the peaks in turbity, which occurred on an almost daily basis, were recorded by both sensors. However, the peaks were lower in the measurements performed with the UV-probe (10 – 50 %). However, both the general trend as well as all significant changes were observed by both systems (Figure 3.11, example of the period 3 – 10 January, 2005). The higher background turbidity observed with the UV-probe is most likely the result of the build up of the sediments in the flow through cell. The smaller height of turbidity peaks could be the result of mixing with less turbid waters in the sampling system. When positioned directly in the source water, the results would most likely match more closely.

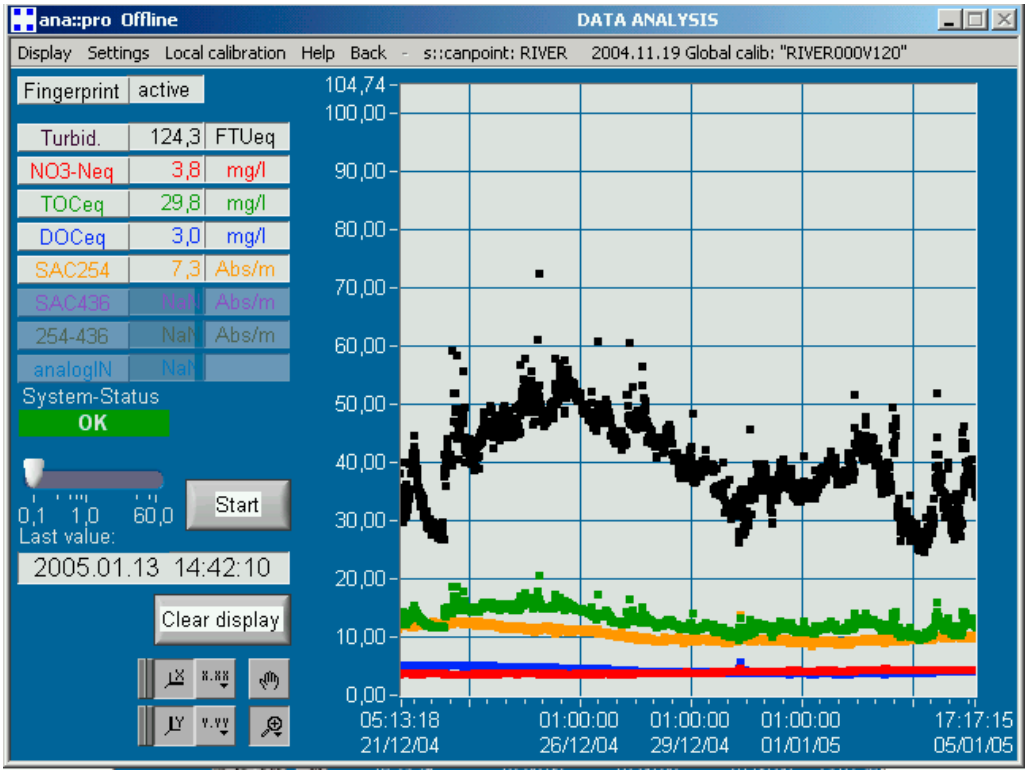

Figure 3.10: Strong fluctuations in turbidity observed when monitoring surface water

[2] Data was used with permission from Waterleidingbedrijf Amsterdam.

