



**CONTAMINANT ALARM SYSTEMS**  
TECHNICAL NOTES V 1.2US

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[www.s-can.at](http://www.s-can.at) [www.water-security.com](http://www.water-security.com)

# UV-Spectrometry for Contaminant Alarm Systems

## 1 Introduction

The instrumental identification of contaminants in a stage as early as possible is the vital basis for any following intervention activity after the spill.

For larger drinking water distribution systems, in order to put acute health stress on human beings, it is necessary to insert a very high dose of any chemical or biological agent, and position the point of insertion near the consumer, because of high dilution factors. Therefore it will be necessary to monitor larger systems at several points, and not only at the point of entry into the system. Smaller systems are more vulnerable, and insertion in greater distance from the point of use can be effective.

One solution brought into discussion more recently is based on indirect measurement, and on the assumption that either the contamination itself or the carrier matrix can be detected as a deviation from a reference signal or matrix of several signals. A broadband picture of the overall water quality is monitored with the help of a combination of physical and chemical sensors, and use any deviation of a pre-defined reference condition as a warning signal. The reference or baseline is normally generated from historical samples, so the system must be “trained”, which is a critical task that can lead to high false alarms probability if not done properly. A related new approach will be introduced with this communication.

### ***Types of Risks***

Real time monitoring systems are the answer to detect low probability / high impact risks in an early stage, other than chronic or long term risks that can be monitored by occasional sampling and analysis.

1. anthropogenic risks (inadvertent discharges/spills, or intentional discharges)
2. natural risks (flooding, turbidity, algal blooms etc.)

### ***Monitoring strategies***

1. measurement of specific substance concentrations
2. direct measurement of toxicity
3. measurement of characteristics / deviations of a reference status

### ***Monitoring methods***

1. direct measurement of toxicity by microbial cultures and caged organisms
2. immuno-assay technologies, “electronic noses”
3. advanced process analysers (GC/MS, AOX, LC/MS etc.); time resolved optical methods, like UV, IR, ATR or fluorescence spectrometry
4. monitoring of broadband characteristics with the help of diverse conventional physical and chemical sensors and tracking of deviations from a trained reference status

The reference or baseline is generated from historical samples, i.e. by state-of-the-art “black box” statistical methods. Such a system must be “trained”, which is a tricky task that leads to unacceptable false alarm probability as long as non-selective surrogate parameters like pH, conductivity, turbidity, DOC, Nitrate etc. only are available. Even after long training periods, no information is hidden in a set of non-selective signals that can tell the manager if a DOC increase of i.e. + 1 mg/l is to be considered “good” – i.e. by natural fluctuation - or “bad” – i.e. by a contamination. However, a contamination mirrored by an increase of 1 mg/l of DOC could easily be very harmful to drinking water consumers. Without more sensitive and at the same time much more selective sensors, contaminant alarm systems would not be very useful for practical applications.

## 2 s::can's solution

There used to be a wide gap between the sophisticated, highly selective, but difficult to operate and expensive analysers on the one hand, and the non-selective, low-sensitive sensors and analysers, on the other hand. *Real-time UV-spectrometry* exactly fills this gap. No other method is known today that could provide a comparable suitability for alarm systems.

Non-negotiable technical design criteria for valuable real-time alarm systems are:

- 1) extreme long term reliability under harsh and neglected field conditions
- 2) ease of operation for normal water works staff

Long term means a maximum inspection frequency of one month, but typical frequencies of 6 months and less. This condition reduces the applicable techniques to direct measurements without moving parts, with no reagents, and with intelligent management of long term optical, mechanical or electrical instrumentation shifts. Other important factors are low energy consumption, low component costs, but still satisfying accuracy.