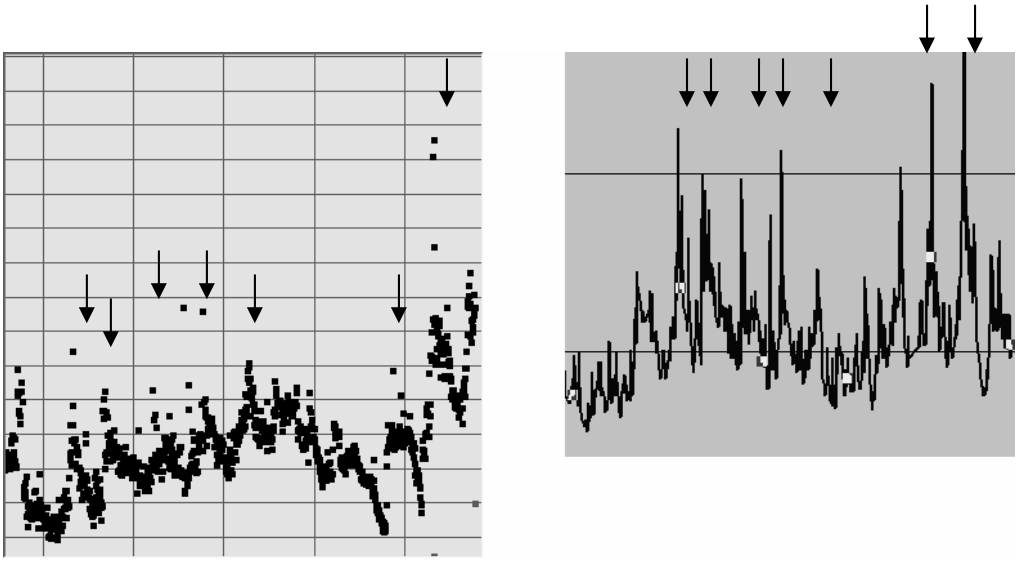

Figure 3.11: Comparison of measurement data, left: Spectro::lyser, right Hach turbidity meter.

Finally, the noise on the baseline was higher in the results obtained with the UV-probe. This is caused by the use of a floating point avarage used with the turbidity meter, which smoothes the baseline significantly. Such an option is also available in the Ana::pro software, but was not activated in this evaluation.

It can thus be concluded that turbidity measurements with this set-up are not ideal, but the results represent that actual fluctuations in the turbidity well. However, for more accurate readings automatic cleaning is advised and the use of the flow through cell is not recommended in highly turbid waters.

The TOC calculated by the instrument proved to be directly related to the turbidity, and fluctuations in the latter resulted in similar fluctuations in the former parameter. DOC, nitrate and UV_{254} did not show this relation. The latter three parameters are therefore better suited to monitor non-turbidity related events in water quality. In this evaluation the values measured by the UV-probe were not compared with laboratory measurements, as no local calibration of the instrument was performed and without such a local calibration achieving quantative data will not be possible.

Apart from the large fluctuations in turbidity, only a single event was observed, on december 30, where UV_{254},, DOC and [NO_3^-] all increased (UV_{254} 14 up from 9.5, DOC, 5.7 up from 4 and [NO_3^-] 4.6 up from 4) without a corresponding increase in turbidity or TOC. Furthermore, the variance in these parameters (DOC 3.7 – 4.1, UV_{254} 8.5 – 10.0, [NO_3^-] 3.8 – 4.2) in the preceding and following two days was much smaller than the observed deviation.This change in the water composition did not trigger any of the biological monitors, Daphnia, Algae, Fish and Bacteria toximeters, that are sampling the same water flow. However, elevated levels of a number of phtalates were observed on the same day using routine monitoring (HPLC). This event, and possibilities for data analysis thereof, is described in more detail in section 3.5.

Pre-treated water

As with drinking water a very stable signal was obtained when monitoring the pre-treated water. Gradual changes were observed but no spikes or severe noise (figure 3.12).