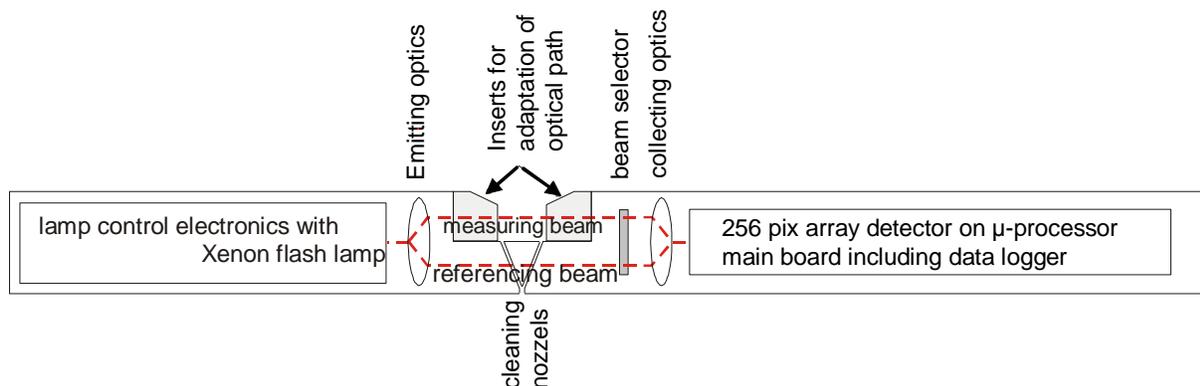
Engineers of s::can Messtechnik, Vienna, Austria, and Senrad Inc., N.Y., USA, have developed in a joint project a completely new method to detect slightest changes and deviations from the "normal" reference state of a water, instrumentally based on their well-proven *spectro::lyser™*, and on their recently released software package *ana::larm*.

### Hardware: The spectro::lyser™

The *spectro::lyser™* is an extremely sensitive submersible UV-Vis-Spectrometer with 100 mm optical pathlength. Changes at a low ppb level of DOC-equivalents can be traced.

The instrument's size is 500/44 mm, 1,1kg, it utilises no chemicals, no membrane, no pumps, no filters, no wipers - nothing but 12 V low power energy. There are no moving parts - it is not even serviceable - and is built to run without ever leaving the water, at almost zero operating costs.

More than 500 instruments world wide are running in most diverse applications, and prove reliability in most harsh environments.



The patented 2-beam optical design ensures drift-free measurements over many months. It works by blasting UV light from a high-energy long-life Xenon lamp (left hand) directly onto the liquid. The Zeiss 256 pixel diode array detector at the opposite side monitors the entire optical spectrum - from deep UV to the visible - and with the help of advanced chemometric algorithms running in the onboard mini computer, the smallest amounts of various pollutants can be quantified, even in a complex matrix.

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The interface is digital (RS485/Modbus) and can be connected to any PC or data acquisition / SCADA system. The instrument is available with full stand-alone capability (integrated data logger and battery), or as a part of a network of autonomous solar-powered field station, providing the telemetric control and data transfer from several field sensors or stations to a central data bank / management system, accessible via any web browser (see p.10).

### **Software: ana::larm**

ana::larm is the product of 3 years of intensive development, with contributions from several University partners, research institutes, and built on data of several European research projects. It has been developed specifically for contaminant alarm systems based on thousands of spectra, and is already successfully used in several applications in Europe.

The training of the alarm parameters can be done by the instrument automatically, or is done manually guided by the provided PC software. It allows the very simple half- or fully automatic setup and configuration of up to 8 spectral alarm parameters within a few minutes. It will react on any type of organic contamination that provides an absorption signal in the UV range. The alarm sensitivity for many organic contaminants is between 1 and 500 ppb. At the same time it is most insensitive against any fluctuation of the matrix within the natural / "normal " / range, and thus keeps false alarms to an unmatched minimum. There will not be a useful alarm for substances that do not provide any signal in the UV range.

The approach and methods used are absolutely new and unique, and will open a completely new perspective for water monitoring beyond the trending of "classical" concentration parameters. Compared to other online monitoring instruments on the market, we feel that the spectro::lyser™ in combination with the alarm software module provides today's best possible protection against any kind of "abnormal" water composition or contamination.

### **Implementation of Real-Time-UV-Spectrometry into Alarm Systems**

*One strategy* is to use the standard calibration algorithms for substances like T(D)OC, Nitrate, Turbidity, organic substances like aromates, phenols, hydrocarbons, and others, and to monitor those substances with time and space. Specifications are given in the relevant technical notes. With this, it can replace several complicated and expensive on-line analysers at the same time.

Although UV-Vis-spectroscopy is sensitive down to the low ppb-range for many organic pollutants, it will often not be selective enough to indicate the type of micropollutant at the drinking water level. Therefore, a closer analysis must follow in cases of elevated signals. However, the signal will often represent a sum parameter, but also as such, it will be orders of magnitude more sensitive than i.e. DOC measurements.

*The other strategy* is to use the UV spectrum as a whole, in order to detect even the smallest changes between the measured spectra and reference spectra at any wavelength, often changes that become only evident in differential spectra. See p.7. As an example, variations of substance concentrations are derived from direct absorption values, and changes of the characteristics of a water are detected from 1. and 2. order derivatives.

Sometimes the detected changes can not directly be correlated to known substances, but nevertheless provide a sensitive alarm parameter. Immediately, actions can be started, like shutting down valves in order to prevent that potentially dangerous substances can enter the drinking water system. Next (automatically) take a sample and find out in the lab about the origin of the spectral anomaly.

There are several ways to exploit the provided spectral information:

- qualitative interpretation of spectral deviations from a site specific reference spectrum (peaks, shoulders, gradients, analysis of derivative spectra)
- changes of spectral features over time (anthropogenic changes, like from spills, are typically faster than natural changes)

- compare spectral differences between measuring points of a measuring network - we call this delta-spectrometry™.

One target in a European LIFE project was to compare the spectrometrical approach with a standard Daphnids test. Nitrobenzene was used as a test / tracer substance. It was quite surprising that the Daphnids showed no reaction even at high Chloroform concentrations, but the spectral measurement could easily detect even very low concentrations. Because of the project's success, the method is now used by large utilities in addition to the conventional alarm parameters.

As an additional benefit, through the detailed knowledge about the evolution of water quality parameters over space and time, non-alarming but chronic polluter identification can be brought forward.

### ***Important: How to Define Alarms vs. the Baseline of "Normality"***

As for all alarm systems, a well defined approach to quality data interpretation is needed for each individual case. Specific baselines must be evaluated, and deviations of such that lead to an alarm must be defined. Because of the multidimensional information provided, UV spectrometry offers a much higher information potential about the "normal" baseline than single signals like turbidity or DOC.

A new approach for baseline definition - geographically resolved "Delta Spectrometry" :

A "reference" is measured in real time at a point where unimpaired water quality can be guaranteed, near the source of the system, or after the controlled treatment.

At strategically chosen sampling points in the monitoring network, (spectral) water quality is measured in real-time and sent to the central station where the data (spectra) are again compared in real time, in order to detect any change or deviation between sampling point and the reference with highest possible resolution.

For sure, all logistic measures, like most restrictive access denies, must be taken to ensure that the reference point stays always absolutely unaffected and free from any pollution. The combination of several sensors to a sensor array further reduces the probability of false alarms.

## **3 s::can's answers**

### ***➤ quick response to suspect quality changes ?***

The standard measuring time is 30 seconds, but can be reduced down to 5 seconds. The absolute response time depends on the time needed for the evaluation of alarm algorithms, in connection to other sensors involved in a sensor network.

### ***➤ real-time measurement ?***

The time delay is negligible, compared to biological systems or analysers.

### ***➤ high sensitivity, at the same time low false alarm probability ?***

Sensitivity is down to the ppb region with a 100 mm pathlength probe for many substances, and with this, much more sensitive than conventional DOC analysers. Also, selectivity will always be considerably higher than of DOC analysers.

Therefore, false alarm probability will by principle be always much lower than i.e. turbidity, UV254, or DOC alarms.