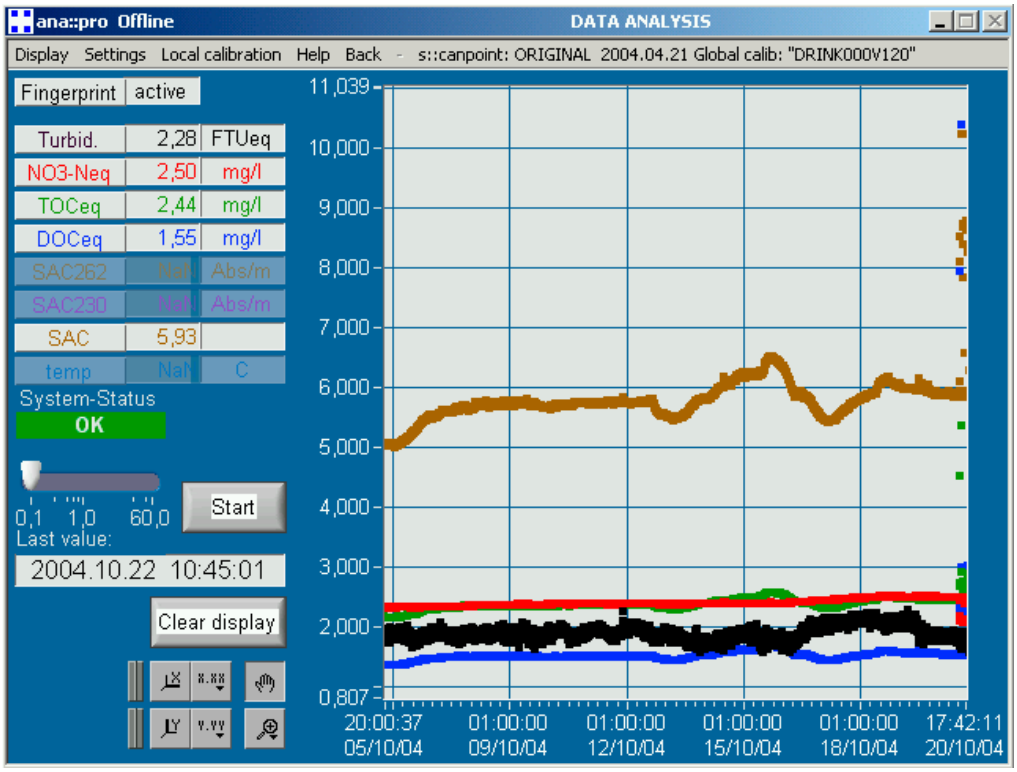

Figure 3.12: Scale of the natural variations in the pre-treated water in comparison with the spiking of ascorbic acid at 2 mg/L (far right).

The minimum concentration of ascorbic acid that could be detected in the pre-treated water was determined using the SENSIBEL set-up in an identical way as described for drinking water in section 3.2. When spiking ascorbic acid, the corresponding change in the fingerprint, as well as an increase in absorption at UV_{254}, was visible down to 0.15 mg/L. Below this concentration, starting at 0.1 mg/L, no change could be detected. This corresponds with the results obtained in drinking water. The fact that no signal at all was observed below 0.15 mg/L in both drinking water and pre-treated water suggests that the SENSIBEL is not capable of spiking at 0.1 mg/L when using a stock solution of 1 g/L.

No large (more than 50% increase in value) and rapid (within 12 hours) change of any monitored parameter was observed during the period of monitoring. The instrumentation available at the WRK plant, which consists of turbidity sensors and HPLC-UV, confirms that no events occurred during

this period that could have been detected using the UV-probe.[3] An elevated level of MTBE was detected for several days during the monitoring period, but this compound is invisible in UV/Vis spectroscopy. Furthermore, an elevated level of turbidity was recorded between the 18th and 25th of October: increased from ~0.025 to 0.05 – 0.06 FTU. A somewhat smaller increase, relative to the background level, was recorded with the Spectro::lyser; 3.0 up from 2.0 – 2.5 FTUeq. Furthermore, the increase by the UV-probe was observed only during the 23rd – 25th of October. As the UV-probe was sampling a different pipe, the lower increase could be the result of either a lower response by the instrument or by a different composition of the water.

Although the trends in turbidity observed by the Spectro::lyser correspond with those measured by the Hach turbidity monitor installed at the WRK plant, a difference of a factor 100 between the reported values was found. The most likely explanation for this discrepancy is an incorrect calibration of one of the two instruments.

Furthermore, the fluctuations in the measurements with the Spectro::lyser were larger. This latter effect was the result of the floating average used in the Hach instrument, which dampens out rapid fluctuations. Such a floating average option is available in the Ana::pro software but was not used during this evaluation.

Practical issues
While using the Spectro::lyser in pre-treated water some practical observations on its use were also made. Before starting the evaluation on the site of the WRK, a new background spectrum was recorded. However, this was not done properly, which resulted in the probe being unable to record the turbidity during the first two weeks of the evaluation. This was corrected by recording a new background using milliQ water. The most likely cause for this problem was insufficient cleaning of the probe before recording the background spectrum. Therefore, caution should be taken when replacing the background with a new one, and it is advisable to check the new background by measuring a standard sample to verify the operation of the probe.

Furthermore, it was remarkable that the probe could be operated without significant fouling over a period of two months in the pre-treated water. This could be done while using an insert, a configuration that is more prone to fouling than one without an insert present. The probe and insert were cleaned after 1 month, but no change in the measuring results was observed after cleaning. This indicates that the Spectro::lyser can be operated in relatively clean water (e.g. drinking water quality) for a period of 2 months, or possibly more, without a strong influence of fouling on the measurements.