### ***➤ clear interpretability of signal and alarms ?***

... can be reached by a) by real-time reference point ("Delta-Spectrometry") or b) sufficient baseline training

➤ *broad band response to diverse contamination sources (at the cost of low selectivity) ?*

A broad spectrum of contaminations - but not all - can be detected. The identification of single substances or substance groups is limited to those substances that 1) are detectable in the UV-spectrum and 2) were implemented in the detection procedure.

Examples: Phenol, Benzene, Toluene, Xylene, many pesticides, some nerve gases, part of the hydrocarbons / petroleum, crude oils, naphthalene, and many others. Not possible: i.e. short-chained aliphatics. For other substances, it can only be stated THAT a substance, but not WHICH one has been detected.

➤ *reliability ?*

s::can instruments were designed and built for highest operational safety and reliability, can withstand the most aggressive environment, and are most tolerant against neglect. There are no serviceable parts, and the sealed instrument can not be opened. s::can instruments can run for years without ever leaving the water.

➤ *reproducibility ?*

Because of the efficient 2-beam-design, the long term spectral signal reproducibility is higher than of any other known instrument on the market.

➤ *robustness and long term stability of sensors and stations under harsh conditions ?*

There is no service interval. The recommended maintenance interval in drinking water applications is 6 months and can be extended; the instruments are tolerant against high temperature and pressure gradients; the sensors can be installed in creeks at high water level fluctuations, in ground water wells, in pipe lines, in by-passes, etc.

➤ *remote accessibility ?*

The instruments can be remotely accessed via their remote terminals if necessary, and automated data transfer to a central station / data bank / can easily be achieved.

➤ *low costs, allowing multi-point systems to cover larger areas distributions networks ?*

The purchase and installation cost of one instrument is a fraction of i.e. a DOC analyser; the running costs are almost zero.

➤ *high security access, secure data exchange, high security reserves on all levels ?*

Depending on the application, highest security levels can be reached on a hardware and software level.

## 4 References

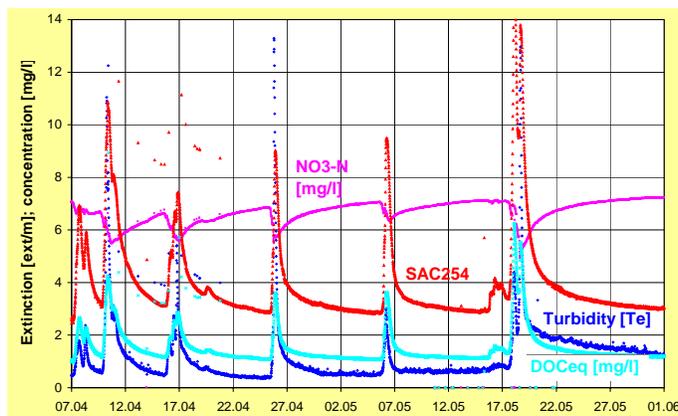
- The potential of UV-spectrometry for alarm systems is mentioned in the new USA "Guidelines for Designing an Online Contaminant Monitoring System", 2004, [www.asce.org/static/1/wise.cfm#WISE](http://www.asce.org/static/1/wise.cfm#WISE), describing s::can's approaches.
- Recently, the spectro::lyser™ was tested with positive results for contaminant monitoring by the well repudiated KIWA drinking water research institute in the Netherlands (Report BTO 2005.002, available from [www.kiwa.nl](http://www.kiwa.nl), or from s::can Vienna).
- The City of Vienna has been running 15 stations to their highest satisfaction since the year of 2000 in an always growing network for drinking water protection.
- The Swiss Army has tested the spectro::lyser™ recently with positive results for contaminant monitoring (report summary available upon request).
- The spectro::lyser™ is used in several other European drinking water systems for contaminant alarm and water security purposes.

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## 5 Real Case Studies

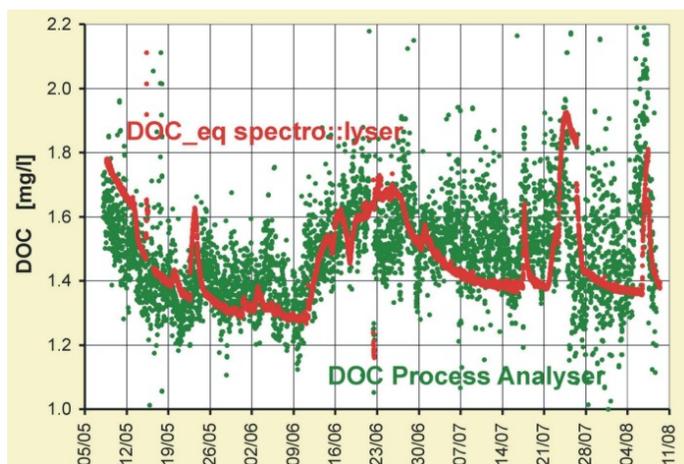
### Early Warning, Alarm and Control Systems based on Real-time Spectrometry



A groundwater well in Switzerland suffers frequently from the influence / filtrate of a nearby river, and from agricultural pressure / manure.

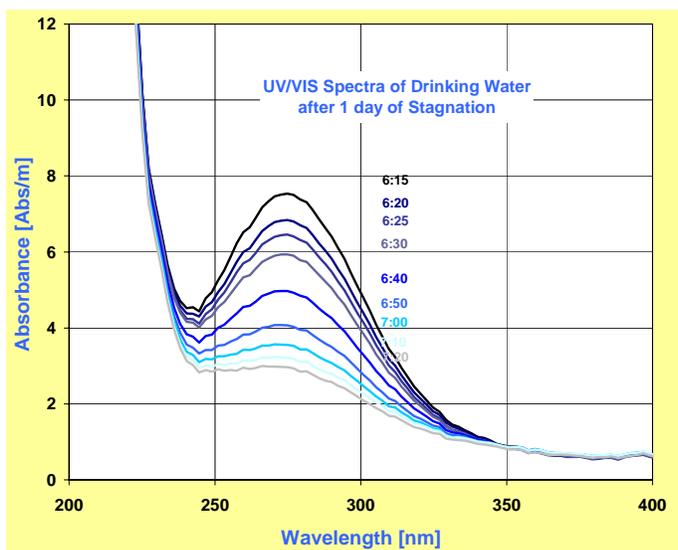
The parameters DOC\_eq and Turbidity, as well as an advanced spectral derivative are used for the control of drinking water extraction, and for the identification of manure.

The application is running since 04/2001 without any break for maintenance.



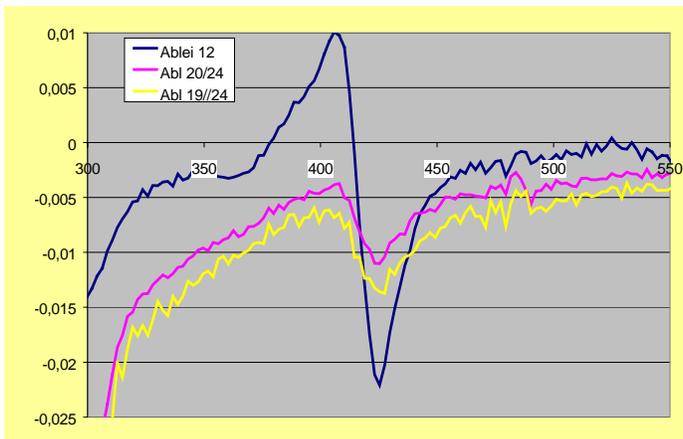
A major hydro power company has to monitor the organic carbon content of the artificial exfiltrate from their water basins into groundwater. They used to do the measurements by D/TOC analysers. Because of operational costs and unreliability / needed regular maintenance, they wanted to exchange the analysers.

This figure shows clearly how much more sensitive and selective the information from spectral measurement is compared to the online TOC measurement.



Measurements in a drinking water well show an extreme peak in the region of 280 nm when the tap is opened after 1 day of stagnation. The measurement is highly reproducible and was found, although less pronounced, in many different drinking water systems.