3.5 Data managment / Alarm modus

After completing a measurement series, or after downloading data files from either the instrument or the connected process computer, it is possible to

[3] Data was used with permission from Waterleidingbedrijf Amsterdam.

review the data using either the Ana::pro software or using a spreadsheet programme. The offline mode used for this reviewing allows one to call up the values of the parameters, the generation of time series for the parameters (see figures above) and the recalculation of parameters using the fingerprint data. Furthermore, the generation of 3D plots of the fingerprint spectra can be highly illustrative (figure 3.13), but this is currently only possible in a spreadsheet programme.

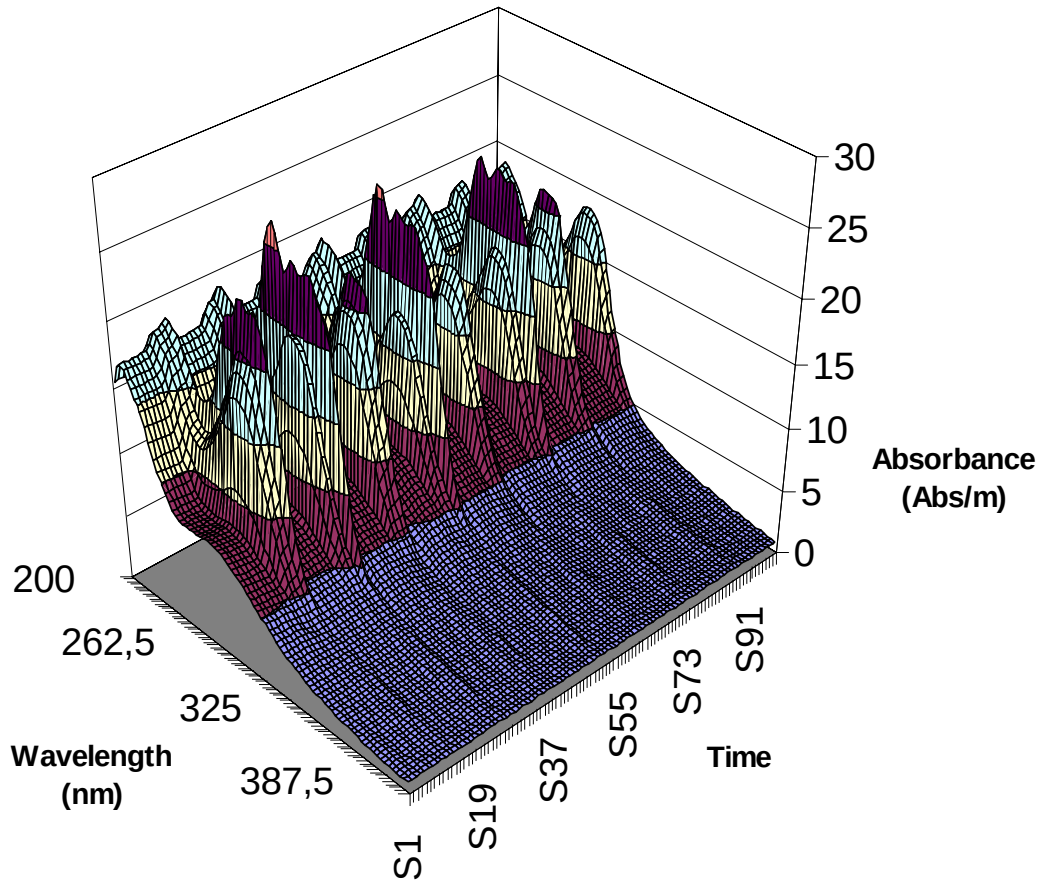

Figure 3.13: 3D-plot of the fingerprint spectra recorded over a period of 1 day during which benzoic acid and ascorbic acid were sub sequentially spiked every 6 hours.

Less illustrative visually than the 3D-plot, but very useful in detecting of changes in the water composition is the alarm module currently under development for use with the Ana::pro software tool. During this project a development version of this tool was briefly evaluated.

When using the alarm tool the standard parameters, e.g. turbidity, TOC, DOC etc, are replaced with 7 alarm parameters. The standard parameters could not be reviewed when using the alarm tool; however, they can be calculated at a later date when reviewing the data. The alarm parameters are defined by S::can in such a way that a change in the fingerprint spectrum is reported with high sensitivity and so that each parameter covers a different range of wavelengths or characteristic of the spectrum.

The levels at which the system gives an alarm can be set per parameter by the user. The sensitivity of the alarm settings can be adjusted depending on the natural fluctuations in the sample matrix. In order to do this, a series of at least 100 reference measurements is required, which give a good representation of the variations in the matrix under normal conditions. After tuning the alarm levels for the monitored matrix, they can be adjusted further without the need for additional reference measurements.

During the evaluation at the WRK plant, alarm settings were produced for both the source water and for the pre-treated water. In the case of the pre-treated water the reference signal is relatively stable, allowing sensitive alarm monitoring. At this setting an alarm was given every time ascorbic acid was spiked to the water, even at the 0.15 mg/L. No other significant events were recorded using these alarm settings.

Setting alarm levels for the source water was more difficult, as large fluctuations were present in turbidity. However, when leaving out the data from the period the water flow through the probe was blocked, a reasonable alarm setting could be obtained. With this setting, one single, unidentified, event was observed. In the fingerprint, this event could be observed as a small but significant increase in DOC, [NO_3^-] and UV_{254} values. The response of the alarm parameters was much stronger, as shown in figure 3.14. This shows that even in a strongly fluctuating matrix the instrument can be used detect changes in water quality. The identity of this contaminants or mixture of contaminants has not been confirmed. However, it is known from routine monitoring that increased levels of phtalates were present in the source water during the day of the observed event. Although this suggests there might be a relation between these two observations, this conclusion can not be drawn on the basis of the available information.

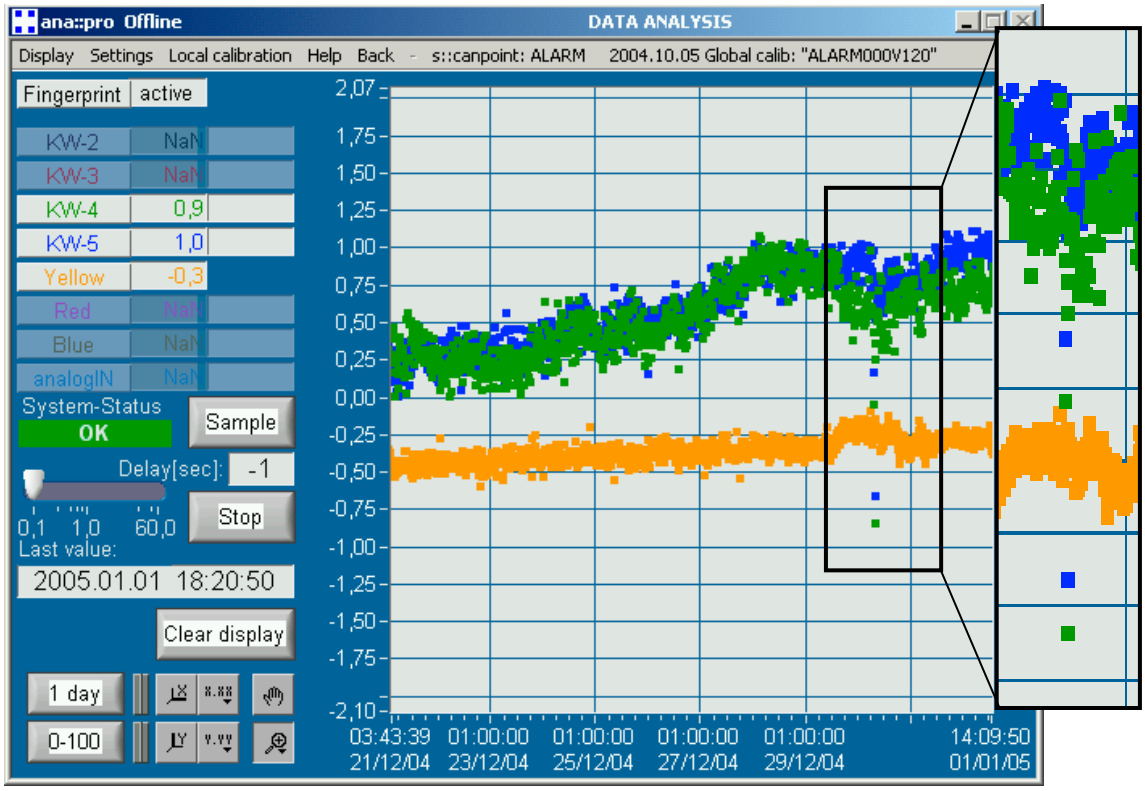

Figure 3.14: Response of alarm parameters to changing water quality.