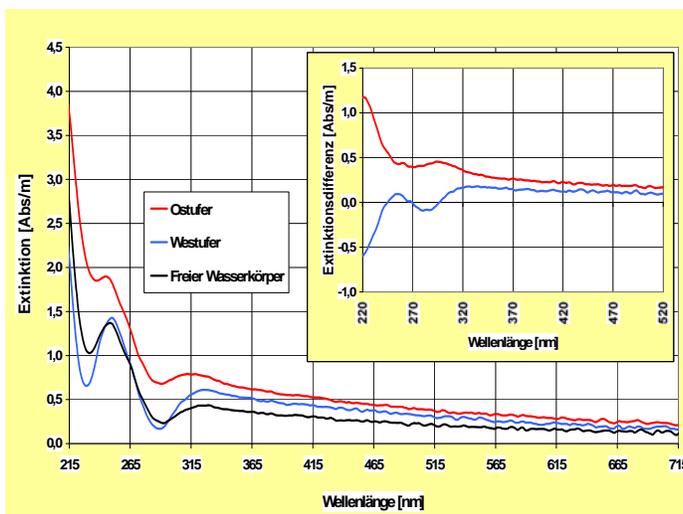
This absolutely new level of real-time information is expected to be most valuable for the investigation and monitoring of hygienic, microbial and other risks, and is one of the most prominent applications for water distribution network monitoring.



A discharge into a small Austrian creek was identified by derivative spectrometry:

The absorption spectra between 300 and 460 nm showed only a small shoulder in the region of 415 nm at some of the spectra.

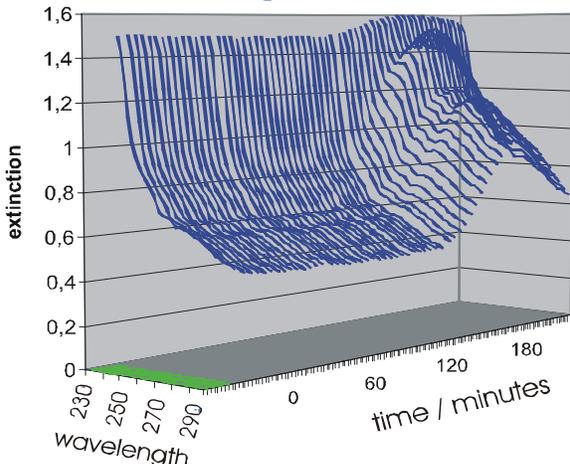
In this figure, the derivative spectra are printed, featuring clearly identifiable signals in the same region, which are used for discharge identification and warning.



This figure shows the spectra from the east bank (red fingerprint), west bank (blue) and open water (black) of an alpine lake.

The differences visible in the absorbance spectra in the wavelength range of 215 to 350nm become more distinct using the “Delta-Spectrometry” method. Comparison of the east and west bank spectra to the fingerprint of the free water body, serving as a reference, will yield the difference (delta) spectra shown in the upper right corner of the graph above. Due to differing substance groups, the spectra take various shapes within the range determinant for the relevant organic substance. This method is capable of capturing very small variations in water composition, which is of particular benefit in early warning systems.

**Change of “Göllersbach”-river spectra during a short rainfall**

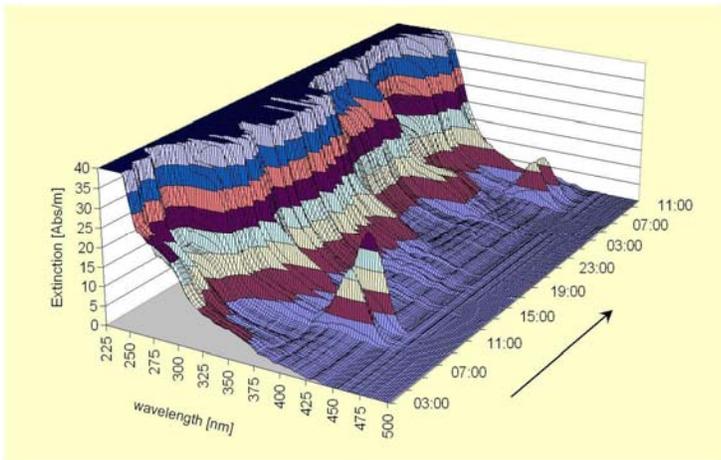


3-D monitoring of the “fingerprint” of a little Austrian creek over time.