4 Conclusions

In this project the S::can Spectro::lyser UV-probe was briefly evaluated. The instrument acquired for this evaluation was fitted with a 100 mm sample cuvette and could recorded the absorption/transmission spectra of samples between 200 – 735 nm. This information is important as the version of the instrument will influence the maximum sensitivity and resolution that can be achieved.

Laboratory and field tests have shown that the Spectro::lyser is an instrument that is robust and easy to operate. The data presented by the software tool is clear and easy to interpret. Advanced data handling, such as setting of alarm levels requires more experience with the system, but with the support of the company S::can this is not a problem.

The maximum sensitivity for contaminations in drinking water achieved was in the order of µg/L (phenylurea herbicides). Compounds with a lower extinction coefficient will be detectable in higher concentrations only (mg/L). Furthermore, when measuring in a matrix with a high sediment load or a high concentration of DOC the path length of the instrument has to be reduced, which also reduces the sensitivity of the instrument for contaminations.

As the UV—probe is a stand-alone spectrophotometer, and uses neither concentration step nor chromatography to separate the components present in a sample, it is not suited as a tool to screen water samples for very low concentrations of (unknown) pollutants. The recorded spectra represent the sum of all components present in the water. However, this makes the probe a useful tool for monitoring natural fluctuations in the composition of drinking and surface water and for monitoring water for sudden changes in overall quality. Especially the alarm module in the software is useful in this type of application. In this role the probe will not be able to identify specific contaminants, due to the low specificity of UV-spectra, and will only be sensitive for compounds that absorb UV-light.

In the work performed in this project, only water without residual disinfectant was tested. Results in chlorinated or chloraminated water might be different from those obtained with drinking water in the Netherlands. This remains to be investigated.

For automated alarm monitoring, which is a feature available with the UV-probe, additional tests should be done to establish the natural background signal and variations therein, over an extended period of time and at different locations. Only if the regime within which natural variation occur is known can it be determined whether the alarm function is useful and can alarm settings be prepared.

The S::can Spectro::lyser does not only measure a UV/Vis spectrum of a water sample, it calculates a number of parameters on the basis of this spectrum. Because of this, it can be used as a direct replacement for on-line turbidity sensors and UV sensors, as it will yield information of similar accuracy if a local calibration is performed. However, the standard instruments are less expensive to acquire and maintenance costs are estimated to be similar. Therefore, the UV-probe is interesting for use when additional information on water quality is desired, beside UV-absorption and turbidity. In that case a lot of additional information, e.g. nitrate concentrations and indications of the organic components in the water as well as the spectral fingerprint, will be obtained at relatively low extra costs. For example, use of the instrument for monitoring raw water, filtration and coagulation steps would provide a much better insight in the process in comparison with conventional turbidity sensors and UV sensors used for such purposes. Thus, it can be concluded that the probe has a substantial added value over conventional sensors with more limited capabilities, but as it is somewhat more expensive, it should be considered mainly in applications where this additional information will actually be used.

5 Literature

Brandt, A. "Handleiding voor het gebruik van de SensiBel-opstelling", Kiwa report *BTO 2001.101*, 2001.

Steiner, W. E.; Clowers, B. H.; Haigh, P. E.; Hill, H. H. "Secondary Ionisation of Chemical Warfare Agent Simulants: Atmospheric Pressure Ion Mobility Time-of-Flight Mass Spectrometry", Anal. Chem. **2003**, *75*, 6068 – 6076.

I Appendix – Operational issues

Selecting an instrument
Various types of the Spectro::lyser are available: path lengths of the measuring cell vary from 100 mm to 1 mm, spectral bandwidth can be either 200 – 400 nm or 200 – 735 nm. Furthermore, probes optimised for measuring only specific parameters (e.g. turbidity and nitrate) that do not offer the user the possibility to look at the entire fingerprint are also available.

Before acquiring a probe, the application needs to be carefully considered. The matrix in which it is to be used determines the path length required, 100 mm being suited for drinking water only, while surface water will require either 35 mm or most likely a 10 mm path length. The UV/Vis instrument is the most versatile but has a lower resolution in comparison with the UV instrument. As a results the UV is able to distinguish nitrate and nitrite absorption peaks, whereas the UV/Vis probe is not capable of separating these two absorption peaks.

Finally, for measuring changes in overall water quality, and in order to use the alarm tool, the fully capable instrument is required.

Preparing the instrument for first use
The instrument is delivered ready to use. After installation of the software, the instrument can be connected to a computer and power supply and is ready to start measuring. The manual provided by S::can clearly describes how the software should be installed and how the basic functions of the instrument can be operated.

Storage of recorded data
All data recorded is automatically stored by the instrument. The data is written to files labelled with the data and time of the first measurement stored into that particular file. Renaming of the files is not possible within the S::can software, but can be done manually without causing errors in the programme. Care must be taken when exiting a measurement series: the software asks whether data should be saved. If "NO" is selected, all data will be lost. Therefore, it is best to always select "YES" and to later remove any unnecessary data.

Each data file can contain only a maximum number of fingerprint spectra. After the file is filled, the software automatically starts to write the data to a new file. When measuring at a rate of one fingerprint recorded every 5 minutes, a new file will be started every 4.5 days.

When operating in the data logger mode, the number of fingerprints that can be stored is limited. One can instruct the instrument to measure until its internal memory is full or to continue measuring, in which case it will overwrite the oldest data. Data stored in the logger mode can be retrieved by connecting the probe to a computer.

Installation of the probe
When installing the probe a number of things should be considered. When the instrument is deployed directly into the water, it should not be held in place by the power/data cable alone. Preferably the probe is fixed in position, as this will prevent failure of the data cable and also ensure a constant orientation of the probe in the water. The optimum orientation of the probe will depend on the local conditions, but in general this should not have a very strong effect on the measurement as long as the autocleaning system is used. In water with a high velocity cavitation can occur which disturbs the measurements. Without the use of the autocleaning system orientation is more important as a horizontal orientation of the optical windows can result in rapid accumulation of sediment deposits.

When using the instrument in a flow through set-up, autocleaning will be more difficult or even impossible. In highly turbid waters (surface water) the orientation of the probe is critical for such a application, with the absence of horizontally oriented flat surface being required to prevent sediment build-up. Furthermore, regular cleaning, at least once every 3 days, is required to ensure proper operations of the instrument. In less turbid water, such as drinking water, these issues are not relevant and cleaning of the probe with a lower frequency suffices (e.g. once a month). Cleaning frequencies given here are only an indication, as the optimal frequency will vary with every application.

Calibration
Upon delivery, the probe comes with an internal calibration of the "global calibration" type that is available from S::can. Such a global calibration is a software algorithm which has been composed on the basis of a large number of measurements collected by S::can. It can be considered as a calibration for an average water composition. With this global calibration installed, the instrument will be able to provide qualitative data. However, for quantitative data, local calibration will be required. A software tool is available to support local calibrations: after measuring a number of samples with a known parametric value, these data points are use to make calibration curve and adjust the measured values. A clear description of how to use the local calibration tool is provided in the manual of the instrument. It must be noted that calibration data are best collected when measurements are performed. In theory it is also possible to retrieve data points from existing files and use these for local calibration, but this proved to be not practical.

A background spectrum, or reference spectrum, is recorded in the factory. The background used is distilled water. Refreshing of the background spectrum, to compensate for possible changes in the instrument, can be done by the user. For routine measurements, rerecording of the background spectrum is not recommended. It is very easy to introduce errors in the measured data by poorly recording of the background spectrum (e.g. improperly cleaned windows, cavitation in the water). Frequent (daily) recording a new background is recommended when using the instrument in

the laboratory for measuring concentrations at the edge of the detection limit of the instrument.

Recording the natural background

The sensitivity at which identification of abnormal events in the water is possible depends on the natural fluctuation in the matrix. If the Spectro::lyser is to be used as an alarm system, it is necessary to gain insight into the natural changes that can occur in the matrix. This will require measuring of the fingerprint spectrum of the water for a period of preferably several months. If the water to be monitored shows strong seasonal changes, monitoring over at least a year will be desirable. Using this data, the system can be "trained", it can be set to recognise abnormal changes in water quality. The data acquired during this training period can be used to define the alarm levels. The chance of a false positive and negative alarms will depend strongly on this alarm level and the validity of the data collected during the training period. All data acquired after this training period can be used at will to refine the natural background and alarm levels.