The effect of a rainfall on water quality can be seen. Calibrated parameters like Nitrate, DOC, or turbidity can be traced.

Also, the spectral fingerprint can be used as a whole to trigger necessary activities, like stopping an extraction pump, or starting an auto-sampler.

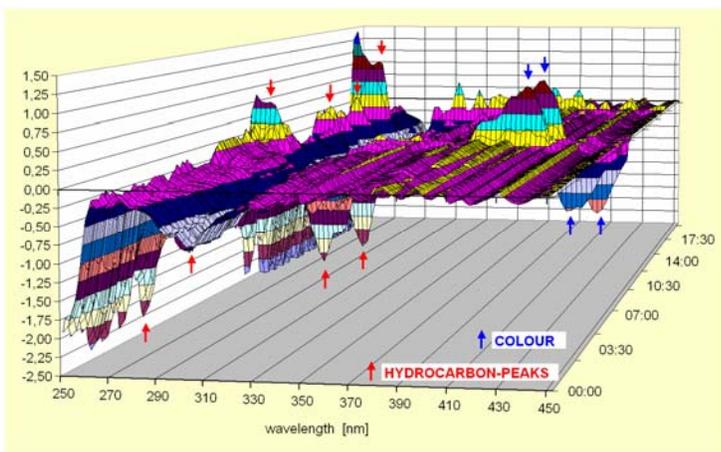
With the help of referenced Delta Spectrometry (as pictured above), the distinguishing between natural and anthropogenic causes for spectral deviations is possible.



STEP 1:

3-D monitoring of a heavily polluted channel over time.

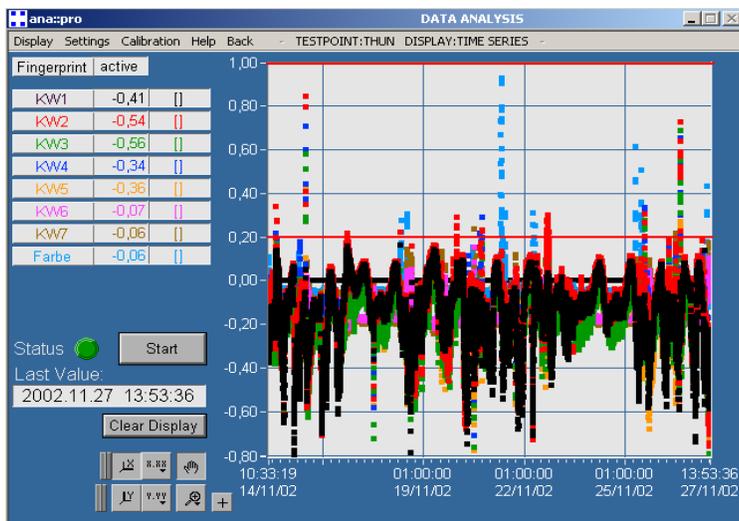
Even without sophisticated mathematical tools, peaks, valleys, and shoulders, originating from abnormal emissions to the water body, can be seen.



STEP 2:

3-D-derivative spectrometry for the detection of abnormal emissions

The derivative of the online spectra are used to identify deviations from “normal” spectral features. Depending on the wavelength range the deviations can be qualified and roughly correlated to substance groups.

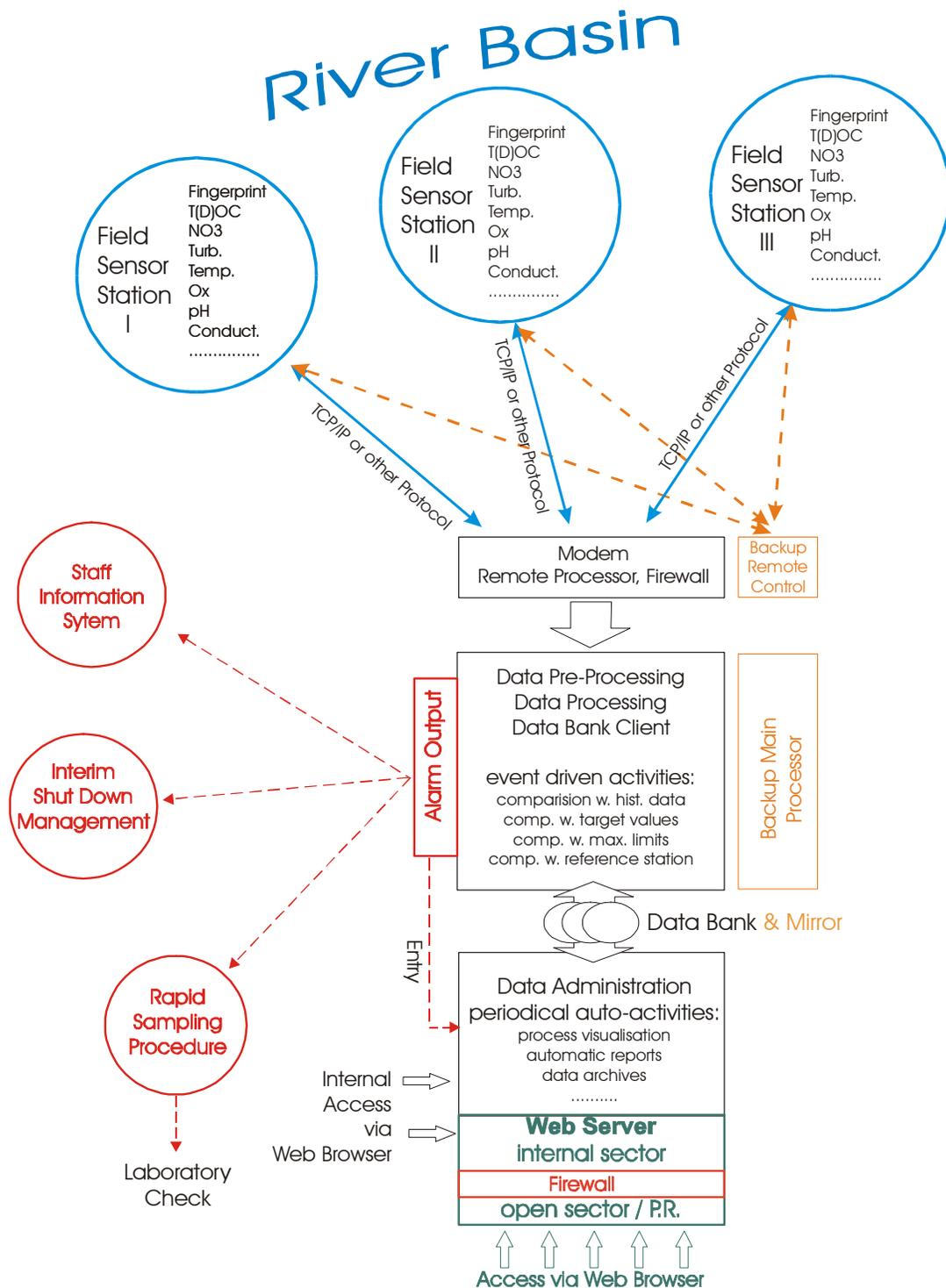


STEP 3: s::can’s alarm software

implements up to 8 virtual contaminant fractions based on derivative spectrometry. Sensitivity can be adjusted individually with respect to risks involved and acceptable false alarm levels.

20 % - alarm: slight deviation from normal spectrum. Automatical sampling triggered, no additional action needed, waiting for lab analysis (> red line at 0,20)

100 % - alarm: strong peak on normal spectrum. automatical sampling plus urgent action at site needed (> red line at 1,00).



Sensor Network for Monitoring and Alarm Systems by:



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